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Dioxotungsten(VI) Complexes of Hydrotris(3,5-dimethylpyrazol-1-yl)borate Including the X-ray Crystal Structure of the Tungsten Selenophenolate Complex *cis*-$\{\mathrm{HB(Me_2C_3N_2H)_3}\}\mathrm{WO_2(SePh)}$

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The syntheses, and spectroscopic, structural and electrochemical properties of *cis*-dioxotungsten(VI) complexes $\mathrm{LWO_2X}$ [L = hydrotris(3,5-dimethylpyrazol-1-yl)borate; X = $\mathrm{Cl^-}$, $\mathrm{NCS^-}$, $\mathrm{OMe^-}$, $\mathrm{O_2CH^-}$, $\mathrm{OPh^-}$, $\mathrm{SPh^-}$, $\mathrm{S_2PPh_2}$-S^-, $\mathrm{SePh^-}$] are described. Reaction of $\mathrm{LWO_2Cl}$ with group 1 salts $\mathrm{M^IX}$ and 18-crown-6 in refluxing toluene was employed in the syntheses of derivatives with X = $\mathrm{NCS^-}$, $\mathrm{OPh^-}$, $\mathrm{SPh^-}$, and $\mathrm{SePh^-}$, while reaction of $\mathrm{LWO_2(SePh)}$ with methanol and $\mathrm{LWO_2(SPh)}$ with formic acid yielded $\mathrm{LWO_2(OMe)}$ and $\mathrm{LWO_2(O_2CH)}$, respectively. The complex $\mathrm{LWO_2(S_2PPh_2}$-$S)$ was prepared by reacting $\mathrm{LW(S_2PPh_2}$-$S)\mathrm{(CO)_2}$ with pyridine *N*-oxide. The complexes exhibit two $\nu(\mathrm{WO_2})$ infrared bands, at 935−960 $\mathrm{cm^{-1}}$ and 900−915 $\mathrm{cm^{-1}}$, and ^{1}H NMR spectra consistent with C_s symmetry. Orange crystals of *cis*-$\mathrm{LWO_2(SePh)}$ are monoclinic, space group $P2_1/c$, with a = 18.385(6) Å, b = 8.102(1) Å, c = 18.284(5) Å, β = 117.15(2)°, V = 2423(2) Å^3, and Z = 4. The structure was solved by direct methods and refined to R = 0.035 (R_w = 0.033) for 3668 reflections with $I \geq 3.0\sigma(I)$. The mononuclear complex exhibits a distorted octahedral coordination sphere composed of a selenophenolate ligand [W−Se = 2.535(1) Å], two terminal oxo groups [W═O = 1.716(4) and 1.721(4) Å], and a facially tridentate L ligand. In acetonitrile, the complexes undergo a one-electron reduction at very cathodic potentials ($E_{1/2}$ = −1.71 to E_{pc} = −1.05 V vs SCE), some 560−620 mV more negative than observed for analogous molybdenum complexes (*Inorg. Chem.* **1996**, *35*, 7508). The complexes are very stable and do not participate in clean oxygen atom transfer or coupled electron−proton transfer reactions.

Introduction

There is growing evidence for the presence of oxotungsten centers in many pterin-containing tungsten enzymes.[2,3] Indirect evidence for oxo ligation was obtained from the crystal structure of the aldehyde ferredoxin oxidoreductase from *Pyrococcus furiosus* (*P. furiosus*, Pf-AOR)[4] and earlier EXAFS studies of an inactive form of this enzyme.[5] Recent EPR, variable temperature MCD, and further EXAFS studies of this and related enzymes provide direct spectroscopic evidence for oxo ligation. Thus, despite considerable heterogeneity at the tungsten center at all oxidation levels, oxo and hydroxo (protonated oxo) ligands are invoked for all the catalytically competent W(V) and W(VI) forms of active Pf-AOR.[6] However, some forms of this enzyme are postulated to contain mercapto (protonated thio) ligands in place of hydroxo ligands, and there has been speculation that W−S redox and trithiolene ligation may be involved in the generation of a high-potential form of the enzyme.[6] Closely related but less well-studied enzymes also appear to contain oxotungsten centers; these include the formaldehyde ferredoxin oxidoreductases from *P. furiosus* and *Thermococcus litoralis* and various formate dehydrogenases (FDH).[2,3] Advances in the area of oxotungsten inorganic chemistry[7,8] are essential to a full understanding of the nature and biological role of these enzyme centers. Oxo complexes containing dithiolene and selenium donor ligands would appear to be particularly relevant as enzyme models.

Several groups have developed significant structural and functional models for various tungsten enzymes. Bis(dithiolene) dioxo−W(VI) and oxo−W(V) and −W(IV) complexes of the type $[\mathrm{W^{VI}O_2(dt)_2}]^{2-}$, $[\mathrm{W^{V}O(dt)_2}]^{-}$, and $[\mathrm{W^{IV}O(dt)_2}]^{2-}$ [dt = $\mathrm{S_2C_2(CN)_2}^{2-}$ (mnt),[9,10] $\mathrm{S_2C_6H_4}^{2-}$ (bdt),[11] $\mathrm{S_2C_{10}H_6}^{2-}$ (ndt)[12]] have been reported by Sarkar and Nakamura and their respective co-workers. The W(VI) complexes possess distorted octahedral structures, while the W(V) and W(IV) complexes are square pyramidal in geometry.[9−12] The mnt complexes exhibit a variety of reactions of biological relevance, including a ligand extrusion reaction between $[\mathrm{WO_2(mnt)_2}]^{2-}$ and $\mathrm{MoO_4}^{2-}$, the oxidation of crotonaldehyde to crotonic acid (cf., AOR),[10] and the reduction of $\mathrm{CO_2/HCO_3}^-$ to formate (eq 1, cf., FDH).[9] The complex

$$[\mathrm{WO(mnt)_2}]^{2-} + \mathrm{HCO_3}^- \rightarrow [\mathrm{WO_2(mnt)_2}]^{2-} + \mathrm{HCO_2}^- \tag{1}$$

$$[\mathrm{WO_2(bdt)_2}]^{2-} + \mathrm{PhCH(OH)COPh} \rightarrow [\mathrm{WO(bdt)_2}]^{2-} + \mathrm{PhCOCOPh} + \mathrm{H_2O} \tag{2}$$

$[\mathrm{W^{VI}O_2(bdt)_2}]^{2-}$ cleanly oxidizes benzoin to benzil in a reaction

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(eq 2) which closely resembles enzyme processes.[11,13] On the basis of an observed deuterium isotope effect, the rate determining step is proposed to involve abstraction of the α-hydrogen atom of the benzoin by an oxo ligand of $[WO_2(bdt)_2]^{2-}$.[13] The $[WO_2(dt)_2]^{2-}$ complexes do not readily undergo classic oxygen atom transfer reactions with, for example, PPh_3. Finally, the related non-dithiolenic complex $[WO_2\{O_2CC(S)Ph_2\}_2]^{2-}$ is capable of oxidizing benzoin to benzil but does not react with PPh_3 or thiophenol at 25−60 °C (cf., Mo analogue, which undergoes reactions with all three reagents).[14] This complex also catalyzes the oxidation of benzoin by nitrate.[14] These very important model studies have not been augmented by any extensive, systematic studies of dioxo−W(VI) chemistry.

