to provide information on charge distribution.

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Supplementary Material Available: For both Fe(Cat-N-BQ)(Cat-N-SQ) and $Ni(Cat\text{-}N\text{-}BQ)_2$, tables listing crystal data and details of the structure determinations, anisotropic thermal parameters, and hydrogen atom locations (11 pages); listings of observed and calculated structure factors (85 pages). Ordering information is given on any current masthead page.

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Aspects of the Oxygen Atom Transfer Chemistry of Tungsten

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The oxygen atom transfer chemistry of most elements that form stable metal–oxo compounds, among them tungsten, is unsystematically developed at present. Reported here are certain aspects of the oxo transfer chemistry of tungsten Schiff base and N,N-disubstituted dithiocarbamate (R_2dtc) complexes, which are compared with the far more extensively examined chemistry of molybdenum with these ligands. A reproducible preparation of $WO_2(acac)_2$ (**4**, acac = acetylacetonate(1−)) is described. Compound **4** and the Schiff bases $H_2(sap)$ and $H_2(ssp)$ afford the complexes $WO_2(sap)$ (**5**, sap = 2-(salicylideneamino)phenolate(2−)), $WO_2(5\text{-}t\text{-}Busap)$ (**6**), and $WO_2(ssp)$ (**7**, ssp = 2-(salicylideneamino)benzenethiolate(2−)). When recrystallized from methanol, **6** gave $[WO_2(5\text{-}t\text{-}Busap)(MeOH)]\cdot MeOH$, which was obtained in monoclinic space group $P2_1$ with $a = 6.832$ (2) Å, $b = 11.299$ (4) Å, $c = 13.354$ (7) Å, $\beta = 99.02$ (4)°, and $Z = 2$. With use of 2997 unique data ($I > 3\sigma(I)$), the structure was refined to R (R_w) = 3.50% (4.80%). The complex contains a *cis*-dioxo group, a coordinated methanol molecule trans to one oxo ligand, and a *mer* arrangement of the tridentate ligand, whose oxygen atoms are mutually trans and are cis to the oxo ligands. The two W=O bond lengths differ by 0.12 Å. In contrast to their Mo analogues, **6**–**8** are unreactive to reductive oxo transfer with a number of basic tertiary phosphines under moderately forcing conditions. The compounds do undergo O/S substitution with $(Me_3Si)_2S$, yielding $WS_2(sap)$ and $WS_2(ssp)$. The $Mo^{VI}S_2$ *group* is unknown. Reactions of $W(CO)_3(R_2dtc)_2$ with $Mo_2O_3(Et_2dtp)_4$ (**14**, Et_2dtp = *O,O′*-diethyl dithiophosphate(1−)) afford in high yield $WO_2(R_2dtc)_2$ (R = Me, $R_2 = (CH_2)_5$ (**11**)) in examples of intermetal oxo transfer reactions. These compounds are much less stable than their Mo analogues and are very sensitive to water and dioxygen. The probable oxo donor is $MoO_2(Et_2dtp)_2$ (**16**), known to be in equilibrium with **14** and $MoO(Et_2dtp)_2$, which was isolated from the reaction. Compound **11** is unreactive to Ph_3P, in distinction to its Mo counterpart, which is relatively rapidly reduced in a strongly exothermic reaction. However, **11** is cleanly reduced by $(MeO)_3P$ to $W_2O_3((CH_2)_5dtc)_4$. The reaction sequence presumably follows that in Mo systems, viz., reduction to the $W^{IV}O$ complex followed by a fast reaction of this species with the starting complex to afford the μ-oxo $W^V{}_2O_3$ product. Certain thermodynamic features of these reactions are discussed, and it is shown that, in terms of a previously introduced oxo transfer reactivity scale, **16** is a moderately strong oxo donor. The collective observations reflect a greater thermodynamic barrier to the reduction of W(VI) vs Mo(VI). Accordingly, $W^{IV}O$ complexes, unless stabilized by π-acid ligands, should be strong oxo acceptors. Recent reports of the initial cases of $W^{IV} \rightarrow W^{VI}$ oxo transfer reactions are considered in terms of the reactivity scale.

