complex which results in the enhancement of the reactivity of the aliphatic carbon–sulfur bonds. Selective coupling of one dithioacetal group of bisdithioacetals can thus be achieved conveniently. This discovery has led to further investigation on the activation of thioethers as well as other C–X bonds.

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Supplementary Material Available: Experimental procedures and spectroscopic data (IR, ^{1}H and ^{13}C NMR, and HRMS) for compounds **13–20**, (1*E*,3*E*)-**23**, and (1*E*,3*E*)-**24** (3 pages). Ordering information is given on any current masthead page.

cis-Dioxobis(benzenedithiolato)tungsten(VI) and the Related Monooxotungsten(V) and -(IV) Complexes. Models of Tungsten Oxidoreductases

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Recently a variety of tungsten-containing enzymes have been found, e.g., formate dehydrogenase, carboxylic acid reductase (aldehyde oxidase), and aldehyde oxidoreductase (aldehyde ferredoxin oxidoreductase).[1-6] The EXAFS spectroscopic analysis of aldehyde oxidoreductase from *Pyrococcus furiosus* has suggested the presence of octahedral dioxotungsten(VI) species.[5,6] The metal center is considered to be surrounded by many thiolate ligands that include molybdopterin as those in the metal centers of molybdooxidases.[4,7-12] The molybdopterin is a dithiolene ligand connecting phosphate and pterin derivatives. The resonance Raman study on dimethyl sulfoxide reductase has suggested the chelating coordination of the dithiolate to a Mo(VI) center.[13] Similar coordination seems to be involved in the metal center of W-containing oxidoreductases.

Our successful synthesis of model oxotungsten complexes having a dithiolene-like skeleton is based on a novel method utilizing the low solubility of monooxotungsten(V) benzenedithiolate complex $(PPh_4)[W^VO(bdt)_2]$ (**1**),[14] excluding the preferred formation of $[W^V(bdt)_3]^-$ in the ligand-exchange reaction between

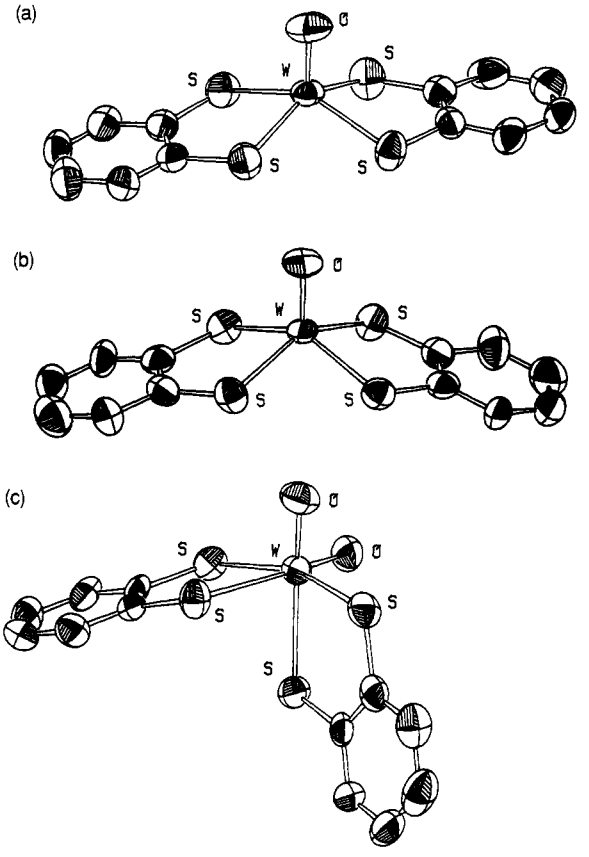

Figure 1. The ORTEP drawings of (a) $(PPh_4)[W^VO(bdt)_2]$ (**1**), (b) $(NEt_4)_2[W^{IV}O(bdt)_2]$ (**2b**), and (c) $(PPh_4)_2[W^{VI}O_2(bdt)_2]$ (**3a**).

