Inorganic Chemistry

Mononuclear Sulfido-Tungsten(V) Complexes: Completing the Tp*MEXY (M = Mo, W; E = O, S) Series

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S Supporting Information

ABSTRACT: Orange Tp*WSCl₂ has been synthesized from the reactions of Tp*WOCl₂ with boron sulfide in refluxing toluene or Tp*WS₂Cl with PPh₃ in dichloromethane at room temperature. Mononuclear sulfido-tungsten(V) complexes, Tp*WSXY {X = Y = Cl, OPh, SPh, SePh; X = Cl, Y = OPh; XY = toluene-3,4-dithiolate (tdt), quinoxaline-2,3dithiolate (qdt); and Tp* = hydrotris(3,5-dimethylpyrazol-1yl)borate} were prepared by metathesis of Tp*WSCl₂ with the respective alkali metal salt of X^{-}/XY^{2-} , or $[NHEt_3]_2(qdt)$. The complexes were characterized by microanalysis, mass spectrometry, electrochemistry, and infrared (IR), electron para-



magnetic resonance (EPR) and electronic absorption spectroscopies. The molecular structures of Tp*WS(OPh)2, Tp*WS(SePh)₂, and Tp*WS(tdt) have been determined by X-ray crystallography. The six-coordinate, distorted-octahedral W centers are coordinated by terminal sulfido (W \equiv S = 2.128(2) - 2.161(1) Å), terdentate facial Tp*, and monodentate/bidentate O/S/Se-donor ligands. The sulfido-W(V) complexes are characterized by lower energy electronic transitions, smaller g_{isot} and larger A_{iso} ⁽¹⁸³W) values, and more positive reduction potentials compared with their oxo-W(V) counterparts. This series has been probed by sulfur K-edge X-ray absorption spectroscopy (XAS), the spectra being assigned by comparison to Tp*WOXY (X = Y = SPh; XY = tdt, qdt) and time-dependent density functional theoretical (TD-DFT) calculations. This study provides insight into the electronic nature and chemistry of the catalytically and biologically important sulfido-W unit.

INTRODUCTION

The discovery that tungsten enzymes are present in microorganisms living in extreme environments (extremophiles) $^{1-3}$ has stimulated interest in the bioinorganic and biomimetic chemistry of tungsten.⁴ Tungsten-dependent organisms appear to have evolved before molybdenum-dependent organisms, the change from W- to Mo-catalyzed biochemical processes being an evolutionary response to the slow oxygenation of Earth's biosphere, except in niche environments where tungstendependent organisms persist, around 2.3 billion years ago.^{2,5} Accordingly, Mo and W enzymes (excluding nitrogenase) share a number of features: they contain mononuclear active sites where the metal center is coordinated by one or two pyranopterin-substituted dithiolene ligands (molybdopterin (MPT) or a derivative) and a complement of oxo-, sulfido-, or amino acid-based coligands, and where the metal center generally cycles through + IV, + V, and + VI oxidation states during turnover.^{1–3}

The focus of biomimetic studies to date has included the replication of coordination sphere components and overall composition, active site structure, and reactivity/function in small metal site mimics.⁴ Many comparative studies have highlighted similarities as well as significant differences in the redox behavior and biomimetic reaction chemistry of Mo and W.⁶ There is now growing interest in establishing the electronic origins of the chemistries of Mo versus W and of their ligand complements, e.g., O-versus S/Se-coordination, and how these may determine enzyme stability, function, and mechanism in, e.g., mesophilic versus hyperthermophilic organisms and oxic versus anoxic environments.^{2,6,7} Access to analogous Mo and W complexes amenable to comparative chemical, spectroscopic, and theoretical interrogation is prerequisite to progress in this area.

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A wide range of oxo- and to a lesser extent sulfido-Mo and -W complexes have been prepared and studied as mimics for Mo and W enzymes.⁴ The most closely targeted models feature biologically relevant dithiolene coligands (cf. MPT). However, the majority of mononuclear sulfido(dithiolene)-M (M = Mo, W) complexes are M(VI) or M(IV) species because the propensity for comproportionation and M(V) dimer formation that restricts access to *mononuclear* M(V) species in sterically unencumbered systems.^{8,9}

While mononuclear oxo-M(V) complexes are relatively wellknown, there are far fewer examples of mononuclear sulfido-M(V) species.¹⁰ The incorporation of sterically bulky coligands has proven the most effective strategy for preventing dimer formation and facilitating the isolation of mononuclear oxoand sulfido-M(V) complexes bearing organic coligands. Trofimenko's first and second generation scorpionate (pyrazolylborate) ligands have been most useful in this regard.¹¹ Thus, the first sulfido-Mo(V) complex, Tp*MoSCl₂, reported by Young et al.,¹² features the hydrotris(3,5-dimethylpyrazol-1yl)borate ligand (Tp*-). A range of derivatives have been prepared from this complex and detailed structural, spectroscopic and theoretical studies have been undertaken to probe their electronic structure.¹³⁻¹⁵ Related species have been prepared in situ and characterized by EPR spectroscopy.¹⁶ Sulfido-Mo(V) species are also postulated as intermediates in the synthesis of Tp*MoO(pterinyl-dithiolene).¹⁷ More recently, the bulkier hydrotris(3-isopropylpyrazol-1-yl)borate ligand (Tp^{iPr-}) has been instrumental in the isolation of complexes containing terminal oxo as well as terminal sulfido ligands on a single Mo(V) center, viz., [CoCp₂][Tp^{iPr}MoOS-(OAr)] $(Cp^- = cyclopentadienyl, OAr^- = phenolate$ derivative).¹⁸ Other oxo-sulfido-Mo(V) complexes have been prepared in situ and studied by EPR spectroscopy.¹⁹ Singh et al. have claimed the isolation of one such complex.²⁰ Johnson et al. have also used sterically bulky amido ligands to stabilize the sulfido-Mo(V) complex MoS(NRAr)₃ ($R = C(CD_3)_2CH_3$, Ar = $C_6H_3Me_2-3,5$ ²¹ An unstable bis(dithiolene)-Mo(V) complex, $NEt_4[MoS(S_2C_6H_8)_2]$, has also been reported but its isolation was thwarted by rapid dimerization.⁹ Very few mononuclear sulfido-W(V) complexes are known; they include structurally characterized WSCl₃(MeSCH₂CH₂SMe),²² PPh₄[WSCl₄],²³ and Tp*WS{ $S_2C_2(CO_2Me)_2$ }.²

Here, we report the synthesis and characterization of the first extended series of sulfido-W(V) complexes, viz., Tp*WSXY {X = Y = Cl, OPh, SPh, SePh; X = Cl, Y = OPh; XY = toluene-3,4-dithiolate (tdt), quinoxaline-2,3-dithiolate (qdt)}, outlined in Chart 1. Their preparation "completes" the set of four oxo/ sulfido-M(V) Tp* complexes, viz., Tp*MoOXY, Tp*MoSXY,

Chart 1. Structures of Complexes Synthesized and Ligands Used in This Study



Tp*WOXY, and Tp*WSXY, whose synthesis and study was initiated by Enemark and co-workers in the 1980s.^{12,25} The crystal structures of Tp*WS(OPh)₂, Tp*WS(SePh)₂, and Tp*WS(tdt)·C₄H₈O are also reported, doubling the number of structurally characterized sulfido-W(V) complexes. Moreover, access to these complexes provides the foundation required for detailed, comparative spectroscopic and computational investigations of the different sets of compounds to examine their biological and catalytic significance.

EXPERIMENTAL SECTION

Synthesis of Complexes. The compounds $TpWOCl_2^{26}$ and $Tp^*WS_2Cl^{27}$ were synthesized according to the published methods. Quinoxaline-2,3-dithiol was prepared following the method of Morrison and Furst.²⁸ All reactions were performed under an atmosphere of pure dinitrogen employing standard Schlenk techniques. Solvents were carefully dried and deoxygenated before use. Chromatographic separations and purifications were performed on 50×2.5 cm² diameter columns using Merck Art. 7734 Kieselgel 60.