Here, we report the synthesis and spectroscopic, structural, and electrochemical properties of a wide range of *cis*-dioxotungsten(VI) complexes containing the tripodal N_3-donor hydrotris(3,5-dimethylpyrazol-1-yl)borate ligand (L). The spectroscopic and electrochemical properties of the complexes as a function of the ligands X are documented, and the crystal structure of $LWO_2(SePh)$ is described. Aspects of the reactivity of these complexes are also reported. The results are consistent with the general chemical and electrochemical characteristics of oxotungsten complexes, as defined by the pioneering work of Spence,[15] Wieghardt,[16] Holm,[17] and others.[18] Further interest in complexes of this type stems from their use as starting materials for novel oxo−thio and bis(thio) complexes.[19−21]

A brief survey of the dioxomolybdenum and dioxotungsten chemistry of L provides a context for this work. A wide variety of molybdenum complexes of the type *cis*-$LMoO_2X$ have been prepared as models for pterin-containing molybdenum enzymes such as sulfite oxidase and nitrate reductase.[22−29] These complexes exhibit distorted octahedral structures and participate in a number of important oxygen atom transfer (OAT)[23−29] and coupled electron−proton transfer (CEPT) reactions;[26−29] these reactions involve biological substrates such as nitrate and dimethyl sulfoxide and lead to the generation of oxo−Mo(IV) and oxo−hydroxo−Mo(V) species of biological relevance. An extensive chemistry[22−29] and a single model exhibiting the important centers and reactions involved in dioxo−Mo(VI)-containing enzymes[28,29] have evolved from work in this area. A number of mononuclear dioxo−hydrocarbyl complexes of the type $LMoO_2R$ (R = Me, CH_2SiMe_3) have also been reported.[30,31] The first mononuclear dioxo−W(VI) complex of L to be reported was LWO_2Cl.[19] It has been employed in the synthesis of dioxo−hydrocarbyl complexes, LWO_2R (R = Me, Et, Ph),[19,30,32] and converted to analogous oxo-thio and bis(thio) derivatives, LWOSCl and LWS_2Cl.[19,20] As well, the selective oxyfunctionalization of the LWO_2R complexes by singlet oxygen and dioxirane has been described by Sundermeyer and co-workers.[33] More recently, the dioxo−hydroxo− and trioxo−W(VI) complexes $LWO_2(OH)$ and $[LWO_3]^-$ have been prepared and characterized.[30,33,34]

Materials and Methods

Reagents (AR grade or better) were used as supplied or were purified by standard procedures.[35] Potassium thiocyanate was dried at 150 °C under a dynamic vacuum for 15 h. Literature methods were used for the preparations of KL,[36] HS_2PPh_2,[37] $(NEt_4)_2[WO_2(NCS)_4]$,[38] LWO_2Cl,[19,32] $LWO_2(OH)$,[34] $[WO_2Cl_2]_n$,[39] and $[WO_2Br_2]_n$.[39] Unless stated, reactions were performed under an atmosphere of pure dinitrogen, employing standard Schlenk techniques; workups were performed in air. Solvents were carefully dried, deoxygenated, and distilled before use.[35] Infrared spectra were obtained on Jasco A-302 or Perkin-Elmer 983G infrared spectrophotometers using pressed KBr disks with polystyrene as reference. ^1H NMR spectra were obtained using a Varian Unity 300 MHz FT NMR spectrometer, and electronic spectra were recorded on a Hitachi 150-20 UV spectrophotometer. Electron impact (70 eV) mass spectra were obtained on a JEOL AX 505H mass spectrometer. Column chromatography was performed using Merck Artikel 7734 Kieselgel 60. Microanalyses were performed by Atlantic Microlabs, Norcross, GA. Cyclic voltammetric samples were prepared as 5−10 mM solutions in dried 0.1 M Bu^nNBF_4/acetonitrile and run on a Cypress Electrochemical System II with 3 mm glassy carbon working electrode and platinum auxiliary and reference electrodes. Solutions were purged with dinitrogen before use and maintained under a dinitrogen atmosphere during experiments. Reported peaks were referenced to the saturated calomel electrode (SCE) by use of an internal standard (ferrocene; 0.390 V vs SCE).[40]

Syntheses

$LWO_2(NCS)$. Method 1. A suspension of LWO_2Cl (0.250 g, 0.456 mmol), anhydrous KNCS (0.50 g, 5.1 mmol), and 18-crown-6 (5 mg) was refluxed in toluene (15 mL) for 6 days. The solvent was removed on a rotary evaporator, and the residue was dissolved in 1:1 dichloromethane/water (100 mL). The dichloromethane phase was separated

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and dried over magnesium sulfate and then enriched in hexanes to precipitate white microcrystals. Yield: 0.167 g (64%). The analytical sample was recrystallized from 1,2-dichloroethane/hexane.

Method 2. A mixture of $(NEt_4)_2[WO_2(NCS)_4]$ (1.000 g, 1.41 mmol) and KL (0.498 g, 1.48 mmol) was refluxed in acetonitrile for 18 h, and the resulting purple mixture was poured into water (100 mL). The purple solid was filtered, washed with water and then methanol, and recrystallized (3 times) from dichloromethane/methanol to give white crystals. Yield: 0.119 g (15%). Anal. Calcd for $LWO_2(NCS)\cdot 0.35C_2H_4Cl_2$, $C_{16.7}H_{23.4}BCl_{0.7}N_7O_2SW$: C, 33.11; H, 3.89; N, 16.19. Found: C, 33.05; H, 3.84; N, 16.21 (the partial 1,2-dichloroethane of crystallization was confirmed by NMR spectroscopy).

$LWO_2(OPh)$. A suspension of LWO_2Cl (0.250 g, 0.456 mmol), NaOPh (0.064 g, 0.55 mmol), and 18-crown-6 (5 mg) was refluxed in toluene (15 mL) for 1.5 h and then filtered through a short bed of silica gel. The silica was washed with dichloromethane (8 × 5 mL), and the combined filtrate and washings were enriched in hexanes to precipitate white microcrystals. Yield: 0.228 g (83%). Anal. Calcd for $C_{21}H_{27}BN_6O_3W$: C, 41.61; H, 4.49; N, 13.87. Found: C, 41.67; H, 4.51; N, 13.77.

$LWO_2(SPh)$. A suspension of LWO_2Cl (0.500 g, 0.913 mmol), 18-crown-6 (5 mg), and NaSPh (0.130 g, 0.984 mmol) was refluxed in toluene (15 mL) for 13 h and then evaporated to dryness. The residue was extracted with dichloromethane (20 mL) and filtered through a short bed of silica gel, which was washed free of yellow color using dichloromethane. The filtrate and washings were enriched in hexane, and the resulting orange crystals were collected and washed with hexane. Yield: 0.466 g (82%). Anal. Calcd for $C_{21}H_{27}BN_6O_2SW$: C, 40.53; H, 4.37; N, 13.51; S, 5.15. Found: C, 40.28; H, 4.38; N, 13.44; S, 5.10. Electronic spectrum (CH_2Cl_2): λ, 415 (sh) nm (ϵ, 670 $M^{-1}\cdot cm^{-1}$).