Introduction

Of all elements, the oxygen atom transfer chemistry of molybdenum is the most extensively investigated and best understood. Comprehensive accounts of Mo-mediated oxo transfer reactions are available.[1,2] Our research in this field[2–10] has been motivated by the problem of the mechanism of action of a broad class of enzymes, the molybdenum oxotransferases (hydroxylases).[11,12] The two most widespread transformations are the primary oxo transfer reaction[1] (1), wherein XO/X functions as an oxo donor/acceptor and the oxidation state of the Mo atom is changed by 2 units, and the μ-oxo dimerization reaction (2).

$$Mo^{VI}O_2L_n + X \rightleftharpoons Mo^{IV}OL_n + XO \qquad (1)$$

$$Mo^{VI}O_2L_n + Mo^{IV}OL_n \rightleftharpoons Mo^{V}{}_2O_3L_{2n} \qquad (2)$$

For reaction 1 and similar processes, a thermodynamic reactivity scale for substrates X/XO has been devised.[1,5] Reaction 2 is a reversible equilibrium when L is a N,N-disubstituted dithiocarbamate or related chelating monoanionic sulfur ligand,[1,13] but more frequently it is an irreversible process. This reaction occurs unless it is impeded by the steric properties of the ligand[4–9,14] or unless the Mo(IV) product of reaction 1 is trapped by added ligand.[10,15,16] Ligand systems that have figured prominently in the oxo-transfer chemistry of molybdenum include the dithiocarbamates,[1] the sterically bulky tridentates[17] $L\text{-}NS_2$[4–9] and $HB(Me_2pz)_3$,[14] and the tridentate Schiff bases sap and ssp.[10,15,18,19]

Our recent analysis of metal-mediated oxo transfer reactions[1] makes evident the lack of systematic development of the atom

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(1) Holm, R. H. *Chem. Rev.* **1987**, *87*, 1401.
(2) Holm, R. H. *Coord. Chem. Rev.*, in press.
(3) Reynolds, M. S.; Berg, J. M.; Holm, R. H. *Inorg. Chem.* **1984**, *23*, 3057.
(4) Berg, J. M.; Holm, R. H. *J. Am. Chem. Soc.* **1985**, *107*, 917, 925.
(5) Harlan, E. W.; Berg, J. M.; Holm, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 6992.
(6) Caradonna, J. P.; Harlan, E. W.; Holm, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 7856.
(7) Holm, R. H.; Berg, J. M. *Acc. Chem. Res.* **1986**, *19*, 363.
(8) Caradonna, J. P.; Reddy, P. R.; Holm, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 2139.
(9) Craig, J. A.; Holm, R. H. *J. Am. Chem. Soc.* **1989**, *111*, 2111.
(10) Craig, J. A.; Harlan, E. W.; Snyder, B. S.; Whitener, M. A.; Holm, R. H. *Inorg. Chem.* **1989**, *28*, 2082.
(11) *Molybdenum Enzymes*; Spiro, T. G., Ed.; Wiley-Interscience: New York, 1985.
(12) Bray, R. C. *Q. Rev. Biophys.* **1988**, *21*, 299.
(13) (a) Matsuda, T.; Tanaka, K.; Tanaka, T. *Inorg. Chem.* **1979**, *18*, 454. (b) Tanaka, T.; Tanaka, K.; Matsuda, T.; Hashi, K. In *Molybdenum Chemistry of Biological Significance*; Newton, W. E., Otsuka, S., Eds.; Plenum: New York, 1980; pp 361–367.
(14) Roberts, S. A.; Young, C. G.; Cleland, W. E., Jr.; Ortega, R. B.; Enemark, J. H. *Inorg. Chem.* **1988**, *27*, 3044.
(15) Boyd, I. W.; Spence, J. T. *Inorg. Chem.* **1982**, *21*, 1602.
(16) Kaul, B. B.; Enemark, J. H.; Merbs, S. L.; Spence, J. T. *J. Am. Chem. Soc.* **1985**, *107*, 2885.
(17) Abbreviations: acac, acetylacetonate(1−); Cp*, pentamethylcyclopentadienyl(1−); Et_2dtp, *O,O′*-diethyl dithiophosphate(1−); $HB(Me_2pz)_3$, hydrotris(3,5-dimethylpyrazolyl)borate(1−); $L\text{-}NS_2$, 2,6-bis(2,2-diphenyl-2-sulfidoethyl)pyridine(2−); pip, piperidyl; pyO, pyridine *N*-oxide; R_2dtc, N,N-disubstituted dithiocarbamate(1−); sap, 2-(salicylideneamino)phenolate(2−); solv, solvent ligand; ssp, 2-(salicylideneamino)benzenethiolate(2−).
(18) Topich, J.; Lyon, J. T., III. *Polyhedron* **1984**, *3*, 55, 61.
(19) Topich, J.; Lyon, J. T., III. *Inorg. Chem.* **1984**, *23*, 3202.