Tp*WSCl₂. Method 1. A mixture of Tp*WOCl₂ (156 mg; 0.27 mmol) and B_2S_3 (200 mg; 1.70 mmol) was refluxed in toluene (20 mL) for 4 d, then treated with MeOH (5 mL), and reduced to dryness. The residue was shaken with CH₂Cl₂ (20 mL) then eluted on a silica column with 3:2 CH₂Cl₂/hexane. A faint green band (Tp*WS₂Cl; 7 mg) was followed by the orange product. Recrystallization from CH₂Cl₂/MeOH gave orange crystals. Yield: 92 mg (57%). A later green band contained Tp*WCl₃ (14 mg; 13% based on Cl).

Method 2. A mixture of Tp*WS₂Cl (80 mg; 0.14 mmol) and PPh₃ (38 mg; 0.14 mmol) in dichloromethane (5 mL) was stirred for a 19 h at ambient temperature. The yellow solution was then eluted on a 50 cm silica column with 3:2 dichloromethane/hexanes as eluent. The major orange-yellow band was collected and recrystallized from dichloromethane/hexanes. Dark orange crystals were retrieved from a second recrystallization from dichloromethane/methanol. Yield: 62 mg (77%).

Anal. Calcd for $C_{15}H_{22}BN_6SCl_2W$: C, 30.85; H, 3.80; N, 14.39; S, 5.49; Cl, 12.14. Found: C, 30.93; H, 3.82; N, 14.37; S, 5.58; Cl, 12.20. IR (CsI, cm⁻¹): 2960 w, 2925 w, ν (BH) 2555 m, ν (CN) 1540 s, 1445 s, 1410 s, 1385 s, 1350 s, 1210 s, 1200 s, 1075 s, 1065 s, 1040 s, 985 m, 930 w, 875 w, 855 m, 815 m, 790 s, 735 w, 690 m, 645 m, 595 w, ν (W \equiv S) 515 s, 475 w, 375 w, ν (WCl) 330, and 310 s. Electronic spectrum (CH₂Cl₂): 10 160 (60), 26 320 (sh, ~ 900), 32 100 (sh, ~ 10 400), 34 480 (sh, ~ 16 500), and 35 600 cm⁻¹ (17 200 M⁻¹ cm⁻¹). ESI mass spectrum: m/z 585 [M]⁺.

Tp*WS(OPh)Cl. Phenol (74 mg; 0.79 mmol) was added to sodium (18 mg; 0.78 mmol) in toluene (5 mL) and refluxed for 40 min. The cooled suspension of NaOPh was joined by a THF solution (~40 mL) of Tp*WSCl₂ (200 mg; 0.34 mmol), and the mixture refluxed for 2 d. The solvent was removed under vacuum and the residue anaerobically column chromatographed using neat benzene as eluent. The first yellow-orange band was collect, recrystallized from THF/hexanes, and dried in vacuo. Yield: 21 mg (10%).

IR (KBr, cm⁻¹): 2926 m, ν (BH) 2552 m, ν (OPh) 1588 s, ν (CN) 1543 s, 1478 s, 1449 s, 1414 s, 1384 m, 1360 s, 1204 s, 1067 s, 1045 m, 856 s, 813 m, 796 w, 758 m, 691 m, 641 m, 607 w, ν (W \equiv S) 486 m. Electronic spectrum (MeCN): 10 100 (40), 16 900 (sh, ~10), 31 400 (sh, ~7900), 35 700 (13 000), 45 100 (sh, ~2000), and 47 600 cm⁻¹ (26 800 M⁻¹ cm⁻¹). ESI mass spectrum: *m*/*z* 643 [M + H]⁺.

Tp*WS(OPh)₂. White crystalline NaOPh was freshly prepared by combining phenol (74 mg; 0.79 mmol) with sodium (18 mg; 0.78 mmol) in refluxing toluene (5 mL) for 1 h. Yellow Tp*WSCl₂ (200 mg; 0.34 mmol) was quickly added to the cooled suspension under a positive pressure of nitrogen, and the mixture refluxed for 3 d. The solvent was evaporated and the residue column chromatographed using benzene as eluent. A prominent yellow band was collected, reduced to dryness, and recrystallized from THF/hexane. Yield: 31 mg (13%).

Table 1. Crystallographic Data

	$Tp*WS(OPh)_2$	Tp*WS(SePh) ₂	Tp*WS(tdt)·C ₄ H ₈ O
formula	$C_{27}H_{32}BN_6O_2SW$	C ₂₇ H ₃₂ BN ₆ SSe ₂ W	C ₂₆ H ₃₆ BN ₆ OS ₃ W
fw	699.30	825.22	739.45
crystal size, mm ³	$0.15 \times 0.15 \times 0.10$	$0.10 \times 0.10 \times 0.02$	$0.15 \times 0.05 \times 0.05$
crystal system	triclinic	orthorhombic	monoclinic
space group	PĪ	Pbca	$P2_{1}/c$
<i>a,</i> Å	9.9067(7)	15.046(1)	13.771(4)
b, Å	11.0138(7)	26.833(3)	10.380(3)
<i>c,</i> Å	14.2504(9)	14.465(1)	21.227(6)
α , °	76.888(1)	90	90
<i>β</i> , °	85.383(1)	90	103.156(6)
γ, °	65.518(1)	90	90
<i>V</i> , Å ³	1378.0(2)	5840(1)	2955(1)
Z	2	8	4
Т, К	130(2)	130(2)	130(2)
$ ho_{ m calcd}$, g cm ⁻³	1.685	1.877	1.662
μ , mm ⁻¹	4.304	6.549	4.153
refl. collected/ $2\Theta_{max}$	7277/50.00	34672/55.05	14462/50.00
unique refl./R _{int}	4780/0.0195	6701/0.1274	5211/0.0972
no. of param./restr.	353/0	349/6	354/0
R1 ^a /goodness of fit ^b	0.0261/1.030	0.0643/1.027	0.0463/0.791
$w R2^c (I > 2\sigma(I))$	0.0609	0.1110	0.0771
residual density, e $Å^{-3}$	+1.05/-0.69	+1.23/-2.10	+1.76/-1.27
^{<i>a</i>} Observation criterion: $I > 2\sigma(I)$. R1 =	$= \sum F_0 - F_c / \sum F_0 ; \ ^b \text{GoF} = \left[\sum w \right]$	$F_0^2 - F_c^2)^2]/(n-p)]^{1/2}; \ ^c wR2 = [\Sigma[w]$	$w(F_0^2 - F_c^2)^2] / \Sigma [w(F_0^2)^2]^{1/2}$ where

 $w = 1/\sigma^2(F_0^2) + (aP)^2 + bP, P = (F_0^2 + 2F_c^2)/3.$

Anal. Calcd for $C_{27}H_{32}BN_6O_2SW$: C, 46.37; H, 4.61; N, 12.02; S, 4.59. Found: C, 45.74; H, 4.66; N, 11.67; S, 4.52. IR (KBr, cm⁻¹): 2960 w, 2926 m, ν (BH) 2545 m, ν (OPh) 1589 s, ν (CN) 1543 s, 1479 s, 1449 s, 1415 s, 1381 m, 1362 s, 1281 s, 1261 s, 1246 s, 1202 s, 1077 m, 1067 s, 1057 m, 1046 m, 1022 w, 997 w, 878 m, 856 s, 803 w, 791 w, 691 s, 644 s, ν (W \equiv S) 486 s, 474 m. Electronic spectrum (THF): 9100 (66), 16 800 (sh, ~40), 32 300 (sh, ~14 500), and 36 100 cm⁻¹ (20 100 M⁻¹ cm⁻¹). ESI mass spectrum: m/z 700 [M + H]⁺.

Tp*WS(SPh)₂. A fresh suspension of NaSPh was prepared by mixing thiophenol (85 mg; 0.77 mmol) and sodium (18 mg; 0.78 mmol) in toluene (5 mL) and refluxing for 1 h. A yellow solution of Tp*WSCl₂ (200 mg; 0.34 mmol) in THF (30 mL) was then added, and refluxing continued for 38 h. The solvent was evaporated and the residue column chromatographed using benzene as eluent. A dark brown band was collected, reduced to dryness, and the complex was retrieved by diffusion of hexanes into a chilled, saturated THF solution of the compound. Yield: 38 mg (15%).