$LWO_2(SePh)$. A stirred solution of Ph_2Se_2 (0.285 g, 0.912 mmol) in tetrahydrofuran (10 mL) was titrated with a tetrahydrofuran solution of $LiEt_3BH$ (1 equiv) until the yellow color disappeared. Under vacuum, the solvent was removed and the flask was heated at 50 °C for 20 min to remove Et_3B. The resulting LiSePh was dissolved in tetrahydrofuran (2 × 5 mL), and the solution was injected onto solid LWO_2Cl (0.500 g, 0.912 mmol). The resulting mixture was stirred for 24 h, filtered free of salts, and then reduced to 2 mL under vacuum. Orange crystals were precipitated with dry methanol. Yield: 0.317 g (52%). Anal. Calcd for $C_{21}H_{27}BN_6O_2SeW$: C, 37.69; H, 4.07; N, 12.56. Found: C, 37.75; H, 4.06; N, 12.58. Electronic spectrum (CH_2Cl_2): λ, 435 nm (ϵ, 615 $M^{-1}\cdot cm^{-1}$).

$LWO_2(OMe)$. A solution of $LWO_2(SePh)$ (0.110 g, 0.164 mmol) in dichloromethane (20 mL) was treated with methanol (5 mL) and stirred in air in a stoppered flask for 17 h. The resulting pale yellow solution was reduced to dryness, and the residue was redissolved in dichloromethane (3 mL) and eluted on a 20 cm silica gel column using dichloromethane as eluent. The light yellow and following colorless bands were discarded. The eluent was changed to tetrahydrofuran, and the product was collected as a colorless band. Recrystallization from dichloromethane/methanol produced white crystals. Yield: 0.076 g (85%). Anal. Calcd for $C_{16}H_{25}BN_6O_3W$: C, 35.32; H, 4.63; N, 15.45. Found: C, 35.44; H, 4.60; N, 15.34.

$LWO_2(O_2CH)$. A solution of $LWO_2(SPh)$ (0.150 g, 0.241 mmol) in toluene (10 mL) was treated with formic acid (10.0 μL, 0.265 mmol) and stirred for 3 days. White crystals were steadily deposited. The volume was reduced to 5 mL under vacuum, hexane (30 mL) was added, and the white crystalline product was filtered and washed with hexane. Yield: 0.131 g (97%). Anal. Calcd for $LWO_2(O_2CH)\cdot 0.5CH_2Cl_2$, $C_{16.5}H_{24}BClN_6O_4W$: C, 33.00; H, 4.03; N, 14.00. Found: C, 33.28; H, 4.04; N, 13.92. The formation of a CH_2Cl_2 hemisolvate from CH_2Cl_2/hexane was confirmed by NMR.

$NH_4[S_2PPh_2]$. Ammonia gas was passed through an aerobic solution of HS_2PPh_2 (2.00 g, 7.99 mmol) in toluene (20 mL) for 5 min, and then hexane (10 mL) was added. The white microcrystalline product was filtered, washed with hexane, and recrystallized from dichloromethane/hexanes. Yield: 2.14 g (100%). IR (KBr, cm^{-1}) ν(NH), 3050 s, br, 1630 m, 1480 w, 1470 w; ν(P−Ph), 1430 s; δ(NH), 1400 s, br, 1305 w, 1165 w, 1095 s, 1070 w, 1025 w, 995 w, 745 m, 700 s, 690 s, 640 s, 610 s, 600 w; ν(PS), 560 s, 490 m, 480 m, 445 w. ^1H NMR (MeOH-d_4): δ 7.30 (m, 6H), 8.03 (m, 4H). Anal. Calcd for $C_{12}H_{14}NPS_2$: C, 53.91; H, 5.28; N, 5.24. Found: C, 53.71; H, 5.31; N, 5.21.

Table 1. Crystallographic Data and Refinement Details for $LWO_2(SePh)$

empirical formula	$C_{21}H_{27}BN_6O_2SeW$	ρ_{calcd}, g cm^{-3}	1.834
fw	669.1	$F(000)$	1296
space group	monoclinic $P2_1/c$	μ, cm^{-1}	6.304
a, Å	18.385(6)	max/min transm factors	0.909/1
b, Å	8.102(1)		
c, Å	18.284(5)	no. of data measd	6161
β, deg	117.15(2)	no. of unique data	5983
V, Å^3	2423(2)	no. of obsd data [$I \geq 3.0\sigma(I)$]	3668
Z	4		
h, k, l range	$-23 < h < +21$,	R	0.035
	$-10 < k < 0$,	R_w	0.033
	$0 < l < +23$	ρ_{max}, e Å^{-3}	0.76
T (°C)	20		

$LW(CO)_2(S_2PPh_2)$. A mixture of $NH_4[S_2PPh_2]$ (1.234 g, 4.61 mmol) and $LWI(CO)_3$ (3.194 g, 4.62 mmol) was heated in toluene (30 mL) at 80 °C with stirring. The flask was left open to the nitrogen line. The reaction was stopped as soon as the dark color of $LW(CO)_3I$ was exhausted, and a thick, bright orange mixture was present (*ca.* 70 min). Further heating was avoided to prevent formation of $[LW(CO)_2]_2(\mu\text{-}S)$.[41] The mixture was stripped dry under a vacuum, and then the residue was extracted with dichloromethane and filtered free of NH_4I. Enrichment of the filtrate with methanol gave an orange precipitate, whose quality was improved by a second recrystallization. Yield: 3.147 g (88%). Smaller quantities were freed from traces of $[LW(CO)_2]_2(\mu\text{-}S)$ by eluting a dichloromethane solution on a 50 cm silica column with 3:2 dichloromethane/hexanes. After elution of two green bands, the eluent was changed to dichloromethane and the product was collected as a saffron-orange band. An independent synthesis and details of the characterisation of this complex appear elsewhere.[42]

$LWO_2(S_2PPh_2)$. A solution of $LW(CO)_2(S_2PPh_2)$ (2.570 g, 3.27 mmol) and pyridine *N*-oxide (0.96 g, 10.1 mmol) was stirred in 1,2-dichloroethane (20 mL) for 20 min and then at 55 °C for 40 min, and then was stripped dry. Recrystallization of the residue from dichloromethane/methanol gave white crystals. Yield: 1.85 g (74%). Anal. Calcd for $C_{27}H_{32}BN_6O_2PS_2W$: C, 42.54; H, 4.23; N, 11.02; S, 8.41. Found: C, 42.66; H, 4.21; N, 11.11; S, 8.32.