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Table I. Absorption and Infrared Spectral Data for Molybdenum and Tungsten Compounds

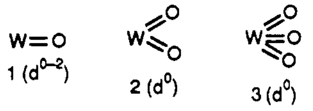
	λ_{max}, nm (ϵ_M)[a]		$\nu_{M(O/S)}$,[d] cm^{-1}	
	Mo	W	Mo	W
MO_2(sap)	349 (9430), 421 (5670)[f]	365 (5490), 406 (8000)[b]	905, 935	908, 951
MO_2(5-*t*-Busap)	350 (9800), 422 (5580)[f,g]	369 (6170), 413 (8350)	910, 940	911, 949
MO_2(ssp)	374 (6070), 452 (sh, 1360)[f]	371 (4780), 434 (2700)[c]	900, 934	919, 956
$MO_2(Me_2dtc)_2$[e]	299 (11 700), 378 (3350)	306 (5600)	898, 938	900, 940
$MO_2(pipdtc)_2$[e]	300 (13 700), 380 (4000)	307 (6400)	883, 918	899, 940
$M_2O_3(pipdtc)_4$[e]	374 (sh, 6800), 514 (13 000)[i]	327 (sh, 12 000), 506 (12 000)[j]	935	945
WS_2(sap)		363 (sh, 7120), 430 (sh, 4970)		510
WS_2(5-*t*-Busap)		368 (sh, 6800), 440 (3740)		500, 510[h]
WS_2(ssp)		375 (6320), 430 (3350)		510

[a] DMF solutions except as noted; see also Figure 2. [b] Also, 280 nm (13 200). [c] Also, 303 nm (13 100). [d] sap and ssp complexes in DMF solutions; others in KBr. [e] 1,2-Dichloroethane solutions. [f] Reference 10. [g] MeOH solution. [h] DMF adduct. [i] 3.5 mM. [j] 4.8 mM.

Table II. Crystallographic Data for $[WO_2(5\text{-}t\text{-Busap})(MeOH)]\cdot MeOH$

formula	$C_{19}H_{25}NO_6W$	space group	$P2_1$
fw	547.26	*T*, K	298
a, Å	6.832 (2)	λ, Å	0.710 69 (Mo Kα)
b, Å	11.299 (4)	ρ_{calcd} (ρ_{obsd}), g/cm^3	1.79 (1.76)
c, Å	13.354 (7)	μ, cm^{-1}	58.3
β, deg	99.02 (4)	$R(F_o)$, %	3.50
V, Å^3	1018.0 (7)	$R(F_o^2)$, %	4.80
Z	2		

transfer chemistry of all metals that form stable oxo complexes. Among these is tungsten, which has been shown to support the mononuclear functional groups W=O (**1**), WO_2 (**2**), and WO_3 (**3**).[1,20] There are very few documented oxo transfer reactions



of tungsten.[1] Among those one might anticipate is the counterpart of reaction 1, at least in the reverse direction. Here a ready oxidation of oxophilic W(IV) is probable when ligands stabilizing this oxidation state are absent. Likewise, certain W(II) compounds should be oxidizable to products containing groups **1** or **2**. One cause of the lack of information about tungsten-mediated oxo transfer is the dearth of well-characterized $W^{VI}O_2$ and $W^{IV}O$ compounds, although such reactions are of course not confined to these oxidation states. For example, there is only one report of $WO_2(R_2dtc)_2$ complexes,[21,22] and the reaction of one of these with tertiary phosphines is claimed to yield unidentified products.[21] In comparison, a number of $MoO_2(R_2dtc)_2$ complexes have been prepared, and they undergo clean reduction in reaction 1 with X = R_3P.[1] Further, no $W^{VI}O_2$ complexes with Schiff bases such as sap and ssp are known despite the large number prepared with molybdenum[10,15,18,23] and their demonstrated reactivity in atom transfer.[10,18,19] Other $W^{VI}O_2$ compounds, some of them organometallics, have been described,[24-26] but their oxo transfer reactivity has not been tested. The large majority of mononuclear $W^{IV}O$ compounds are stabilized by π-acid ligands such as tertiary phosphines and acetylenes[27-29] and are coordinatively saturated, and some are notably reactive.[29] We have initiated an examination of the oxo transfer reactions of tungsten. Because of the large body of information available on the structures and reactivities of corresponding complexes of molybdenum, the most obvious and yet the most meaningful comparisons, we have pursued the synthesis and reactivity of analogous tungsten compounds derived from dithiocarbamate and tridentate Schiff base (sap, ssp) ligand types. The leading results of that investigation are reported herein.