Anal. Calcd for $C_{27}H_{32}BN_6S_3W$: C, 44.34; H, 4.41; N, 11.94; S, 13.15. Found: C, 44.94; H, 4.59; N, 11.12; S, 12.50. IR (KBr, cm⁻¹): 2962 m, 2924 m, 2854 w, ν (BH) 2554 m, ν (SPh) 1576 m, ν (CN) 1543 s, 1473 m, 1448 s, 1412 s, 1381 w, 1354 s, 1262 s, 1203 s, 1097 s, 1074 s, 1037 s, 1023 s, 857 m, 812 w, 738 m, 691 m, 647 m, ν (W \equiv S) 491 m. Electronic spectrum (THF): 13 600 (630), 19 000 (sh, ~2300), 22 400 (sh, ~3700), 25 400 (6200), 34 722 (13 900), 37 600 cm⁻¹ (18 100 M⁻¹ cm⁻¹), and 41 700 (16 500). ESI mass spectrum: *m*/*z* 733 [M + H]⁺.

Tp*WS(tdt). A refluxing mixture of sodium (18 mg; 0.78 mmol) and toluene-3,4-dithiol (50 μ L; 0.38 mmol) in toluene (10 mL) solution produced a white suspension of Na₂tdt. To this was added Tp*WSCl₂ (200 mg; 0.34 mmol) in THF (40 mL), and the mixture was refluxed for 26 h. The solvent was removed in vacuo and the residue column chromatographed using 3:2 THF/hexanes as eluent. The first green band was collected, recrystallized from THF/methanol, and dried under vacuum. Yield: 90 mg (40%).

Anal. Calcd for $C_{22}H_{28}BN_6S_3W$: C, 39.59; H, 4.23; N, 12.59; S, 14.41. Found: C, 40.05; H, 4.28; N, 12.21; S, 14.50. IR (KBr, cm⁻¹): 2964 m, 2924 m, ν (BH) 2557 m, ν (CN) 1543 s, 1451 s, 1412 s, 1383 w, 1357 s, 1262 m, 1203 s, 1103 w, 1075 m, 1037 m, 857 m, 812 m, 801 s, 790 m, 690 m, 652 m, ν (W=S) 487 m. Electronic spectrum

(THF): 11 600 (240), 14 900 (300), 23 200 (sh, ~4000), 25 400 (6200), 33 700 (10 300), and 40 500 cm⁻¹ (27 900 M⁻¹ cm⁻¹). ESI mass spectrum: m/z 668 [M + H]⁺.

Tp*WS(qdt). Quinoxaline-2,3-dithiol (106 mg; 0.54 mmol) and triethylamine (160 μ L; 1.14 mmol) were stirred in THF (15 mL) for 1 h, upon which Tp*WSCl₂ (300 mg; 0.51 mmol) was added, and the mixture refluxed for 3 d. During that time two additional 100 μ L aliquots of NEt₃ were added to restore base lost during reflux. The mixture was then filtered and the solvent was removed under vacuum. The resultant solid was dissolved in benzene and eluted on a silica column with 9:1 benzene/THF. The first orange band (Tp*WSCl₂) was discarded, while the second band (brown) was collected and reduced to dryness. The complex was recrystallized from THF/ hexanes and dried in vacuo. Yield: 43 mg (12%).

IR (KBr, cm⁻¹): 2927 m, ν (BH) 2557 m, ν (CN) 1544 s, 1450 s, 1415 s, 1384 m, 1357 s, 1250 m, 1218 w, 1195 s, 1169 s, 1107 s, 1074 s, 1066 s, 1043 w, 858 m, 814 w, 795 m, 754 s, 690 w, 644 w, 596 m, ν (W \equiv S) 495 m, 471 w. Electronic spectrum (CH₂Cl₂): 13 500 (360), 14 900 (sh, ~300), 23 000 (sh, ~7600), 26 500 (21 000), 34 500 (sh, ~12 400), 36 100 cm⁻¹ (14 300 M⁻¹ cm⁻¹). ESI mass spectrum: *m*/*z* 707 [M + H]⁺.

Tp*WS(SePh)₂. A yellow solution of diphenyl diselenide (160 mg; 0.51 mmol) in THF (5 mL) was treated with 1.0 M LiBEt₃H (Superhydride; ~1200 μ L) until the yellow color of the solution was discharged. The solvent and volatile BEt₃ were removed under vacuum at 50 °C for 40 min. To this residue was added Tp*WSCl₂ (200 mg; 0.34 mmol) and THF (20 mL), and the mixture was refluxed for 28 h. The solvent was evaporated under reduced pressure, and the residue reconstituted in benzene and was column chromatographed. The third band (dark brown) was collected, and EPR showed this to be a mixture of the desired product and presumably a hydrolyzed specie. This fraction was eluted on a silica column employing 2:1 benzene/ hexanes, and an intense dark brown band was collected. The product was carefully recrystallized with THF/hexanes, collected by filtration, washed with ice-cold hexanes, and dried in vacuo. Yield: 25 mg (9%).

IR (KBr, cm⁻¹): 2960 w, 2923 m, ν (BH) 2553 m, ν (SePh) 1573 m, ν (CN) 1543 s, 1471 m, 1446 s, 1438 s, 1413 s, 1382 m, 1351 s, 1206 s, 1066 s, 1036 s, 1021 s, 998 w, 857 m, 815 m, 788 m, 733 s, 689 s, 645 m, ν (W \equiv S) 503 m. Electronic spectrum (THF): 12 900 (1100),

19 000 (sh, ~4200), 23 900 (8500), 25 400 (6200), and 36 200 cm⁻¹ (26 300 M⁻¹ cm⁻¹). ESI mass spectrum: m/z 826 [M + H]⁺.

X-ray Crystallographic Data Collection and Refinement of the Structures. Orange blocks of Tp*WS(OPh)₂ were obtained by diffusion of hexanes into saturated a THF solution of the complex, while black plates of Tp*WS(SePh)2 were obtained by slow diffusion hexanes into a THF solution of the compound at -20 °C. Diffraction quality crystals of Tp*WS(tdt) were obtained as black rods by diffusion of hexanes into a saturated THF solution. Crystals were coated in mineral oil and mounted on glass fibers. Data for all complexes were collected with a Bruker SMART Apex CCD detector using Mo-K α radiation (graphite crystal monochromated, λ = 0.71073 Å). Cell parameters were acquired by the SMART software package, and the data reduction performed using SAINT. The temperature during data collection was maintained at 130 K using an Oxford Cryostream cooling device. The structures were solved by direct methods and refined using full-matrix least-squares on F^2 using the SHELXTL program package.²⁹ All non-hydrogen atoms were included in difference maps and anisotropic thermal parameters were employed. Hydrogen atoms were included in calculated positions. Thermal ellipsoid plots were generated using the program ORTEP-3³⁰ integrated within the WINGX³¹ suite of programs. All ORTEP projections have been drawn at the 50% probability level with hydrogen atoms removed for clarity. The labeling schemes for the pyrazole rings containing N11 and N21 follow that shown for the ring containing N31. Crystal data are provided in Table 1.

X-ray Absorption Spectroscopy. X-ray absorption spectroscopy was carried out at the Stanford Synchrotron Radiation Laboratory with the SPEAR storage ring containing 60-100 mA at 3.0 GeV. Sulfur Kedge experiments were performed on beamline 6-2 using an Si(111) double crystal monochromator and wiggler field of 1.0 T. Harmonic rejection was accomplished by using a bent-flat nickel coated mirror downstream of the monochromator adjusted so as to have a cutoff energy of about 4500 eV. Incident intensity was monitored using an ion chamber contained in a (flowing) helium-filled flight path. X-ray absorption was monitored by recording total total electron yield while simultaneously monitoring X-ray fluorescence using a 3-grid fluorescent ion chamber with electron yield accessory (The EXAFS Company, Pioche, NV, U.S.A.). The energy scale was calibrated with reference to the lowest energy peak of the sodium thiosulfate standard (Na₂S₂O₃·5H₂O) which was assumed to be 2469.2 eV. Samples were examined at ambient temperature. Data were averaged, and a smooth background was removed from all spectra by fitting a polynomial to the pre-edge region and subtracting this polynomial from the entire spectrum. Normalization of the data was accomplished by fitting a flattened polynomial or straight line to the postedge region and normalizing the postedge to 1.0. Fits to the pre-edges modeled by pseudo-Voigt lines were carried out using the program EDG FIT³² with a fixed 1:1 ratio of Lorentzian to Gaussian contributions.