$(PPh_4)[W^VO(SPh)_4]$[15] and bdt-H_2. Use of the above method allows extension to the synthesis of monooxotungsten(IV) thiolate complexes, which have been considered to be extremely unstable due to the negative W(IV)/W(V) redox potential in $(PPh_4)[W^VO(SPh)_4]$.[15] Thus, $(PPh_4)_2[W^{IV}O(bdt)_2]$ (**2a**) and $(NEt_4)_2[W^{IV}O(bdt)_2]$ (**2b**) were synthesized by a simple borohydride reduction of **1** or $(NEt_4)[W^VO(bdt)_2]$.[16] **2a** and **2b** readily react with trimethylamine *N*-oxide to give dioxotungsten(VI) complexes, $(PPh_4)_2[W^{VI}O_2(bdt)_2]$ (**3a**) and $(NEt_4)_2[W^{VI}O_2(bdt)_2]$ (**3b**), in ca. 70% yield.[17] The O-atom transfer to **2b** by trimethylamine *N*-oxide is relatively fast ($k_{obsd} = 5 \times 10^{-3}$ s^{-1} M^{-1}) at room temperature, compared with that ($k_{obsd} = 0.2 \times 10^{-3}$ s^{-1} M^{-1}) to $[Mo^{IV}O(bdt)_2]^{2-}$ under stoichiometric conditions. The reduction gives only trimethylamine and $(NEt_4)_2[W^{VI}O_2(bdt)_2]$ since the ^{1}H NMR spectrum of a solution of trimethylamine *N*-oxide and $[Mo^{IV}O(bdt)_2]^{2-}$ indicates clean conversion during the reduction. **2a** and **2b** exhibit a negative redox potential of W(IV)/W(V) at −0.63 V vs SCE in *N*,*N*-dimethylformamide (DMF), when compared with that (−0.35 V vs SCE)[18] of Mo-

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(14) $(PPh_4)[W^VO(SPh)_4]$ (250 mg, 0.26 mmol) prepared by the modification of a reported procedure[28] was suspended in 140 mL of 1,2-dimethoxyethane/diethyl ether (1/2, v/v). To the suspension was added bdt-H_2 (80 mg, 0.51 mmol) dropwise at room temperature. The mixture was stirred for 96 h, and the blue powder obtained was collected with filtration. Dark blue microcrystals formed by recrystallization from acetonitrile/diethyl ether/*n*-hexane in 48% yield. Anal. Calcd for $C_{36}H_{28}OPWS_4$: C, 59.07; H, 4.13. Found: C, 58.77; H, 4.13. UV–visible absorption: 353 (sh, 3600 M^{-1} cm^{-1}), 462 (1200), 618 nm (3100). ESR: $g_{av} = 1.960$, $A_{av} = 50 \times 10^{-4}$ cm^{-1}.
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(16) To an acetonitrile solution (200 mL) of $(PPh_4)[W^VO(bdt)_2]$ (**1**) (680 mg, 0.83 mmol) was added PPh_4BH_4 (1.2 g, 6.6 mmol). The solution was kept at −20 °C for 2 days. Precipitating red plate crystals of **2a** were collected by filtration, washed with acetonitrile, and dried under vacuum. Yield: 680 mg (71%). Anal. Calcd for $C_{60}H_{48}OP_2WS_4$: C, 62.17; H, 4.17. Found: C, 59.60; H, 4.14. **2b** was obtained by the NEt_4BH_4 reduction of $(NEt_4)[W^VO(bdt)_2]$. Anal. Calcd for $C_{28}H_{48}ON_2WS_4$: C, 45.40; H, 6.53; N, 3.78. Found: C, 45.32; H, 6.56; N, 3.88. ^{1}H NMR (DMF-d_7): δ 7.73 (q, 4 H, J = 5.4, 3.2 Hz), 6.68 (q, 4 H, J = 5.4, 3.2 Hz).
(17) To a DMF solution (70 mL) of **2a** (680 nm, 0.59 mmol) was added Me_3NO (90 mg, 1.2 mmol) at room temperature. The red solution turned yellow in 5 min. Diethyl ether (20 mL) was added dropwise after 2 h. Yellow needles obtained were collected by filtration and dried under vacuum. Yield: 490 mg (70%). Anal. Calcd for $C_{60}H_{48}O_2P_2WS_4$: C, 61.33; H, 4.10. Found: C, 61.50; H, 4.14. **3b** was synthesized by the same procedure. Anal. Calcd for $C_{28}H_{48}ONWS_4$: C, 44.44; H, 6.39; N, 3.70. Found: C, 44.21; H, 6.33; N, 3.74. ^{1}H NMR (DMF-d_7): δ 7.73 (q, 4 H, J = 5.4, 3.2 Hz), 6.68 (q, 4 H, J = 5.4, 3.2 Hz).