Experimental Section

Preparation of Compounds.[17] All operations were performed under a pure dinitrogen atmosphere unless otherwise noted. Solvents were dried by standard methods and degassed immediately before use. WO_2Cl_2 (Alfa), $W(CO)_6$ (Aldrich), and bromine (Fluka) were used as received. 2,4-Pentanedione (Aldrich) and trimethyl phosphite (Aldrich) were distilled prior to use. The Schiff bases H_2(ssp) and H_2(sap), and the 5-*tert*-butyl variant H_2(5-*t*-Busap), were prepared from equal molar quantities of salicylaldehyde or 5-*tert*-butylsalicylaldehyde (prepared by the Duff reaction[10,30]) and *o*-aminothiophenol or *o*-aminophenol in ethanol, followed by recrystallization of the crude products from hot ethanol. Anhydrous $Na(Me_2dtc)$ and Na(pipdtc) were prepared by the reaction of the corresponding amine and CS_2 in the presence of NaOMe in methanol and were recrystallized from THF/hexane. $MoO_2(pipdtc)_2$ was obtained from the reaction of equimolar amounts of piperidine and CS_2 in methanol in an ice bath, followed by the addition of $MoO_2(acac)_2$[31] in methanol. The yellow product was purified by recrystallization from dichloromethane/hexane. The compounds $Mo_2O_3(Et_2dtp)_4$,[32] $W(CO)_4Br_2$,[33] and $W(CO)_3(pipdtc)_2$ and $W(CO)_3(Me_2dtc)_2$[27a,34] were prepared by literature methods. Spectroscopic characterization data of new compounds are given below and in Table I; in NMR measurements the solvent was $Me_2SO\text{-}d_6$ unless noted otherwise.

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(20) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley-Interscience: New York, 1989; pp 172-173.

(21) Chen, G. J.-J.; McDonald, J. W.; Newton, W. E. *Inorg. Chim. Acta* **1976**, *19*, L67.

(22) Another compound of this type has recently been synthesized: Lee, L.-K.; Cooper, N. J. Manuscript in preparation.

(23) (a) Rajan, O. A.; Chakravorty, A. *Inorg. Chem.* **1981**, *20*, 660. (b) Topich, J. *Inorg. Chem.* **1981**, *20*, 3704. (c) Dey, K.; Maiti, R. K.; Bhar, J. K. *Transition Met. Chem.* **1981**, *6*, 346.

(24) (a) Drew, M. G. B.; Fowles, G. W. A.; Rice, D. A.; Shanton, K. J. *J. Chem. Soc., Chem. Commun.* **1974**, 614. (b) Ružič-Toroš, Ž.; Kojič-Prodič, B.; Gabela, F.; Šljukič, M. *Acta Crystallogr.* **1977**, *B33*, 692. (c) De Wet, J. F.; Caira, M. R.; Gellatly, B. J. *Acta Crystallogr.* **1978**, *B34*, 762. (d) Zheng, P.-J.; Cui, M.-F.; Gu, Y.-D.; Jin, X.-L. *Huaxue Xuebao* **1985**, *43*, 389. (e) Faller, J. W.; Ma, Y. *J. Organomet. Chem.* **1988**, *340*, 59.

(25) Rice, C. A.; Kroneck, P. M. H.; Spence, J. T. *Inorg. Chem.* **1981**, *20*, 1996.

(26) Feinstein-Jaffe, I.; Dewan, J. C.; Schrock, R. R. *Organometallics* **1985**, *4*, 1189.

(27) (a) Ward, B. C.; Templeton, J. L. *J. Am. Chem. Soc.* **1980**, *102*, 1532. (b) Templeton, J. L.; Ward, B. C.; Chen, G. J.-J.; McDonald, J. W.; Newton, W. E. *Inorg. Chem.* **1981**, *20*, 1248.

(28) (a) Carmona, E.; Sanchez, L.; Poveda, M. L.; Jones, R. A.; Hefner, J. G. *Polyhedron* **1983**, *2*, 797. (b) Levason, W.; McAuliffe, C. A.; McCullough, F. P., Jr. *Inorg. Chem.* **1977**, *16*, 2911. (c) Carmona, E.; Galindo, A.; Gutiérrez-Puebla, E.; Monge, A.; Puerta, C. *Inorg. Chem.* **1986**, *25*, 3804. (d) Carmona, E.; Galindo, A.; Guille-Photin, C.; Lai, R.; Monge, A.; Ruiz, C.; Sanchez, L. *Inorg. Chem.* **1988**, *27*, 488. (e) Carmona, E.; Galindo, A.; Guille-Photin, C.; Sanchez, L. *Polyhedron* **1988**, *7*, 1767. (f) Chiu, K. W.; Lyons, D.; Wilkinson, G.; Thornton-Pett, M.; Hursthouse, M. B. *Polyhedron* **1983**, *2*, 803. (g) Drew, M. G. B.; Page, E. M.; Rice, D. A. *J. Chem. Soc., Dalton Trans.* **1983**, 61. (h) Butcher, A. V.; Chatt, J.; Leigh, G. J.; Richards, P. L. *J. Chem. Soc., Dalton Trans.* **1972**, 1064. (i) Leipoldt, J. G.; Basson, S. S.; Roodt, A.; Potgieter, I. M. *Transition Met. Chem.* **1986**, *11*, 323. (j) Lippard, S. J.; Russ, B. J. *Inorg. Chem.* **1967**, *6*, 1943.