Other Physical Measurements. Infrared spectra were recorded on a Biorad FTS 165 FTIR spectrophotometer as pressed KBr or CsI discs and far-infrared spectra on a Cary 17 spectrophotometer. X-band EPR spectra were recorded on a Bruker ELEXSYS E500 spectrometer. Fluid solution spectra were simulated using Bruker's Simfonia. Electronic spectra were obtained on PerkinElmer Lambda 2 spectrophotometer. Mass spectra were obtained on Quattro II Micromass Triple Quad and Vacuum Generators VG ZAB 2HF mass spectrometers. Cyclic voltammograms were recorded using an Autolab PGSTAT30 interfaced with GPES 4.9 electrochemistry software. The electrode configuration consisted of a 2 mm glassy carbon working electrode, a platinum auxiliary electrode, and a reference electrode consisting of Ag/AgNO₃ (0.01 M in MeCN) incorporated into a salt bridge containing supporting electrolyte (to minimize Ag^+ leakage). Solutions of the complexes (1-2 mM) were prepared in acetonitrile containing 0.1 M $[N(n-Bu)_4]PF_6$ or dichloromethane containing 0.2 M $[N(n-Bu)_4]PF_6$ as electrolyte. All reduction potentials are referenced versus the ferrocenium/ferrocene (Fc^{+/0}) couple. Elemental analyses were performed by Atlantic Microlab Inc., Georgia, USA.

Calculations. All calculations in this work were performed with the electronic structure program ORCA.³⁴ Geometry optimizations were carried out using the B3LYP functional.³⁵ A segmented all-electron relativistically contracted (SARC) basis set of triple-Z-quality (def2-TZVP) was used for tungsten with enhanced integration accuracy (SPECIALGRIDINTACC 14).³⁶ A scalar relativistic correction was applied using the zeroth-order regular approximation (ZORA) method.³⁷ An all-electron polarized triple- ζ -quality (def2-TZVP) basis set of the Ahlrichs' group was used for the other atoms.³⁸ Auxiliary basis sets for all complexes used to expand the electron density in the calculations were chosen to match the orbital basis. The self-consistent field (SCF) calculations were tightly converged (1 \times $10^{-8} E_{\rm h}$ in energy, $1 \times 10^{-7} E_{\rm h}$ in the density change, and 1×10^{-7} in the maximum element of the DIIS error vector). The geometry search for all complexes was carried out in redundant internal coordinates without imposing geometry constraints. Canonical orbitals were constructed using the program Molekel.³

Time-dependent (TD-DFT) calculations of the sulfur K-pre-edges using the BP86⁴⁰ functional were performed on the crystallographic or geometry optimized coordinated as previously described.⁴¹ Due to the limitations in the accurate treatment of excited states in DFT, absolute transition energies cannot be obtained by this method. Nevertheless, the relative transition energies and the relative intensities are, in general, reliably modeled. The sulfur 1s orbitals were localized using the Pipek–Mezey criteria,⁴² and the TD-DFT equations were solved⁴³ individually for each sulfur atom, excluding all but excitations originating from the sulfur 1s orbital.⁴⁴ It was established that a constant shift of +57.52 eV was required for this regime of basis sets and applied to the transition energies to align calculated and experimental data. Plots were obtained using a line broadening of 1.0 eV.

RESULTS AND DISCUSSION

Synthesis and Characterization. Reaction of blue $Tp*WOCl_2$ with boron sulfide over 4 days in refluxing toluene yielded orange $Tp*WSCl_2$ (57%) and green $Tp*WCl_3^{26,45}$ (13% based on Cl) following chromatographic workup. Unfortunately, boron sulfide is no longer commercially available and other sulfiding agents tested were ineffective in converting $Tp*WOCl_2$ into $Tp*WSCl_2$. Alternatively, the compound can be prepared from $Tp*WS_2Cl$ by sulfur atom transfer to PPh₃ in chlorinated solvents, where chlorine atom transfer converts the initial formed sulfido-W(IV) complex to $Tp*WSCl_2$ in 70% yield. The compound is soluble in chlorinated solvents, slightly soluble in acetonitrile and aromatic solvents and insoluble in water, alcohols and hydrocarbons, and indefinitely stable in air and wet solvents.

Metathesis reactions of Tp^*WSCl_2 and ligand salts afforded yellow-brown sulfido-W(V) compounds. Generally, due to the sluggish nature of substitution at W(V) and the potential for downstream reactions, the syntheses require prolonged reaction times and produced only limited quantities of the title compounds (9–40%) after purification by column chromatography. The compounds were very sensitive to hydrolysis to the oxo-W(V) analogues (especially in the presence of silica gel) and all manipulations required strictly anaerobic conditions. Most of the compounds were soluble in THF and chlorinated solvents, slightly soluble in acetonitrile and aromatic solvents and insoluble in water, alcohols, and hydrocarbons. Tp*WS-(SPh)₂ and Tp*WS(SePh)₂ show high solubility in most organic solvents (except cold hexanes) but were slowly converted to Tp*WSCl₂ in chlorinated solvents.

The compounds have been characterized by a variety of techniques, the results being consistent with the presence of pure, single component compounds with the proposed formulation. All compounds exhibited strong $[M + H]^+$ parent

ions in mass spectrometric analyses and IR bands characteristic of the constituent ligands. The chloro complex, Tp*WSCl₂, exhibited a strong ν (W–S) band at 515 cm⁻¹ and strong symmetric and antisymmetric ν (WCl₂) stretches at 330 and 310 cm⁻¹, respectively. The other sulfido complexes exhibited an intense ν (W=S) band in the region 503–486 cm⁻¹. The oxo complexes displayed a single, strong ν (W=O) band in the region 950–941 cm^{-1.26} Bands characteristic of the Tp* ligand (ν (BH) 2557–2545 cm⁻¹ and ν (CN) 1544–1540 cm⁻¹) as well as the monodentate coligands (ν (C–C) ca. 1580 cm⁻¹) were also observed.

Electronic Spectroscopy. The electronic absorption spectra reveal a ligand field (LF) transition in the near-IR region at $\sim 10\ 000\ \text{cm}^{-1}$ (Figure 1). The relatively low energy



Figure 1. Electronic absorption spectra of Tp^*WSCl_2 , $Tp^*WS(OPh)_2$, $Tp^*WS(SPh)_2$, and $Tp^*WS(SePh)_2$ recorded in dichloromethane solutions at ambient temperature. The dashed gray trace is the spectrum for the corresponding oxo-W(V) homologue.

of the LF transition in the sulfido complexes reflects the smaller HOMO–LUMO gap associated with the weaker π -donor. Such transitions in analogous oxo-W(V) complexes are higher in energy at around 15 000 cm⁻¹ (Figure 1).²⁶ This band is assigned as a transition from the singly occupied $d_{x^2-y^2}$ ground state orbital (SOMO) to d_{yz} and/or d_{xz} orbitals. These sixcoordinate complexes have pseudo- $C_{2\nu}$ symmetry, where the zaxis is parallel to the W–S bond and the x-axis bisects the X/Ydonor atoms. Intense ligand-to-metal charge transfer (LMCT) bands obscure this LF transition in S- and Se-donor complexes. For the phenolate and chloride complexes, there are intense bands at ~20 000 cm^{-1} due to O 2p and Cl 3p CT to the ground state as seen in other analogues.^{25,26,46} For Tp*WS-(SPh)₂ and Tp*WS(SePh)₂, low-energy CT bands are attributed to S/Se \rightarrow W d_{x²-y²} transitions and have extinction coefficients $\varepsilon > 1000 \text{ M}^{-1} \text{ cm}^{-1}$. The oxo-W(V) analogues exhibit similar electronic spectra.²⁶ However, in keeping with

the relatively weak LF of the heavier congeners, there is a bathochromic shift of ca. 2500 cm^{-1} in the bands for the sulfido complexes compared to their oxo counterparts, and a bathochromic shift of ca. 600 cm^{-1} in the bands for the selenophenolate complexes compared to their thiophenolate analogues. The high intensity of these bands reflects the presence of considerable metal–ligand covalency, the intensity of the bands for the selenophenolate complexes being enhanced by the large spin-orbit coupling constant for Se.