Crystal Structure of $LWO_2(SePh)$. Orange crystals of $LWO_2(SePh)$ were grown in darkness under nitrogen, by slow diffusion of dry methanol into a saturated dichloromethane solution of the complex. Intensity data for a crystal 0.08 × 0.23 × 0.26 mm were measured at room temperature (20 °C) on a Rigaku AFC6R diffractometer fitted with graphite monochromatized Mo Kα radiation, $\lambda = 0.710\,73$ Å. The ω: 2θ scan technique was employed to measure 6161 data up to a maximum Bragg angle of 27.5°. The data set was corrected for Lorentz and polarization effects,[43] and an empirical absorption correction was applied.[44] Relevant crystal data are given in Table 1.

The structure was solved by direct methods employing SHELXS86[45] and refined by a full-matrix least-squares procedure based on F.[43] Non-H atoms were refined with anisotropic displacement parameters, and H atoms were included in the model in their calculated positions (C−H = 0.97 Å). The refinement was continued until convergence, employing σ weights (i.e. $1/\sigma^2(F)$) for 3668 data with $I \geq 3.0\sigma(I)$. Final refinement details are collected in Table 1, and the numbering scheme employed is shown in Figure 1 (drawn with ORTEP[46] at 35% probability ellipsoids). The teXsan[43] package, installed on an Iris Indigo workstation, was employed for all calculations.

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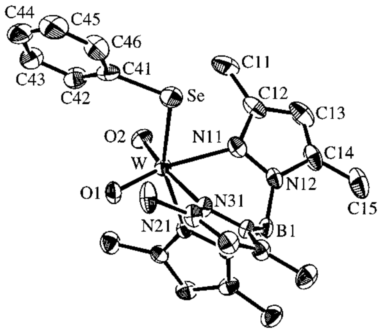

Figure 1. Molecular structure and atom labeling scheme for LWO_2(SePh). The labeling of the atoms in the pyrazole rings containing N(21) and N(31) parallels that shown for the ring containing N(11).

Results and Discussion

Synthesis and Characterization. Four different synthetic strategies were employed in the synthesis of the LWO_2X complexes. The first, which proved to be very limited in scope, involved the reaction of tungsten-containing starting materials with KL. Thus, reaction of $[WO_2Cl_2]_n$ and KL in *N*,*N*-dimethylformamide produced LWO_2Cl in *ca.* 70% yield,[19,32] while reaction of $(NEt_4)_2[WO_2(NCS)_4]$ with KL in refluxing acetonitrile produced LWO_2(NCS) in 15% yield; the latter reaction was complicated by the formation of large amounts of unidentified, intensely-colored byproducts. The reaction of $[WO_2Br_2]_n$ and KL in *N*,*N*-dimethylformamide or acetonitrile did not provide access to the analogous bromo derivative. The second strategy involved substitution of the chloride ligand of LWO_2Cl. The derivatives LWO_2X were prepared in 52−83% yields by reaction of LWO_2Cl with alkali metal salts M^IX (M^IX = KNCS, NaOPh, NaSPh, LiSePh). With one exception, the formation of these derivatives required forcing conditions (refluxing toluene) and was aided by small quantities of 18-crown-6. The exception was LWO_2(SePh), which formed within 24 h when LWO_2Cl and LiSePh were reacted (without crown ether) at room temperature in tetrahydrofuran. A higher yield of LWO_2(NCS) (64%) was obtained by this method, but the reaction was very sluggish (6 days). The scope of these reactions was also limited as LWO_2Cl failed to react with, e.g., NaOMe, Me_3SiNEt_2, AgF, NaF, KSeCN, KF, $KOBu^t$, KBr, NaS_2PPh_2, $NH_4S_2PPh_2$, or NaO_2CH, despite prolonged reflux in toluene and the presence of 18-crown-6. Analogous $LMoO_2X$ ($X = OPh^-$, SPh^-, S_2PPh_2-S^-) complexes are formed by reaction of $LMoO_2X$ ($X = Cl^-$, Br^-) with NEt_3 and HX,[25,26] but similar reactions were unsucessful starting from LWO_2Cl. The third strategy involved the substitution by hard ligands of the soft thiophenolate and selenophenolate ligands of LWO_2(SPh) and LWO_2(SePh). Complexes prepared in this manner were generally not accessible by methathesis reactions involving LWO_2Cl. Infrared and ^1H NMR studies showed that LWO_2(SePh) was converted in wet acetonitrile to LWO_2(OH)[34] and that LWO_2(SPh) reacted with phenol over 3 days in toluene to give LWO_2(OPh). The complexes LWO_2(SPh) and LWO_2(SePh) reacted in air with methanol to give LWO_2(OMe) and thiophenol or diphenyldiselenide, respectively; the reaction involving LWO_2(SePh) was the faster of the two. The formate complex $LWO_2(O_2CH)$ was obtained by reacting LWO_2(SPh) with 1.1 equiv of formic acid in toluene. While hard ligands displaced soft ones at dioxo−W(VI) centers, they did not appear to replace other hard ligands; thus, ^1H NMR studies showed no conversion of LWO_2(OPh) to LWO_2(OMe) in methanol over a 1 month period. Hard-for-soft ligand exchange may account for the air and water sensitivity of dioxo−W(VI) S-donor complexes such as $(phen)WO_2(SPh)_2$,[47] $WO_2(S_2CNR_2)_2$,[17,18a,b] and $[WO_2(bdt)_2]^{2-}$.[11] The displacement of a soft sulfur or selenium donor ligand from $[WO_x]^{n+}$ centers may conceivably relate to substrate binding or activation in tungsten enzymes.[48,49] Finally, dioxo complexes can be prepared by oxidative decarbonylation of low-valent carbonyl complexes.[42] The complex $LWO_2(S_2PPh_2)$ was not accessible from LWO_2Cl but could be prepared by oxidation of $LW(CO)_2(S_2PPh_2)$ with excess pyridine *N*-oxide in 1,2-dichloroethane. Use of a single equivalent of pyridine *N*-oxide led to the formation of red crystalline $LWO(CO)(S_2PPh_2)$.[50] The complex LWO_2(OH) was also prepared by oxidative decarbonylation of $LWI(CO)_3$, in this case by dimethyl sulfoxide.[34]

The diamagnetic, crystalline complexes are colorless ($X = NCS^-$, OMe^-, OPh^-, O_2CH^-, S_2PPh_2-S^-) or orange ($X = SPh^-$, $SePh^-$). They are soluble in chlorinated solvents and tetrahydrofuran and are appreciably soluble in aromatic hydrocarbons. The complexes LWO_2(EPh) (E = S, Se) are reasonably soluble in alcohols and diethyl ether, but the other complexes are insoluble in these solvents. All are insoluble in alkanes. These complexes are indefinitely stable as solids and in solution, with the exception of LWO_2(SPh) and LWO_2(SePh), which are sensitive to water, alcohols, and acids. The complex LWO_2(SPh) may be recrystallized in air from undried solvents but LWO_2(SePh) must be handled in and recrystallized from dry solvents.