(29) Parkin, G.; Bercaw, J. E. *J. Am. Chem. Soc.* **1989**, *111*, 391. This article describes the preparation and properties of Cp^*_2WO, an exceptionally reactive compound.

(30) Duff, J. C. *J. Chem. Soc.* **1941**, 547.

(31) Jones, M. M. *J. Am. Chem. Soc.* **1959**, *81*, 3188.

(32) Chen, G. J.-J.; McDonald, J. W.; Newton, W. E. *Inorg. Chem.* **1976**, *15*, 2612.

(33) (a) Bowden, J. A.; Colton, R. *Aust. J. Chem.* **1968**, *21*, 2657. (b) Cotton, F. A.; Falvello, L. R.; Meadows, J. H. *Inorg. Chem.* **1985**, *24*, 514.

(34) Templeton, J. L.; Ward, B. C. *Inorg. Chem.* **1980**, *19*, 1753.

$WO_2(acac)_2$ (4). The following method is adapted from the literature[35] but is simpler and has proven to be highly reproducible with somewhat better yields. A suspension of 2.5 g (8.7 mmol) of WO_2Cl_2 and 25 mL (0.24 mol) of 2,4-pentanedione in 150 mL of benzene (dried over 3-Å molecular sieves) was refluxed for 48 h and filtered while still hot. The solvent was removed from the filtrate to yield a yellowish white crude product. This material was recrystallized by adding ether to a saturated dichloromethane solution, affording 1.6 g (44%) of product as an off-white crystalline solid that was pure by an NMR criterion. ^1H NMR ($CDCl_3$): δ 2.18 (s, 3), 2.19 (s, 3), 5.80 (s, 1).

WO_2(sap) (5). This preparation was performed in the air. A solution of 1.0 g (2.4 mmol) of $WO_2(acac)_2$ in 150 mL of methanol was treated with 0.55 g (2.7 mmol) of H_2(sap), and the mixture was stirred overnight. The precipitate was collected by filtration and washed successively with methanol (2 × 10 mL), dichloromethane, and ether to afford 1.0 g (97%) of the product as a red-brown microcrystalline solid. The product was dried overnight at 150 °C prior to analysis. ^1H NMR: δ 6.92–7.88 (m, 8), 9.28 (s, 1, *H*CN). Anal. Calcd for $C_{13}H_9NO_4W$: C, 36.56; H, 2.12; N, 3.28; W, 43.05. Found: C, 36.64; H, 2.16; N, 3.23; W, 42.90.

WO_2(5-*t*-Busap) (6). The compound was prepared by using a procedure analogous to that for **5** and was obtained as an orange-red microcrystalline solid in 90% yield. It was dried before analysis. ^1H NMR: δ 1.30 (s, 3), 6.88–7.88 (m, 7), 9.32 (s, 1, *H*CN). Anal. Calcd for $C_{17}H_{17}NO_4W$: C, 42.26; H, 3.55; N, 2.90; W, 38.05. Found: C, 42.23; H, 3.56; N, 2.76; W, 37.7.

WO_2(ssp) (7). The compound was prepared by using a procedure analogous to that for **5**, with a reaction time of 2 days, and was obtained in 96% yield as a brown solid, which was dried before analysis. ^1H NMR: δ 6.94–7.88 (m, 8), 9.07 (s, 1, *H*CN). Anal. Calcd for $C_{13}H_9NO_3SW$: C, 35.23; H, 2.05; N, 3.16; S, 7.23; W, 41.49. Found: C, 35.19; H, 2.04; N, 3.20; S, 7.17; W, 41.40.