Complexes containing bidentate dithiolene ligands exhibit two low-energy features compared to one for Tp*WS(SPh)₂ (Figures S1 and S2 of the Supporting Information). This shows the stark contrast in the electronic structure when two thiolates are replaced by a dithiolate, and has been ascribed to dithiolene coordination separating and lowering the transition energies.⁴⁷ An intense absorption feature at 26 500 cm⁻¹ for Tp*WS(qdt) is attributed to a $\pi \rightarrow \pi^*$ transition of the quinoxaline unit.^{26,48}

EPR Spectroscopy. Isotropic X-band EPR spectra are typical of W(V) d¹ centers where large spin-orbit coupling drives g-values substantially lower than that of the free-electron $(g_e = 2.0023)$. The shift to higher field compared to the oxo series gives an inherently larger linewidth for these sulfido complexes, and hyperfine features that stem from coupling to ^{183}W ($I = \frac{1}{2}$; 14.31% abundant) were not observed (Figure 2). For example, the peak width at half-height (fwhm) for the phenolate complexes is ~90 G. Thus, isotropic spectra were simulated to estimate the ¹⁸³W hyperfine coupling constant (Table 2). The isotropic g-value is lower for sulfido-W(V)compared to oxo-W(V) resulting from a smaller HOMO-LUMO gap that increases the mixing between ground and excited states.¹² LF transitions for these sulfido complexes are ~5000 cm⁻¹ less than their oxo-W(V) counterparts (vide supra). As expected, A-values are larger, and vary with different equatorial donor ligands (Figure S3). Large A_{iso} are observed for hard oxygen and chlorine ligands; lower values for softer Sand Se-donor ligands, a consequence of increased metal-ligand covalency. The g_{iso} becomes larger as the spin-orbit coupling of the ligand increases, and is consistent with large differences in the ground state composition with higher covalency in complexes with heavier chalcogens.

Frozen-glass spectra are highly rhombic, as expected of these low-symmetry complexes (Figure 2). Only the tungsten hyperfine associated with g_1 is clearly visible in complexes with bidentate ligands, while appearing as shoulders in species with monodentate ligands. The anisotropy decreases when comparing monodentate SPh with bidentate tdt and qdt, suggesting that the solid state C_1 symmetry is retained in the frozen glass. The formation of a metallodithiolene increases the covalency, and the higher *g*-values maybe ascribed to an increase in the ground-to-excited state transitions as a result of $p\pi$ -d π interactions. The electronic absorption spectra for Tp*WS(tdt) and Tp*WS(qdt) clearly show low-energy LMCT bands that contribute to the increase in *g*.

Crystal Structures. The molecular structures of $Tp*WS(OPh)_2$, $Tp*WS(SePh)_2$, and Tp*WS(tdt) have been determined by single crystal X-ray diffractometry. Thermal ellipsoid plots are shown in Figures 3, 4, and 5; selected bond distances and angles are listed in Tables 3 and 4.

The distorted octahedral complexes $Tp^*WS(OPh)_2$ and $Tp^*WS(SePh)_2$ contain a terminal sulfido ligand, two monodentate OPh or SePh ligands, and a facial, terdentate Tp^* ligand. The W-S1 distances of 2.161(1) and 2.128(2) Å, respectively, are typical of $\{W \equiv S\}^{3+}$ units in



Figure 2. Comparison of the X-band EPR spectra of (a) Tp^*WSCl_2 , (b) $Tp^*WS(OPh)_2$, (c) $Tp^*WS(SPh)_2$, and (d) $Tp^*WS(tdt)$, recorded in dichloromethane/toluene solutions at room temperature (left panel) and 150 K (right panel).

complex	g_1	g_2	g ₃	$\langle g \rangle^a$	$g_{ m iso}$	Δg^{b}	$A_{\rm iso}^{\ c}$
Tp*WSCl ₂	1.787	1.735	1.686	1.736	1.731	0.101	93
Tp*WS(OPh)Cl	1.786	1.708	1.589	1.694	1.690	0.197	90
Tp*WS(OPh) ₂	1.792	1.693	1.559	1.681	1.675	0.233	90
Tp*WS(SPh) ₂	1.924	1.812	1.784	1.821	1.803	0.140	72
Tp*WS(tdt)	1.947	1.878	1.756	1.861	1.863	0.191	68
Tp*WS(qdt)	1.939	1.875	1.770	1.862	1.864	0.169	69
Tp*WS(SePh) ₂	1.953	1.775	1.722	1.818	1.807	0.231	72

 ${}^{a}\langle g \rangle = (g_1 + g_2 + g_3)/3$; g_i values taken directly from the experimental spectrum. ^bAnisotropy, $\Delta g = g_1 - g_3$. ^cObtained by the simulation of isotropic spectra using *Simfonia* (× 10⁻⁴ cm⁻¹).



Figure 3. ORTEP projection and partial labeling scheme for $Tp*WS(OPh)_2$.

WSCl₃(MeSCH₂CH₂SMe) at 2.146(11) Å,²² [WSCl₄]⁻ at 2.064(5) Å,²³ and Tp*WS{S₂C₂(CO₂Me)₂} at 2.108(3) Å.²⁴ For Tp*WS(OPh)₂, the W–O2 and W–O3 distances are 1.938(3) and 1.971(2) Å, and the associated W–O–C angles are 149.2(3)° and 132.9(2)°, respectively. The W atom sits



Figure 4. ORTEP projection and partial labeling scheme for Tp*WS(SePh)₂.

0.292 Å above the N_2O_2 equatorial plane toward the sulfido ligand and the S1–W–O angles are consequently opened to ca.



Figure 5. ORTEP projection and partial labeling scheme for Tp*WS(tdt).

Table 3. Selected Bond Distances (Å) and Angles (deg) for Complexes^a

distance/angle	Tp*WS(OPh) ₂	Tp*WS(SePh) ₂
W-S1	2.161(1)	2.128(2)
W-X2	1.938(3)	2.514(1)
W-X3	1.971(2)	2.559(1)
W-N11	2.296(3)	2.344(7)
W-N21	2.156(3)	2.151(7)
W-N31	2.140(3)	2.193(7)
S1-W-X2	104.88(9)	102.85(7)
S1-W-X3	101.34(9)	95.69(7)
S1-W-N11	169.48(8)	170.4(2)
S1-W-N21	93.67(9)	94.8(2)
S1-W-N31	92.77(9)	92.5(2)
X2-W-X3	88.0(1)	86.75(3)
X2-W-N11	84.3(1)	86.4(2)
X2-W-N21	91.7(1)	92.6(2)
X2-W-N31	162.3(1)	164.7(2)
X3-W-N11	83.8(1)	87.3(2)
X3-W-N21	164.6(1)	169.4(2)
X3-W-N31	87.4(1)	91.7(2)
N11-W-N21	80.8(1)	82.1(3)
N11-W-N31	78.2(1)	78.3(3)
N21-W-N31	88.3(1)	86.2(3)
W-X2-C41	149.2(3)	111.6(3)
W-X3-C51	132.9(2)	105.9(3)

^aX refers to the chalcogen donor atom of the monodentate coligand, O or Se.