Microanalytical and mass spectrometric data were consistent with the formulation of the complexes as monomers. Mass spectra generally exhibited an $[M]^+$ molecular ion peak cluster and were devoid of peak clusters at higher *m/z* (Table 2). The FAB mass spectrum of $LWO_2(O_2CH)$ (in a thioglycerol matrix) contained a molecular ion at *m/z* 558 (7%) and an $[M - CO_2]^+$ peak cluster at *m/z* 514 (22%).

The infrared spectra of the complexes (Table 2) exhibited bands characteristic of L [ν(BH) = 2540−2560 cm^{-1}] and the co-ligands X, as well as two strong bands at 935−960 cm^{-1} and 900−915 cm^{-1}, assigned to the symmetric (A′) and asymmetric (A″) stretches of the *cis*-$[WO_2]^{2+}$ fragment,[8] respectively. The thiocyanate ligand of LWO_2(NCS) is presumably N-bound, consistent with a strong ν(CN) infrared band at 2040 cm^{-1} [51] and the previously reported structure of $LMoO_2$(NCS).[23]

The ^1H NMR spectra of the complexes were consistent with molecular C_s symmetry (Table 2). As observed for $LMoO_2X$ and LWO_2R (R = hydrocarbyl),[24−33] the methine resonance of the unique pyrazole ring is deshielded with respect to the other methine protons for most of the new complexes. Exceptionally, where $X = SPh^-$ or $SePh^-$, these resonances are coincident. The ^1H NMR signatures of proton-bearing X groups are given in Table 2. Resonances typical of phenyl groups were observed for the $X = EPh^-$ and $S_2PPh_2^-$ complexes, the latter showing features due to unresolved ^{31}P coupling. The methoxide group of LWO_2(OMe) produces a singlet at δ 4.56 which is more deshielded than those of $\{HB(Me_2tz)_3\}MoO_2(OMe)$ (δ 4.38, $HB(Me_2tz)_3$ = hydrotris(3,5-dimethyl-1,2,4-triazolyl)borate) and $LMoO_2$(OMe) (δ 4.24),[26] indicating that the $[LWO_2]^+$ center is more electron withdrawing than $[LMoO_2]^+$. The formate

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Table 2. Characterization Data for LWO$_2$X Complexes

		infrared spectrum (KBr, cm^{-1})			^{1}H NMR spectrum, δ (multiplicity,[a] no. of H) (CDCl$_3$)		
X	*m/z* [M]$^+$ [b]	ν(BH)	ν(WO$_2$)	X ligand[c]	L (methyl)	L (methine)	X ligand[c]
Cl$^-$	548 (8%)	2560 m	960 s, 915 s	ν(WCl) 345 s	2.36 (3H), 2.38 (6H)	5.89 (2H)	
					2.69 (3H), 2.70 (6H)	5.92 (1H)	
NCS$^-$	571 (19%)	2550 m	945 s, 900 vs	ν(NCS) 2040 vs	2.38 (3H), 2.38 (6H)	5.91 (2H)	
					2.65 (9H)	5.94 (1H)	
OMe$^-$	544 (27%)	2555 m	935 s, 900 vs	ν(W−OMe) 525 m	2.35 (9H), 2.58 (6H)	5.84 (2H)	OCH$_3$$^-$, 4.56 (3H)
				ν(CO) 1100 s	2.78 (3H)	5.89 (1H)	
O$_2$CH$^-$	558 (7%)	2555 m	945 s, 910 vs	ν(C═O) 1705 vs	2.38 (6H), 2.39 (3H)	5.89 (2H)	O$_2$CH$^-$, 8.77 (^{1}H)
	514 (22%)[d]			ν(CO) 1185 br,s	2.49 (6H), 2.71 (3H)	5.97 (1H)	
OPh$^-$	606 (31%)	2540 m	940 s, 900 vs	1590 s, 1480 s	2.36 (6H), 2.39 (3H)	5.84 (2H)	phenyl, 6.97 (t, 1H)
				ν(CO) 1255 s	2.40 (6H), 2.85 (3H)	5.94 (1H)	7.13 (d, 2H), 7.32 (t, 2H)
SPh$^-$	622 (10%)	2550 m	945 s, 905 vs	1580 m, 1475 w	2.37 (3H), 2.39 (6H)	5.90 (3H)	phenyl, 7.10 (t, 1H)
					2.69 (3H), 2.76 (6H)		7.33 (t, 2H), 7.74 (d, 2H)
S$_2$PPh$_2$$^-$	762 (14%)	2550 m	950 s, 905 vs	ν(PPh) 1435 s	2.33 (3H), 2.36 (6H)	5.84 (2H)	phenyl, 7.43 (m, 6H)
				ν(PS) 525 s	2.54 (6H), 2.60 (3H)	5.86 (1H)	8.11 (m, 4H)
SePh$^-$	668 (7%)	2550 m	945 s, 905 vs	1575 w, 1475 m	2.36 (3H), 2.39 (6H)	5.90 (3H)	phenyl, 7.12 (t, 1H)
					2.66 (3H), 2.82 (6H)		7.30 (t, 2H), 7.46 (d, 2H)

[a] Singlet resonances unless otherwise indicated. [b] Electron impact mass spectral data, peak intensities indicated by percentage relative to strongest peak at 100%. [c] Assignments given where possible. [d] Obtained using fast atom bombardment mass spectrometry, peak due to [M− CO$_2$]$^+$.

Table 3. Selected Interatomic Distances and Angles for LWO$_2$(SePh)

Bond Distances (Å)			
W−Se	2.535(1)	W−O(1)	1.721(4)
W−O(2)	1.716(4)	W−N(11)	2.283(6)
W−N(21)	2.147(5)	W−N(31)	2.288(5)
Se−C(41)	1.940(7)		
Bond Angles (deg)			
Se−W−O(1)	99.7(2)	O(1)−W−N(31)	87.3(2)
Se−W−O(2)	99.6(2)	O(2)−W−N(11)	90.1(2)
Se−W−N(11)	83.1(1)	O(2)−W−N(21)	94.1(2)
Se−W−N(21)	157.0(1)	O(2)−W−N(31)	168.7(2)
Se−W−N(31)	84.5(1)	N(11)−W−N(21)	78.5(2)
O(1)−W−O(2)	102.2(2)	N(11)−W−N(31)	79.9(2)
O(1)−W−N(11)	166.6(2)	N(21)−W−N(31)	78.9(2)
O(1)−W−N(21)	95.3(2)	W−Se−C(41)	103.5(2)

proton of LWO$_2$(O$_2$CH) resonates at δ 8.77; similar chemical shifts are observed for the formate resonance of Mo(CO)$_2$(PEt$_3$)$_2$(O$_2$CH)$_2$ (δ 8.48) and Mo(CO)$_2$(PPh$_3$)$_2$(O$_2$CH)$_2$ (δ 8.14),[52] Mo(H)(O$_2$CH)(PMe$_3$)$_4$ (δ 8.05),[53] *N*,*N*-dimethylformamide (δ 7.90), and acetaldehyde (δ 9.80).[54]

The electronic spectra of the colorless complexes were devoid of bands in the range 400−900 nm. The yellow-orange colors of LWO$_2$(SPh) and LWO$_2$(SePh) arise from tailing of intense ultraviolet bands into the visible region. The complex LWO$_2$(SPh) has a shoulder at 410 nm (ϵ = 690 M^{-1}·cm^{-1}), and LWO$_2$(SePh) has a distinct band at 434 nm (ϵ = 610 M^{-1}·cm^{-1}). These features are atributed to ligand-to-metal charge-transfer transitions from filled S$_p$ or Se$_p$ orbitals to empty tungsten d orbitals; d → d transitions are impossible with these formally d^0 complexes.