WS_2(5-*t*-Busap)(DMF) (8). To a solution of 1.0 g (2.1 mmol) of WO_2(5-*t*-Busap) in a minimal volume (15 mL) of warm DMF was added 1.76 mL (8.4 mmol) of neat $(Me_3Si)_2S$ (Aldrich). The yellow solution quickly changed to red-brown. The mixture was stirred overnight, during which time some red solid separated. After removal of solvent in vacuo, a red-brown solid was obtained. This material was recrystallized from 3:1 dichloromethane/DMF (v/v) to yield 0.60 g (49%) of the pure product as a brown crystalline solid. ^1H NMR: δ 1.31 (s, 9), 6.90–7.88 (m, 7), 9.26 (s, 1, *H*CN). Anal. Calcd for $C_{20}H_{24}N_2O_3S_2W$: C, 40.83; H, 4.11; N, 4.76; S, 10.90; W, 31.25. Found: C, 40.31; H, 3.88; N, 4.75; S, 9.95; W, 31.10.

WS_2(ssp) (9). To a solution of 1.0 g (2.3 mmol) of WO_2(ssp) in a minimal volume (30 mL) of DMF was added 1.5 mL (7.1 mmol) of $(Me_3Si)_2S$. The initial yellow solution rapidly turned to dark red. The reaction mixture was stirred overnight, and the solvent was removed in vacuo. Dichloromethane (25 mL) was added to the red solid residue, producing a slurry. To the stirred slurry was added 100 mL of ether to cause the separation of additional solid. The mixture was stored at −20 °C overnight. This material was collected, washed with ether, and dried in vacuo to give 0.68 g (62%) of the red-brown microcrystalline product. ^1H NMR: δ 6.90–7.90 (m, 8), 8.98 (s, 1, *H*CN). Anal. Calcd for $C_{13}H_9NOS_3W$: C, 32.85; H, 1.91; N, 2.95; S, 20.24; W, 38.68. Found: C, 33.03; H, 1.98; N, 2.91; S, 19.89; W, 38.80.

WS_2(sap) (10). The compound was prepared by a method analogous to that for **9** and was obtained in 65% yield as a red microcrystalline solid. ^1H NMR: δ 6.90–7.90 (m, 8), 9.22 (s, 1, *H*CN). Anal. Calcd for $C_{13}H_9NO_2S_2W$: C, 34.00; H, 1.98; N, 3.05; S, 13.96; W, 40.04. Found: C, 33.69; H, 2.01; N, 3.16; S, 13.83; W, 40.40.

$WO_2(pipdtc)_2$ (11). To the red solution of 2.0 g (3.4 mmol) of $W(CO)_3(pipdtc)_2$ in 100 mL of dichloromethane was added a solution of 6.6 g (6.7 mmol) of $Mo_2O_3(Et_2dtp)_4$ in 50 mL of dichloromethane. The purple color of the Mo compound was quickly replaced by red, and CO was vigorously evolved. The mixture was stirred at room temperature for 40 min, and the solvent was removed in vacuo. Ether (250 mL) was added in several portions, and the residue was triturated in order to remove pink $MoO(Et_2dtp)_2$, leaving 1.8 g of off-white crude product. This material was recrystallized by adding hexane to a saturated dichloromethane solution; 1.2 g (66%) of fine off-white microcrystalline solid was obtained. ^1H NMR (CD_2Cl_2): δ 1.76 (m, 6), 3.90 (m, 4). Anal. Calcd for $C_{12}H_{20}N_2O_2S_4W$: C, 26.87; H, 3.76; N, 5.23; S, 23.86; W, 34.32. Found: C, 26.74; H, 3.73; N, 5.16; S, 23.76; W, 34.75.

$WO_2(Me_2dtc)_2$ (12). The compound was prepared by a method analogous to that for **11**. The product was obtained in 91% yield as an off-white powder that was pure without recrystallization. ^1H NMR ($CDCl_3$): δ 3.37 (s). Anal. Calcd for $C_6H_{12}N_2O_2S_4W$: C, 15.79; H, 2.65; N, 6.14; S, 28.05; W, 40.35. Found: C, 15.99; H, 2.54; N, 6.20; S, 28.19; W, 40.65.

Table III. Atom Positional Parameters (×10^4) for $[WO_2(5\text{-}t\text{-Busap})(MeOH)]\cdot MeOH$