103°. The W–N11 distance is 0.148(9) Å longer than the other W–N bonds because the trans influence of the sulfido ligand is greater than for the phenolate coligands. A very similar trans influence of 0.164(4) Å and 0.144(4) Å was observed for Tp*WO(OPh)₂ and Tp*WO(PP)₂, respectively, where PP is 2-(*n*-propyl)phenolate.²⁶ The trans influence is smaller for the molybdenum homologues.^{14,49}

The complex Tp*WS(SePh)₂ has very similar parameters to Tp*WS(OPh)₂, with only a noticeable difference in the W–X bond lengths. These distances are essentially identical to the W–Se bonds in Tp*WO(bds), where bds is benzene-1,2-diselenolate.²⁶ The W–Se–C angles of 111.6(3)° and 105.9(3)° are ~30° smaller than for the phenolate ligand, and similar to other W-selenolate species.⁵⁰ The terminal sulfido is canted 103° away from the WSe₂ plane, smaller than

Table 4. Selected Bond Distances(Å) and Angles(deg) for Tp*WS(tdt)

W-S1	2.154(2)	W-S2	2.385(3)
W-S3	2.380(2)	W-N11	2.354(6)
W-N21	2.180(7)	W-N31	2.188(8)
S2-C2	1.781(8)	S3-C3	1.77(1)
C2-C3	1.43(1)		
S1-W-S2	101.03(9)	S1-W-S3	100.89(8)
S1-W-N11	169.1(2)	S1-W-N21	94.1(2)
S1-W-N31	94.1(2)	S2-W-S3	84.47(8)
S2-W-N11	86.8(2)	S2-W-N21	93.3(2)
S2-W-N31	164.5(2)	S3-W-N11	87.3(2)
S3-W-N21	165.0(2)	\$3-W-N31	89.2(2)
N11-W-N21	77.8(2)	N11-W-N31	78.7(2)
N21-W-N31	89.1(3)	W-S2-C2	103.2(3)
W-S3-C3	103.2(3)	S2-C2-C3	120.5(7)
S3-C3-C2	119.4(6)		

for Tp*WS(OPh)₂. The longer W–X bonds lower the orbital electronic repulsion in the first coordination sphere and the deviation from octahedral geometry is slightly reduced. The Se…Se intramolecular distance of 3.485 Å is within the van der Waals contact for these atoms. The trans influence of the sulfido ligand manifests in the lengthening of the W–N11 bond by ca. 0.17 Å compared with the other W–N bonds.

For Tp*WS(tdt), the W-S2 and W-S3 distances are 2.385(3) Å and 2.380(2) Å, respectively. The corresponding W-S-C angles are $103.2(3)^\circ$, which are marginally smaller than that for Tp*MoS(bdt) where bdt = benzene-1,2dithiolate(2–).¹⁴ The W atom rests 0.296 Å above the N_2S_2 equatorial plane. The W-S1 distance of 2.154(2) Å in $Tp^*WS(tdt)$ is shorter than that for $Tp^*WS(OPh)_2$ but longer than the corresponding bond length in Tp*WS(SePh)₂. The sulfido bond length is dependent on the size of the equatorial donor atom, with longer W-X bonds for the heavier chalcogens allowing the terminal sulfido to come closer to the W ion. The dihedral angle between the W-S1 bond and WS₂ plane also decreases. However, the trans influence remains invariant despite the shortening of the W-S1 bond because there is a concomitant lengthening of the W-N21 and W-N31 bonds due to the trans influence of S and Se. Therefore, the relative lengthening of the W–N11 bond is negligible.

The fold angle of the dithiolene ligand in Tp*WS(tdt)defined as the dihedral angle between the WS_2 and S_2C_2 planes-is 28.3°, larger than corresponding distortion in Tp*MoS(bdt) (25.3°) ,¹⁴ Tp*MoO(bdt) (21.3°) ,⁵¹ and Tp*WO(bds) (24.8°) .²⁶ Once erroneously attributed to a nonbonding interaction between the dithiolene carbons and the nearby 3-methyl group of Tp* (C11 in Figure 3),⁵¹ the foldangle has been identified as an important electronic effect: donation from out-of-plane π orbitals of the dithiolene sulfur atoms into vacant metal d orbitals. Seminal work by Fourmigué and co-workers,^{52,53} Lauher and Hoffman,⁵⁴ and Enemark and co-workers,^{55,56} has categorized the relationship between foldangle and metal oxidation state. Metals with a filled redox-active orbital configuration bear fold angles close to zero, while d⁰ systems possess large fold angles in the range of 30°-40°. 52,54 For d¹ systems, the fold angle has been found to rest anywhere between these two extremes. To date, structural studies have yet to conclusively relate the variation of fold angle with the electronic effects exacted by dithiolene substituents.

	W(V/IV)		W(VI/V)			
complexes	$E_{1/2}$ (V) ^{<i>a</i>}	$\Delta E_{\rm pp}~({ m mV})$	$I_{ m pa}/I_{ m pc}$	$E_{1/2}$ (V) ^{<i>a</i>}	$\Delta E_{\rm pp}~({ m mV})$	$I_{\rm pa}/I_{\rm pc}$
Tp*WSCl ₂	-1.235	71	0.92	0.578	66	1.02
Tp*WS(OPh)Cl	-1.475	67	0.91	0.107	65	1.08
Tp*WS(OPh) ₂	-1.748	69	1.10	-0.274	67	1.01
Tp*WS(SPh) ₂	-1.144	70	0.95	-0.114	67	0.99
Tp*WS(tdt)	-0.986	68	0.97	0.306	77	1.14
Tp*WS(qdt)	-0.789	68	0.91	0.593		
Tp*WS(SePh) ₂	-1.126	69	0.88	-0.201	65	1.03
^{<i>a</i>} Reduction potentials referenced to the $Fc^{+/0}$ couple.						

Table 5. Electrochemical Data for Tp*WSXY Complexes

Electrochemistry. All complexes possess a reversible cathodic process defined as a one-electron reduction from W(V) to W(IV). Peak current ratios (I_{pa}/I_{pc}) approach unity and the peak separation lies close the theoretical value for oneelectron (59 mV), as observed for internal ferrocene (Table 5). The complexes with monodentate ligands display a quasireversible anodic process (Figure S4), again defined as a oneelectron oxidation of the metal. This oxidation process is also quasi-reversible for Tp*WS(tdt) but irreversible for Tp*WS-(qdt) (Figure S4). These bidentate sulfur-donor ligand complexes constitute a small group with exceptionally high reduction potentials (-0.986 and -0.789 V for Tp*WS(tdt) and Tp*WS(qdt), respectively). The other compounds are reduced at considerably more negative potentials. The oxygendonor ligand species are oxidized at the lowest potentials, consistent with a highly metal localized ground state. The complexes Tp*WS(SPh)₂ and Tp*WS(SePh)₂ displayed very similar redox behavior.

Several factors impact on reduction potentials in solution. These include the effective nuclear charge on the metal ion, viz., oxidation state, and donor/acceptor effects, the energy of the redox-active orbital and electronic relaxation.⁵⁷ The redoxactive orbital is the "nonbonding" $d_{r^2-v^2}$ SOMO, the energy of which is sensitive to changes in the equatorial ligand field. Thus, strong field Cl and O-donor ligands raise the energy of $d_{x^2-\nu^2}$ making reduction more difficult, while weak field S- and Se-donors lower it leading to more facile reduction. Moreover, soft ligands would stabilize W(IV) relative to W(V) and provide a favorable electronic relaxation energy for the reduction of complexes bearing soft versus hard ligands. Overall, potentials shift more positive when a terminal sulfido replaces an oxo ligand (Figure 6). The shift is more substantial for the hard-donor sulfido-W(V) complexes (X/Y = Cl, OPh)than those with softer coligands (XY = SPh, SePh, tdt, qdt). A similar positive shift is observed when comparing Tp*WOSX and Tp*WS₂X (X = Cl, OPh, SPh, SePh) complexes.^{27,58} This



Figure 6. Comparison of the W(V/IV) reduction potentials for Tp*WEXY (E = O, S; X/Y indicated). Data for Tp*WOXY compounds are taken from ref 26.

observation is attributed to a combination of factors most notably a reduction in the effective nuclear charge and an increase in orbital energies due to the increased level of covalency in the sulfido species, as corroborated by sulfur Kedge XAS data (vide infra). This appears to be the first time this effect has been reported in W(V) chemistry. Biologically, the dithiolene ligand is thought to electronically buffer the metal center against stark alterations in the redox environment,^{56,59} such as the loss of an oxo ligand and concomitant two-electron reduction of the metal during catalytic turnover.