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(IV)/Mo(V) in $[Mo^{VI}O_2(bdt)_2]^{2-}$ in DMF.

$$[W^{IV}O(bdt)_2]^{2-} + Me_3NO \rightarrow [W^{VI}O_2(bdt)_2]^{2-} + Me_3N$$

The X-ray crystal structures of monooxotungsten(V) and -(IV) complexes **1** and **2b** and dioxotungsten(VI) complex **3a** are shown in Figure 1.[18] **1** and **2b** have square pyramidal structures that are isomorphous and isostructural with the reported structures of $(PPh_4)[Mo^{V}O(bdt)_2]$ and $(NEt_4)_2[Mo^{IV}O(bdt)_2]$.[19] The difference between W^{V}=O and Mo^{V}=O[20] distances shows the same trend as that between $(AsPh_4)[W^{V}OCl_4]$[21] and (PPh_4)-$[Mo^{V}OCl_4]$.[22] The mean W^{V}-S distance is 2.366 (3) Å,[23] which is shorter than that (2.377 (2) Å) of the corresponding Mo(V) complex.

2a and **2b** can be considered to be model complexes of reduced W oxidoreductase, which has been reported not to exhibit any ESR signal for a W(V) species.[5,6] The shorter W^{IV}=O (1.727 (9) Å) and the longer W^{IV}—S distances (mean 2.372 (4) Å) of **2b**[24] suggest the presence of a stronger π-interaction between W(IV) and sulfur.

On the other hand, **3a** is a structural model complex of the oxidized W enzymes which have been studied by the EXAFS analysis.[5,6] The X-ray analysis indicates that W^{VI}=O distances in **3a** are 1.727 (9) and 1.737 (6) Å. The W^{VI}-S distances trans to W^{VI}=O and cis to W^{VI}=O are 2.597 (4) Å (mean) and 2.425 (4) Å (mean), respectively. A trans influence is observed with the elongation of the bond distance of W^{VI}—S trans to W^{VI}=O. Similar elongation has been found also for $(NEt_4)_2[Mo^{VI}O_2$-$(bdt)_2]$.[25]

A DMF solution of **3b** exhibits significantly blue-shifted UV-visible absorption maxima at 323 nm (sh, 15000 M^{-1} cm^{-1}), 419 nm (2300), and 483 nm (1300) compared with those at 335 nm (7000), 430 nm (sh, 2400), and 533 nm (1400) for $(NEt_4)_2$-$[Mo^{VI}O_2(bdt)_2]$ in DMF. The excitation profile in the resonance Raman spectra indicates that the absorption maxima at 419 and 483 nm are due to the ligand-to-metal charge-transfer bands of the W^{VI}—S or W^{VI}=O bond.

3b exhibits a reduction peak at −1.34 V vs SCE whereas the corresponding $(NEt_4)_2[Mo^{VI}O_2(bdt)_2]$ complex shows a reduction peak at −0.97 V vs SCE in DMF. Under stoichiometric conditions, **3b** reacts with benzoin at room temperature to give $(NEt_4)_2$-$[W^{IV}O(bdt)_2]$ and benzil without side reaction as in the following equation but reacts extremely slowly with triphenylphosphine. The observed second-order rate (10×10^{-6} M^{-1} s^{-1}) at the initial stage of the stoichiometric reaction between **3b** and benzoin is similar to that (5×10^{-6} M^{-1} s^{-1}) of the corresponding dioxomolybdenum(VI) complex. The addition of an excess of benzoin (10 equiv) to $(NEt_4)_2[W^{VI}O_2(bdt)_2]$ results in formatioin of benzil in 90% yield.