atom	*x/a*	*y/b*	*z/c*
W(1)	2186.9 (5)	5084 (3)	2987.3 (3)
O(1)	4163 (12)	5893 (9)	2618 (7)
O(2)	3178 (11)	3807 (9)	3376 (7)
O(3)	447 (13)	6887 (8)	2523 (8)
O(4)	718 (11)	4690 (7)	1704 (6)
O(5)	2385 (11)	5888 (9)	4319 (7)
O(6)	7023 (15)	7554 (9)	2945 (9)
N(1)	−767 (11)	4818 (7)	3472 (6)
C(1)	1310 (25)	8022 (13)	2505 (17)
C(2)	6937 (30)	8180 (15)	3830 (17)
C(10)	−658 (14)	3818 (9)	1463 (8)
C(11)	−2088 (14)	3574 (8)	2065 (7)
C(12)	−3533 (15)	2697 (9)	1751 (7)
C(13)	−3505 (16)	2041 (9)	898 (8)
C(14)	−2061 (18)	2315 (10)	303 (9)
C(15)	−674 (17)	3187 (11)	564 (9)
C(16)	−5037 (18)	1053 (10)	566 (9)
C(17)	−6376 (25)	835 (14)	1339 (12)
C(18)	−6295 (25)	1466 (14)	−423 (11)
C(19)	−3962 (23)	−100 (11)	363 (14)
C(20)	−2154 (14)	4157 (9)	3015 (7)
C(21)	−848 (13)	5286 (9)	4460 (6)
C(22)	885 (17)	5871 (10)	4871 (9)
C(23)	1062 (20)	6362 (12)	5831 (9)
C(24)	−500 (22)	6308 (13)	6367 (10)
C(25)	−2251 (22)	5773 (13)	5952 (10)
C(26)	−2431 (15)	5258 (11)	4986 (7)

$W_2O_3(pipdtc)_4$ (13). $WO_2(pipdtc)_2$ (1.0 g, 1.9 mmol) was suspended in 50 mL of dichloromethane, and 0.12 mL (1.0 mmol) of neat $P(OMe)_3$ was added. The light yellow solution quickly turned to purple, and a dark microcrystalline precipitate slowly separated. The mixture was stirred for 2 h and was maintained at −20 °C overnight. The black microcrystalline product was collected by filtration, washed with 10 mL of cold dichloromethane, and dried in vacuo to afford 0.85 g (86%) of pure product. ^1H NMR (CD_2Cl_2): δ 1.74 (m, 4), 3.88 (m, 6). Anal. Calcd for $C_{24}H_{40}N_4O_3S_8W_2$: C, 27.27; H, 3.82; N, 5.30; S, 24.22; W, 34.84. Found: C, 27.21; H, 3.76; N, 5.37; S, 24.19; W, 35.36.

Collection and Reduction of X-ray Data. Single crystals of $[WO_2(5\text{-}t\text{-Busap})(MeOH)]\cdot MeOH$ were grown by slowly cooling a saturated methanol solution to −20 °C and maintaining the solution at that temperature for several days. Suitable crystals were sealed in a glass capillary with the mother liquor (to prevent desolvation). Data collection was performed at ca. 25 °C on a Nicolet P3F four-circle automated diffractometer equipped with a Mo X-ray source and a graphite monochromator. Crystallographic information is contained in Table II. Orientation matrices and unit cell parameters were obtained from a least-squares fit of 16 reflections from the rotation photograph. No significant decay of three check reflections monitored every 123 reflections was observed over the course of data collection. The data were processed with the program XTAPE of the SHELXTL structure determination program package (Nicolet XRD Corp., Madison, WI 53711). An empirical absorption correction was applied with the program PSICOR. The compound crystallizes in the monoclinic system. Space group $P2_1$ (No. 4) is consistent with the systematic absences and intensity statistics. It was further confirmed by successful solution and refinement of the structure.

Structure Solution and Refinement. Atom scattering factors were taken from the tabulation of Cromer and Waber.[36] The tungsten atom was found by direct methods (MULTAN) with use of the phase set with the highest combined figure of merit. The structures were refined by the blocked-cascade least-squares method with use of the program CRYSTALS. The remaining non-hydrogen atoms were located by alternating cycles of Fourier maps and least-squares refinements. The asymmetric unit consists of one WO_2(5-*t*-Busap)(MeOH) molecule and one methanol solvate molecule. Isotropic refinement converged at R = 7.1%. All non-hydrogen atoms were refined anisotropically. In the final stages of refinement, hydrogen atoms were included at 0.95 Å from the bonded carbon atom and with 1.2× the isotropic thermal parameter of the bonded carbon atom. Final agreement factors are given in Table II;

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(35) (a) Nikolovski, A. *Croat. Chem. Acta* **1968**, *40*, 143. (b) McDonell, A. C.; Vasudevan, S. G.; O'Connor, M. J.; Wedd, A. G. *Aust. J. Chem.* **1985**, *38*, 1017.

(36) Cromer, D. T.; Waber, J. T. *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974.