The potential of the Mo(V/IV) reduction of Tp*MoS(PP)₂ is 0.4 V more positive than that observed for Tp*WS(OPh)₂.¹⁵ A similar 0.4 V difference was observed for related oxo-W(V) and oxo-Mo(V) complexes.²⁶ This metal-dependent effect may be ascribed to changes in the energy of the $d_x^2_{-y}^2$ SOMO which are primarily a result of relativistic effects. These are important contributors to electronic structure in W complexes, in destabilizing the 5d orbitals relative to the 4d orbitals of Mo, which in turn enhances bond ionicity and stabilization of high oxidations states for the heavier metal.⁷

X-ray Absorption Spectroscopy. Sulfur K-edge experiments were recorded on solid samples of the Tp*WSXY (X = Y = Cl, OPh, SPh, SePh; XY = tdt, qdt) series. The spectra presented in Figure 7 are divided into two groups: the first comprises Tp*WSCl₂, Tp*WS(OPh)₂, and Tp*WS(SePh)₂, where there is only one sulfur atom; the second group of Tp*WS(SPh)₂, Tp*WS(tdt), and Tp*WS(qdt) includes additional features from the equatorial (di)thiolate ligands.

All spectra are dominated by very intense low-energy absorptions just above 2467 eV due to dipole-allowed transitions from the core level to excited states having substantial sulfur p- and metal d-orbital character (Table S8). The appearance of a dominant pre-edge peak at ca. 2468 eV is typical of terminal sulfido ligation (Table 6), having been identified in the spectra of Tp*MoOS(OAr) (OAr = alkyl substituted phenolates),⁶⁰ Tp*MoSXY {X = Y = Cl, OPh, PP; XY = catecholate, bdt \int_{14}^{14} Tp*WOSX and Tp*WS₂X (X = Cl, OPh, SPh, SePh, (-)-mentholate).²⁷ The peak width (fwhm) is considerably greater than the expected best resolution of 0.8 eV (measured for the 1s $\rightarrow \pi^*(3b_1)$ transition of gaseous SO₂) indicating overlapping transitions to single or degenerate levels. The spectra of Tp*WSCl₂, Tp*WS(OPh)₂ and Tp*WS- $(SePh)_{2}$, have a second pre-edge peak at ~2471 eV with a similar fwhm but significantly weaker in intensity. This spectral profile is identical to that reported for Tp*MoSXY (X = Y = Cl, PP; XY = cat), ^{14,20} albeit shifted ~1.5 eV to higher energy due to the presence of the 5d metal ion. The transitions are readily assigned using the LF splitting diagram for the $\{W \equiv S\}^{3+}$ unit shown in Figure 8. There are two acceptor levels with sizable sulfur content: the near degenerate W \equiv S π^* MOs comprising



Figure 7. Normalized S K-edge spectra for (a) Tp^*WSCl_2 , (b) $Tp^*WS(OPh)_2$, (c) $Tp^*WS(SPh)_2$, (d) $Tp^*WS(tdt)$, (e) $Tp^*WS-(qdt)$, and (f) $Tp^*WS(SePh)_2$.

Table 6. Ex	perimental	and	Calculat	ed S	K-Pre-Edge
Transition 1	Energies				

	transition	energy	
complex	experimental calculated		assignment
Tp*WSCl ₂	2467.8	2467.7	$1s \rightarrow d_{xz,vz}$
	2471.0	2470.5	$1s \rightarrow d_{z^2}$
Tp*WS(OPh) ₂	2467.7	2467.6	$1s \rightarrow d_{xz,yz}$
	2470.8	2470.6	$1s \rightarrow d_{z^2}$
Tp*WS(SPh) ₂	2467.6	2467.6	$1s \rightarrow d_{xz,yz}$
	2468.7	2469.8	$1s \rightarrow C-S \pi^*$
Tp*WS(tdt)	2467.7	2467.7	$1s \rightarrow d_{xz,yz}$
	2469.2	2469.7	$1s \rightarrow C-S \pi^*$
	2470.8	2470.4	$1s \rightarrow d_{z^2}$
Tp*WS(qdt)	2467.6	2467.7	$1s \rightarrow d_{xz,yz}$
	2469.2	2469.7	$1s \rightarrow C-S \pi^*$
	2470.1	2470.6	$1s \rightarrow d_{z^2}$
Tp*WS(SePh) ₂	2467.7	2467.6	$1s \rightarrow d_{xz,yz}$
	2470.5	2470.5	$1s \rightarrow d_{z^2}$
$Tp*WO(SPh)_2$	2468.3	2468.7	$1s \rightarrow d_{x^2-y^2}$
	2469.6	2469.8	$1s \rightarrow d_{xz,yz}$
	2471.4	2471.2	$1s \rightarrow C-S \pi^*$
Tp*WO(tdt)	2468.3	2468.4	$1s \rightarrow d_{x^2-y^2}$
	2470.2	2469.9	$1s \rightarrow d_{xz,yz}$
	2471.9	2471.4	$1s \rightarrow C-S \pi^*$
		2472.0	$1s \rightarrow d_{xy}$
Tp*WO(qdt)	2468.4	2468.5	$1s \rightarrow d_{x^2-y^2}$
	2470.0	2470.1	$1s \rightarrow d_{xz,yz}$
	2471.6	2470.9	$1s \rightarrow C-S \pi^*$
		2472.1	$1s \rightarrow d_{xy}$



Figure 8. Ligand field splitting manifold comparing the relative energies of the frontier orbitals of the $\{W\equiv O\}^{3+}$ and $\{W\equiv S\}^{3+}$ units in these pseudo- $C_{2\nu}$ symmetric complexes where the *z*-axis aligned parallel to the W–E bond and the *x*-axis bisecting the X/Y donor atoms.

overlap between the W $5d_{xz,yz}$ and $3p_{x,y}$ orbitals, and the W \equiv S σ^* MO consisting of W $5d_z^2$ and S $3p_z$ character (Table S8). Degeneracy is lifted in the W \equiv S π^* level when the disposition of the X/Y ligands becomes less symmetric, i.e., Tp*WSCl₂ has C_s symmetry; Tp*WS(OPh)₂ is C_1 symmetric. This results in an additional splitting of the W \equiv S π^* MOs that contributes to the broadening of the pre-edge peak to \sim 1.5 eV (fwhm). Timedependent (TD)-DFT calculation of the pre-edge spectrum reveals two additional contributions to line broadening. The first is polarization of the W≡S bond, where the presence of an unpaired electron (α -spin) in the $d_{x^2-y^2}$ SOMO stabilizes the α spin manifold compared to the corresponding β -spin one. This is apparent in the Mulliken spin density map, where residual β spin is found on the sulfido ligand for all complexes (Figure S5). The effect is most pronounced for Tp*WSCl₂, and the slight shoulder on the high energy side of the dominant preedge peak visualized in the second derivative plot (Figure S6) estimates the polarization at 0.65 eV. For the other complexes, the experimental splitting from polarization is 0.5 eV. The TD-DFT reproduction significantly underestimates this effect (Figure 9); the calculated splitting in $Tp*WSCl_2$ is 0.28 eV. The second contributing factor to the peak width is the hidden 1s $\rightarrow d_{x^2-v^2}^2$ excitation. Although nonbonding with respect to the sulfido ligand (Figure 8), it attains some S 3p character by mixing of the equatorial π -donor ligands (Table S8). Its overlap with the 1s \rightarrow d_{*xz*,*yz*} excitations, which is not observed in W \equiv O species, stems from the weaker ligand field generated by the terminal sulfido relative to the terminal oxo. (Figure 8). The calculated pre-edge spectra are an excellent match to the experimental data as all three complexes have similar S 3p content in the W \equiv S π^* and σ^* acceptor orbitals (Table S8). The relative intensity of the first two pre-edge peaks in Tp*WSCl₂ determined from pseudo-Voigt deconvolution is 3.4:1, and in agreement with the calculated ratio of 4:1 derived from the S content of the W \equiv S π^* and σ^* MOs. The 1s $\rightarrow d_{\pi^2}$ peak sits at the onset of the rising-edge which distorts the accuracy of this result.

The compounds $Tp*WS(SPh)_2$, Tp*WS(tdt), and Tp*WS(qdt) exhibit rich S K-edge spectra with overlapping transitions from three coordination sulfur atoms. As well as the ubiquitous terminal sulfido peak at 2467.6 eV, $Tp*WS(SPh)_2$ has a shoulder at 2468.7 eV, Tp*WS(tdt) a second pre-edge peak at 2469.2, and Tp*WS(qdt) two additional peaks at 2469.2 and



Figure 9. Comparison of the experimental (top) and calculated (bottom) S K-pre-edge spectra for Tp^*WSCl_2 , $Tp^*WS(OPh)_2$, and $Tp^*WS(SePh)_2$ obtained from ZORA-BP86 TD-DFT calculations. Calculated intensity in arbitrary units.