Crystal Structure of LWO$_2$(SePh). The molecular structure of LWO$_2$(SePh) is presented in Figure 1, and selected interatomic distances and angles are listed in Table 3. The six-coordinate complex exhibits a distorted octahedral geometry and possesses approximate C_s symmetry. The tungsten center is coordinated by a facially tridentate L ligand, two *cis* oxo ligands, and a selenophenolate ligand. The W−O(1) and W−O(2) distances are equal within experimental error and are in the range typical of oxotungsten units.[8,55] The W−Se distance of 2.535(1) Å is slightly shorter than the average from available structures (of low-valent organometallic species rather than oxoselenolate complexes).[56−58] The W−N(11) and W−N(31) distances are ca. 0.14 Å longer than the W−N(21) distance as a result of the *trans* influence of the oxo ligands. The O(1)−W−O(2) angle of 102.2(2)° enhances favorable π interactions between the oxo and metal orbitals.[8,59,60] The W−N(21) and W−Se vectors are inclined away from the oxo ligands and an N(21)−W−Se angle of 157.0 (1)° pertains. The oxo and selenophenolate ligand are unsymmetrically disposed around the pseudo-3-fold axis associated with the LW fragment with O−W···B(1) and Se−W···B(1) angles of 122 and 109°, respectively. The N(*n*1)−W···B(1) angles fall in a narrow range around 47°. The W atom lies 0.8759(3) Å out of the plane defined by the O(1), O(2), and Se atoms and 1.5157(3) Å out of the plane defined by the N(*n*1) atoms. The pseudomirror plane of the molecule is defined by the pyrazole ring containing N(11) and atoms W and Se; the N(21)−W−Se−C(41) torsion angle is −174.8(4)°. The dihedral angle between this plane and the plane through the phenyl group is 45.6°, and the W−Se−C(41)−C(42) and W−Se−C(41)−C(46) torsion angles are −27.0(7) and 154.2(6)°, respectively. It has been noted that the aryl rings of thiophenolate ligands involved in significant π donation prefer to lie coplanar with the M−S−C plane to facilitate an extended π interaction between the aryl, sulfur, and metal π orbitals.[61,62] The observed skewing of the phenyl ring from the M−Se−C plane suggests that it is *not* involved in π bonding, consistent with the presence of strongly π-donating oxo groups.

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Table 4. Cyclic Voltammetric Data for LWO_2X Complexes[a]

X	$E_{1/2}$, V	E_{pc}, V	E_{pa}, V	I_{pa}/I_{pc}	ΔE_{pp}, mV	comments	other processes
$S_2PPh_2^-$	na	−1.05	no	0	na	irrev	no
NCS^-	na	−1.07	no	0	na	irrev	$E_{1/2} = -1.12$ V
Cl^-	na	−1.21	no	0	na	irrev	$E_{1/2} = -1.32$ V
O_2CH^-	−1.25	−1.29	−1.21	0.56	89	quasi-rev	$E_{1/2} = -1.38$ V
$SePh^-$	na	−1.34	no	0	na	irrev	no
SPh^-	−1.32	−1.35	−1.29	1.00[b]	64	quasi-rev	no
OH^-[34]	na	−1.50	no	0	na	irrev	$E_{pc} = -1.74$ V
OPh^-	−1.53	−1.57	−1.48	1.00	84	rev	no
OMe^-	−1.71	−1.76	−1.66	0.98	92	rev	no

[a] At $v = 100$ mV·s^{-1}. Compounds arranged in order of decreasing (more negative) E_{pc}. Abbreviations: irrev = irreversible, quasi-rev. = quasi-reversible, rev = reversible, na = not applicable, no = not observed. [b] This ratio diminishes at $v < 100$ mV·s^{-1}.

The complex is isomorphous and isostructural with $LMoO_2(SPh)$,[26] and both molecules, especially their LMO_2 fragments, are virtually superimposable (mean MO_2 atom displacement = 0.017 Å). The EPh^- fragments adopt the same orientation but overlap less perfectly upon superposition of the molecules (mean E and maximal C atom displacements, 0.13 and 0.32 Å, respectively); as well, the W−Se and Mo−S vectors are virtually collinear. The structure of $LWO_2(SePh)$ also closely resembles those of other dioxo−pyrazolylborate complexes of tungsten.[19,32]

Complex $LWO_2(SePh)$ is the first oxo selenolate of tungsten and only the second oxo selenolate of any metal to be structurally characterized, the previous example being $MoO\{Ph_2P(O)(CH_2)_2P(Ph)(CH_2)_2PPh_2\}(SeC_6H_2Me_3)_2$.[63] Indeed, mononuclear early transition metal selenolates are scarce, and the structures of only three tungsten complexes have been reported.[56−58]

Electrochemistry. With few exceptions, one-electron reduction of *cis*-$[MO_2]^{2+}$ complexes (M = Mo, W) leads to $[M^VO]^{3+}$ or $[M^V{}_2O_3]^{4+}$ species, rather than stable *cis*-$[M^VO_2]^+$ complexes.[26,64] Elimination and/or condensation reactions account for the formation of these thermodynamically favored species upon reduction.[26] However, ligands capable of retarding these reactions have permitted the chemical or electrochemical generation of long-lived, EPR-active *cis*-$[Mo^VO_2]^+$ complexes and the observation of reversible, one-electron reduction processes by cyclic voltammetry.[25−29,65−68] Very recently, compounds of the type $CoCp_2[LMo^VO_2X]$ (Cp = η^5-C_5H_5; X = ER, E = O, S; R = alkyl, phenyl) have been isolated and spectroscopically and structurally characterized.[69,70] Typically, *cis*-$[WO_2]^{2+}$ complexes are reduced at more cathodic potentials than their molybdenum counterparts,[9−11,15,16] and only one such complex, $[(Me_3tcn)WO_2Cl]Cl$ (Me_3tcn = 1,4,7-trimethyltriazacyclononane), has been reported to undergo a reversible reduction on the cyclic voltammetric time scale.[16]