$$[W^{VI}O_2(bdt)_2]^{2-} + PhCH(OH)COPh \rightarrow [W^{IV}O(bdt)_2]^{2-} + PhCOCOPh + H_2O$$

The formation of $(NEt_4)_2[W^{IV}O(bdt)_2]$ is ascribed to the lack of a comproportionation reaction between $[W^{VI}O_2(bdt)_2]^{2-}$ and $[W^{IV}O(bdt)_2]^{2-}$ to a binuclear W(V) complex probably due to inertness of $[W^{IV}O(bdt)_2]^{2-}$, different from the formation of $W_2O_3(pipdtc)_4$ (pipdtc = *N*-piperidinecarbodithioate) reported in the reaction between $WO_2(pipdtc)_2$ and trimethyl phosphite.[26]

cis-Dioxotungsten(VI) thiolate complex **3b** is thermodynamically stable. However, **2b** and **3b** show almost the same reductive and oxidative reactivities as the corresponding molybdenum complexes. Although each oxidation state of tungsten ion has an ionic radius similar to that of the corresponding molybdenum ion, the stronger π-interaction between W and S leads to significant differences in the chemical properties of the molybdenum complexes. The negative value of the redox potential of monooxotungsten(IV) thiolate complex probably contributes to the observed higher reductive reactivity in W oxidoreductase.

No participation of O-atom transfer in a W enzyme system has been considered owing to the difficulty of formation of the W(IV) species from dioxotungsten(VI) complexes.[26,27] Our results suggest that the chelating coordination of the dithiolene part of pterin cofactor shifts the W(IV)/W(V) redox potential to the positive side and the W(IV) state is involved in the catalytic cycle of W enzymes.

Supplementary Material Available: Tables of atomic positional and thermal parameters, bond distances, and bond angles for **1**, **2b**, and **3a** (43 pages); tables of observed and calculated structure factor amplitudes for **1**, **2b**, and **3a** (98 pages). Ordering information is given on any current masthead page.

(18) Crystal data for **1**: *Cc* (monoclinic), a = 12.719 (3) Å, b = 15.601 (3) Å, c = 16.529 (2) Å, β = 93.53 (1)°, Z = 4, V = 3273.7 (7) Å^3, μ = 39.24 cm^{-1}; 4959 unique reflections were measured, and 3574 with $I_o > 3\sigma(I)$ were used in the refinement to R = 0.041, R_w = 0.043. Crystal data for **2b**: $P2/n$ (monoclinic), a = 18.53 (2) Å, b = 9.231 (2) Å, c = 18.899 (3) Å, β = 93.45 (3)°, Z = 4, V = 3226 (3) Å^3, μ = 39.27 cm^{-1}; 7384 unique reflections were measured, and 5239 with $I_o > 3\sigma(I)$ were used in the refinement to R = 0.052, R_w = 0.075. For **3a**: $P2_1/c$ (monoclinic), a = 13.92 (1) Å, b = 16.672 (9) Å, c = 22.618 (7) Å, β = 103.66 (5)°, Z = 4, V = 5101 (6) Å^3, μ = 25.74 cm^{-1}; 12221 unique reflections were measured, and 5414 with $I_o > 3\sigma(I)$ were used in the refinement to R = 0.044, R_w = 0.045.

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Inhibition of Steroid Biosynthesis by Steroid Sulfonates

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Steroid sulfation plays a major role in the metabolism of steroids.[1] Steroid sulfates such as estrone sulfate and dehydroisoandrosterone sulfate are the predominant form of these steroids found in plasma[2] and are important intermediates in the biosynthesis of estrone in breast tumor cells.[3] Another abundant sulfated steroid, cholesterol sulfate, plays a number of crucial biochemical roles, including the stabilization of cell membranes.[4] This communication reveals a facile method for the synthesis of steroid sulfonates, which are nondegradable analogues of sulfated

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