2470.1 eV. The peaks beyond 2470 eV are transitions to C–S π^* and C–S σ^* orbitals frequently observed in the spectra of dithiolate^{44,61} and thiolate⁶² complexes, and are best assigned as "rising" edge features because they are followed by transitions to the sulfur 4p levels, and finally the continuum.

The first pre-edge peak in each spectrum is broadened by lowering of symmetry, polarization of the W \equiv S bond, and the obscured 1s $\rightarrow d_{x^2-y^2}$ transition whose intensity is amplified by S 3p character from the equatorial ligands. Tp*WS(tdt) has a noticeably weaker first pre-edge peak than the other two. This suggests a degree of decomposition to the oxo-W(V) analogue, Tp*WO(tdt), presumably during sample shipping and handling at the synchrotron. Nonetheless, the spectral features are nearly identical to Tp*MoS(bdt), which exhibits two pre-edge peaks at 2466.6 and 2467.7 eV, and two rising-edge peaks 2470.2 and 2470.9 eV.¹⁴

The calculated spectra nicely reproduce the dominate $1s \rightarrow d_{xz,yz}$ transition but overestimate the energy of the other preedge features (Figures 10 and S24). For Tp*WS(SPh)₂, calculations suggest the second pre-edge peak stems from 1s $\rightarrow C-S \pi^*$ of the thiolate ligands, and then the $1s \rightarrow d_{z^2}$ transition to the W \equiv S σ^* MO. The second pre-edge peak in Tp*WS(tdt) and Tp*WS(qdt) is defined as the $1s \rightarrow C-S \pi^*$ excitation of the dithiolate ligand (denoted π_4).⁶³ This MO is stabilized in qdt compared to tdt by the electron withdrawing pyrazine moiety in the former, and responsible for the positive shift of the reduction potentials (Figure 6). To higher energy, the $1s \rightarrow d_z^2$ transition appears in the spectrum of Tp*WS(qdt) (Figure 10), and masked by the rising-edge in Tp*WS(tdt).

The S K-edge spectra of Tp*WO($(SPh)_2$, Tp*WO((tdt)), and Tp*WO(qdt) are shown in Figure 11, and overlaid with the corresponding sulfido compound. The pre-edge profile stems solely from the (di)thiolate ligands and have been used to corroborate the assignment of their sulfido analogues (vide supra). The first peak is defined as the 1s $\rightarrow d_x^2 - y^2$ transition, which is more intense in Tp*WO(SPh)₂ than either Tp*WO



Figure 10. Comparison of the experimental (top) and calculated (bottom) S K-pre-edge spectra for Tp*WE(qdt) (E = O, S) obtained from ZORA-BP86 TD-DFT calculations. Calculated intensity in arbitrary units.



Figure 11. Overlay of the normalized S K-edge spectra of (a) $Tp^*WO(SPh)_2$, (b) $Tp^*WO(tdt)$, and (c) $Tp^*WO(qdt)$ with their sulfido analogues depicted by the dashed line.

(tdt) or Tp*WO(qdt) due to the more flexible SPh ligands. For the dithiolene complexes, the first pre-edge peak for Tp*WO-(tdt) is significantly weaker than for Tp*WO(qdt) (Figure 11). The S 3p character in the $d_{x^2-y^2}$ SOMO stems from mixing of out-of-plane π MOs of the dithiolene brought about by folding of the ligand along the S…S vector (vide supra). The geometryoptimized structure shows a larger fold angle for Tp*WO(qdt) than Tp*WO(tdt), although further measurements are required to refine this correlation. Moreover, this first pre-edge feature is 0.3 eV lower than the corresponding peak in Tp*WO(SPh)₂, commensurate with their more positive reduction potentials (Figure 6).

The second feature is assigned to the $1s \rightarrow d_{xz,yz}$ transition, where the acceptor orbitals being the W=O π^* MOs have only a minor contribution from the equatorial sulfur donors (Table S8). This peak is considerably larger in Tp*WO(tdt) and Tp*WO(qdt) than Tp*WO(SPh)₂ on account on the rigid

structure of the dithiolene ligands giving better overlap with the $5d_{xz,yz}$ orbitals. The first transition occurs at similar energies for all oxo-W(V) complexes but the second feature occurs at energies 0.4–0.6 eV higher for the dithiolate complexes. This larger LF splitting is the result of a "chelate effect" and is responsible for the higher *g*-values for Tp*WO(tdt) and Tp*WO(qdt).²⁶

The third pre-edge peak is defined as the 1s \rightarrow C-S π^* excitation in each complex, although the large peak width suggests it overlaps with the 1s $\rightarrow d_{xy}(\sigma^*)$ transition (Table 6). Overall, these spectra are shifted to higher energy than their sulfido counterparts (Figure 11) because the d orbital manifold in the latter is more stabilized by the core hole. This is \sim 2.4 eV when comparing the position of the first pre-edge peak in Tp*WS(qdt) with the second in Tp*WO(qdt) which are the $1s \rightarrow d_{xz,vz}$ excitations. The core-hole effect is diminished in the energy 1s \rightarrow C-S π^* transition where the difference is 1 eV between oxo- and sulfido-W(V) analogues. The transition from the dithiolate sulfurs to the W \equiv S π^* MOs occurs at higher energies than the transition originating from the sulfido 1s orbital because the former has a deeper binding energy as a consequence of the uninegative charge of the thiolate sulfur compared to dinegative charge of the terminal sulfido ligand.⁶⁴

CONCLUSIONS

The first series of sulfido-W(V) complexes with the general formula Tp*WSXY has been synthesized via metathesis from Tp*WSCl₂ with ligand salts. This has facilitated spectroscopic and electrochemical interrogation of the complexes and comparisons with known oxo- $W(V)^{26}$ and sulfido- $Mo(V)^{12,14}$ analogues. These d¹ W(V) complexes range in color from yellow-orange to green, with the majority being dark brown. The electronic structure of the sulfido-W(V) unit is very similar to that of the sulfido-Mo(V) unit. Exchanging a terminal oxo for a sulfido ligand lowers the HOMO-LUMO gap by \sim 5000 cm⁻¹, leading to smaller g-values on account of the reduced LF splitting. The effect is offset by soft donor ligands (X,Y) cis to the terminal sulfido, where the difference in g-values and reduction potentials with oxo-W(V) analogues is minimized. The analysis of S K-edge spectra for this series trends with that observed for sulfido-Mo(V),14,20 with a dominant transition to the W \equiv S π^* MOs, albeit shifted \sim 1.5 eV to higher energy due to the larger 5d orbitals of W. The pre-edge region was assigned by comparison with analogous oxo-W(V) complexes and TD-DFT calculations, which revealed subtle variations in the $\{W \equiv S\}^{3+}$ covalency modulated by the donor atom type (O/S/Se) and denticity (e.g., SPh vs tdt) of the equatorial ligands.

Although the presence of a terminal sulfido ligand at the active site in tungstoenzymes has not been definitively ascertained, there is precedent among molybdoenzymes, specifically the all sulfur coordination sphere in two periplasmic nitrate reductases.³ Given the sulfur-rich, highly reducing cellular environments in which tungstoenzymes predominate, 1,2,5 it is conceivable that the sulfido ligand is chemically preferred over an oxo ligand in these proteins. This series of sulfido-W(V) complexes is now available for further studies employing advanced spectroscopic techniques, namely multifrequency EPR and magnetic circular dichroism, as much needed calibrants for examination of native systems.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.7b00331.

Electronic absorption spectra of Tp*WS(tdt) and Tp*WS(qdt); correlation plot of g_{iso} versus A_{iso} ; cyclic voltammograms of Tp*WS(SPh)₂ and Tp*WS(tdt); second derivative, pseudo-Voigt deconvoluted, and calculated S K-edge spectra; geometry optimized coordinates, salient bond distances and angles, Mulliken spin density plots, and atomic contributions to frontier orbitals (PDF)

X-ray crystallographic files in CIF format (CIF)

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Notes

The authors declare no competing financial interest.

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