We have used cyclic voltammetry to explore the electrochemistry of the LWO_2X complexes. Electrochemical data are summarized in Table 4. In acetonitrile, all complexes underwent at least one reductive process at potentials more cathodic than −1.05 V vs SCE. The principal (more positive) process is assigned to a one-electron reduction to the corresponding anion, $[LWO_2X]^-$. Typically, this process was irreversible or quasi-reversible. In only two cases, $LWO_2(OPh)$ and $LWO_2(OMe)$, was the process electrochemically reversible. For these complexes, I_{pa}/I_{pc} values approached unity and both E_p and ΔE_p were independent of scan rate v; ΔE_p values were close to that observed for the standard $[FeCp_2]^+/[FeCp_2]$ one-electron couple under the same conditions, and plots of I_{pc} vs $v^{1/2}$ were linear and passed through the origin. Electrochemically reversible one-electron processes are consistent with these observations.[71] The analogous molybdenum complexes exhibit similar electrochemical behavior.[29] At scan rates greater than 100 mV·s^{-1}, $LWO_2(SPh)$ undergoes an apparently reversible reduction with $E_{1/2} = -1.32$ V. At slower scan rates, peak current ratios steadily diminish, indicating a quasi-reversible process.[71] The irreversible reduction of $LWO_2(SePh)$ [cf., $LWO_2(OPh)$ and $LWO_2(SPh)$] may be due to cleavage of the W−Se bond or of the Se−C bond, as Se−C bond dissociation energies are substantially less than those for S−C and O−C bonds.[72] The electrochemical behavior of $LWO_2(O_2CH)$ is dependent on scan rate; a single quasi-reversible process ($E_{1/2} = -1.25$ V, ΔE_{pp} = 141 mV) is observed at 500 mV·s^{-1}, while, at slower scan rates, a second process at $E_{1/2} = -1.38$ V steadily replaces the first. At $v = 30$ mV·s^{-1}, the first process is irreversible and the second approaches reversibility. The reduction of $LWO_2(S_2PPh_2)$ was irreversible at all scan rates. Four complexes (X = NCS^-, Cl^-, O_2CH^-, OH^-) underwent a second reductive process at potentials more cathodic than the principal process. By analogy with $[MoO_2]^{2+}$ electrochemistry,[73] these processes are attributed to the formation of μ-oxo−W(V) dimers and possible further reduction to W(IV). All cyclic voltammograms were devoid of features at anodic potentials.

Consistent with earlier results,[9−11,15,16] the complexes LWO_2X undergo typically irreversible reduction at very negative potentials ($E_{pc} = -1.05$ to $E_{1/2} = -1.71$ V vs SCE). The E_{pc} values are ligand dependent (recognizing the caveat applying to the E_{pc} values for irreversible processes) and span a range of 710 mV (Table 4). This observation demonstrates that a high degree of electronic fine tuning of the $[WO_2]^{2+}$ center is possible by variation of co-ligands. The $S_2PPh_2^-$, halide and pseudohalide complexes are the most readily reduced, the soft ligand $SePh^-$ and SPh^- complexes exhibit intermediate reduction potentials, and the OPh^- and OMe^- complexes are the most difficult to reduce. All the reduction potentials are more

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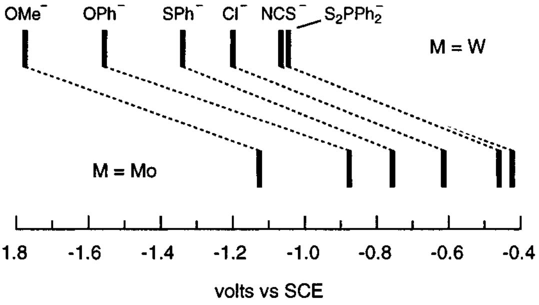

Figure 2. Comparison of the reduction potentials of LMO$_2$X complexes in MeCN (except LMoO$_2$Cl in CH$_2$Cl$_2$). The horizontal scale refers to $E_{1/2}$ or E_{pc} values for the M(VI)/M(V) process, represented by vertical bars for M = Mo (bottom) and W (top) complexes, with specified X ligands. The dashed lines connect the potentials of LMO$_2$X complexes having the same X ligand.

negative than those of potent biological reductants (e.g. NADPH, $E_0' = -0.5$ V; low-potential $[Fe_4S_4]^{n+}$ centers, $E_0' = -0.705$ V[74]), even allowing for significant overpotential effects and the absence of water ($E_0' = -0.42$ V). These considerations suggest that the $[WO_2]^{2+}/[WO_2]^+$ redox couple is biologically irrelevant; however, this does not preclude the biological exploitation of $[WO_2]^{2+}$ centers, as other reductive mechanisms are conceivable. Thus, $[WO_2(mnt)_2]^{2-}$ ($E_{pc} = -1.50$ V vs Ag/AgCl) can be reduced to $[WO(mnt)_2]^{2-}$ by compounds (H$_2$S, PhSH, dithiothreitol, dithionite) with E values significantly more positive than -1.50 V.[9-11] The facility of the latter reactions was interpreted in terms of the formation of precursor complex−substrate adducts with markedly more positive reduction potentials.[10]

The availability[29] of electrochemical data for the molybdenum complexes LMoO$_2$X (X = NCS$^-$, OMe$^-$, SPh$^-$, OPh$^-$) obtained under conditions identical to the data presented here, permits a direct comparison of the the two series of compounds (an earlier comparison contrasted the redox properties of LWO$_2$X in acetonitrile and LMoO$_2$X in dichloromethane[20]). Comparing $E_{1/2}$ or E_{pc} values as appropriate (Figure 2), the tungsten complexes undergo reduction at more cathodic potentials (560−620 mV more negative) than do their molybdenum analogues. This is in keeping with previous results obtained on pairs of Mo/W compounds or limited series of analogues.[15,16] These differences are a manifestation of the decrease in oxidizing power down a group of the periodic table.[18d] In the case of LMO$_2$X complexes, they reflect the relatively high energy of the LUMO orbital of the tungsten complexes compared to that of the molybdenum analogues (the LUMO is a principally metal based π^* combination of d$_\pi$ and oxo p ligand obitals). The different redox potentials of Mo(VI) and W(VI) complexes appear to dramatically influence enzyme turnover, the attenuation of the normal activity of molybdoenzymes upon substitution of Mo by W being attributed to this influence.

Reactivity Studies. OAT and CEPT reactions feature in mechanistic interpretations of the molybdoenzymes.[22,64] Many oxomolybdenum compounds,[22,64,75] and the dimethyl sulfoxide reductase from *Rhodobacter sphaeroides*,[76] catalyze OAT reactions, typically from donors such as Me$_2$SO to acceptors such as phosphines. Moreover, a number of catalytic OAT systems, some of which closely mimic enzyme systems, have been developed.[24,27-29,77-81] These are based on the interconversion of dioxo−Mo(VI) and oxo−Mo(IV) complexes (eq 3,

$$[Mo^{VI}O_2]^{2+} \underset{Me_2SO}{\overset{PR_3}{\rightleftharpoons}} [Mo^{IV}O]^{2+} \tag{3}$$

$$[Mo^{VI}O_2]^{2+} + [Mo^{IV}O]^{2+} \rightarrow \{[Mo^{V}O]_2(\mu\text{-}O)\}^{4+} \tag{4}$$

co-ligands excluded) without the formation of dinuclear μ-oxo−Mo(V) complexes via comproportionation of these species (eq 4). In contrast, dioxo−W(VI) complexes are reluctant to participate in OAT reactions and are generally inert toward reaction with phosphines.[17,18a,b,77] We now describe attempts to reduce the LWO$_2$X complexes using phosphines and benzoin.

At sub-reflux temperatures in a variety of solvents, there was no reaction between LWO$_2$Cl and PPh$_3$ or PBu$^n{}_3$. This is in direct contrast to the facile reactions of phosphines with the dioxo−Mo(VI) and thio−W(VI) analogues, LMoO$_2$X,[25,26,28,29] LWOSX,[21] and LWS$_2$X.[21] The breaking of Mo═O (bond strength *ca.* 98 kcal·mol^{-1}) and W═S (*ca.* 82−92 kcal·mol^{-1})[21] but not W═O (>138 kcal·mol^{-1}) bonds in reactions with PPh$_3$ is in accord with thermodynamic expectations.[82] Indeed, the very similar bond energies of P═O (*ca.* 126−139 kcal·mol^{-1} [83]) and W═O (>138 kcal·mol^{-1}) bonds may account for the difficulty in reducing $[WO_2]^{2+}$ centers using phosphines. In refluxing acetonitrile, LWO$_2$Cl reacted with PPh$_3$ over a 1 week period to give a deep red solution, but the red species could not be isolated or identified. A similar reaction in refluxing tetrahydrofuran (PPh$_3$, 3 days) resulted in the isolation of unreacted LWO$_2$Cl. In refluxing pyridine (115 °C), LWO$_2$Cl reacted with PPh$_3$ in 3 h to produce an intensely colored maroon solution. Chromatographic (aerobic or anaerobic) workup led to the isolation of $[LWO_2]_2(\mu\text{-}O)$ (*ca.* 35%), blue LWOCl$_2$, white LWO$_2$Cl, and a mixture of two unidentified orange oxo species [ν(W═O) = 965 (s) cm^{-1}] (*ca.* 40 mg from 0.50 g of LWO$_2$Cl). The purple color of these solutions may reflect the presence of a mixture of orange and blue products. Having failed to isolate putative LWOCl(py) on workup, attempts were made to trap this complex. Reflux of the maroon solution obtained by reacting LWO$_2$Cl with PPh$_3$ in pyridine with either Me$_3$SiS$_2$CNEt$_2$ (3.5 h) or NaO$_2$PPh$_2$/18-crown-6 (2.5 h) produced no LWO(S$_2$CNEt$_2$) or LWO(O$_2$PPh$_2$). Reflux of the maroon solution with anhydrous NaS$_2$CNEt$_2$/18-crown-6 for 1 day produced only a 1.4% yield of LWO(S$_2$CNEt$_2$);[21] the major product of this reaction was again $[LWO_2]_2(\mu\text{-}O)$.[34] The formation of OPPh$_3$ was confirmed by infrared spectroscopy of the filtrate residue. While it is assumed that LWO(S$_2$CNEt$_2$) is formed in this reaction from transient "LWOCl(py)", it is conceivable that this complex instead forms by reaction of

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NaS_2CNEt_2 with $LWOCl_2$ or the orange oxo products of these reactions, casting further doubt on the intermediacy of LWOCl(py). As $LWO(S_2PPh_2)$ is more robust than $LWO(S_2CNEt_2)$,[21] the reaction of these LWOCl(py) solutions with $NH_4S_2PPh_2$ was attempted. After 6 h of reflux, thin layer chromatography indicated the formation of the same products observed in the previous reactions with $Me_3SiS_2CNEt_2$. After 4 days, new red and yellow products had formed but no $LWO(S_2PPh_2)$ was detected at any stage of the reaction. The yellow product was identified as $LWS(\mu\text{-}S)_2WS(S_2PPh_2)$.[21]

Reaction of $LWO_2(S_2PPh_2)$ with PMe_2Ph in refluxing toluene led to the formation of seven species after 18 h, as judged by TLC (silica, CH_2Cl_2). There was no trace of the expected product $LWO(S_2PPh_2)$. However, a light orange product was isolated by chromatography; its infrared spectrum exhibited the strong $\nu(WO_2)$ (940, 905 cm^{-1}) and $\nu(PPh)$ (1430 cm^{-1}) bands of the starting material but lacked the strong $\nu(PS_2)$ stretch at 565 cm^{-1}. This product was tentatively identified as the phosphinothiolate complex $LWO_2(SPPh_2)$, consistent with abstraction of a sulfur atom from the $S_2PPh_2^-$ ligand in preference to oxygen atom abstraction from the $[WO_2]^{2+}$ unit. The greater strength of W═O (138−161 kcal·mol^{-1}) bonds over P═S (*ca.* 82−92 kcal·mol^{-1}) bonds[83] is consistent with this observation. Other examples of phosphinothiolate complexes include $Cp_2Ti(SPPh_2)$[84] and $CpW[SP(Ph)\{N(SiMe_3)_2\}](CO)_2$.[85]

The α-hydroxyketone benzoin readily reduces $[WO_2(bdt)_2]^{2-}$ and $[WO_2\{O_2CC(S)Ph_2\}_2]^{2-}$ to the corresponding oxotungsten(IV) complexes. Parallel reactions were not observed between $LWO_2(OPh)$ and benzoin in refluxing pyridine (chosen to stabilize transient five-coordinate "LWO(OPh)") or between $LWO_2(S_2PPh_2)$ and less bulky 3-hydroxybutanone (acetoin) in refluxing benzene. These reactions remained colorless at all stages, and unchanged products were isolated.

In contrast to the disappointing outcomes of the reactions described above, the LWO_2X complexes react readily with boron sulfide to generate the corresponding oxo-thio- and bis(thio)−W(VI) complexes, LWOSX and LWS_2X.[19−21] Similarly, Yu and Holm[17] have reported the *in situ* generation of oxo−thio− and bis(thio)−W(VI) Schiff base complexes from their dioxo−W(VI) analogues.

Summary

An extensive series of dioxo−W(VI) complexes of the type LWO_2X has been prepared and characterized, and the first X-ray crystal structure of a (selenolate)oxotungsten complex has been determined. A variety of synthetic methodologies have been employed to generate *cis*-LWO_2X complexes containing hard halide and O- and N-donor ligands ($X = Cl^-$, NCS^-, OMe^-, OPh^-, and O_2CH^-), soft mono- and ambidentate S-donor ligands ($X = SPh^-$ and S_2PPh_2-S^-), and soft Se-donor ligands ($SePh^-$). The complexes have been thoroughly characterized, both spectroscopically and structurally. Electrochemical studies show that the W(VI)/W(V) reduction potentials of the LWO_2X complexes are extremely cathodic, being some 560−620 mV more negative than the corresponding potentials of analogous Mo complexes. The complexes are very stable and fail to participate in clean OAT and CEPT reactions. This behavior underscores the very considerable chemical and redox stability of the $[WO_2]^{2+}$ moiety.

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Supporting Information Available: An X-ray crystallographic file in CIF format is available on the Internet only. Access information is given on any current masthead page.

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