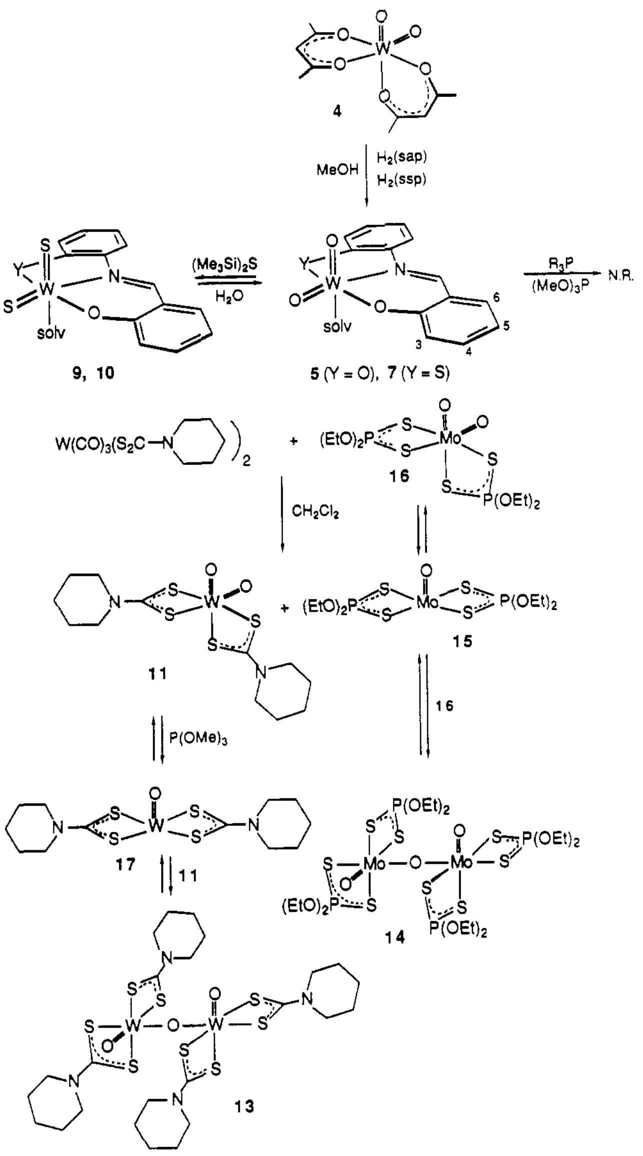

Figure 1. Schematic representations of the structures of Mo and W complexes and their reactions.

positional parameters are listed in Table III.[37]

Other Physical Measurements. All measurements were made under anaerobic conditions except for those of W(VI) Schiff base compounds, which are air-stable. Absorption spectra were obtained on a Perkin-Elmer Lambda 4C spectrophotometer. ^{1}H NMR spectra were recorded on Bruker AM spectrometers operating at 250–500 MHz. Infrared spectra were measured on a Perkin-Elmer 599B spectrophotometer. Tungsten analyses were performed by atomic absorption on a Perkin-Elmer 2380 atomic absorption spectrophotometer.

Results and Discussion

Schiff Base Complexes. (a) Preparations and Structure. $MoO_2(acac)_2$ has been used extensively as a precursor to $Mo^{VI}O_2$ complexes in substitution reactions with protonated ligands. $WO_2(acac)_2$ has been prepared on several occasions as a somewhat unstable, light yellow solid.[15,35] The original yield of 70–80% in the first preparation of this compound[35a] has not proven to be repeatable by ourselves and apparently by others.[35b] A highly reproducible procedure affording the pure compound in 40% yield is reported here. Its use as a starting material for $W^{VI}O_2$ complexes is limited to one example.[35b] We have found $WO_2(acac)_2$ useful in preparing complexes derived from the tridentate Schiff bases sap and ssp. These and other reactions carried out in this work are depicted in Figure 1. Spectroscopic characterization data are contained in Table I, and selected absorption spectra are presented in Figure 2.

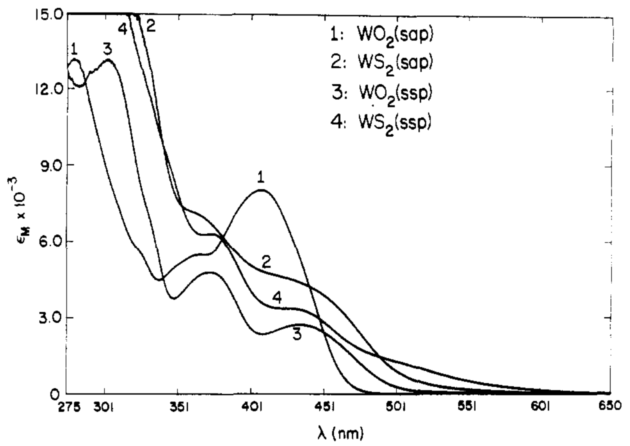

Figure 2. Absorption spectra of the indicated W(VI) complexes. Solvents and spectral data are given in Table I.

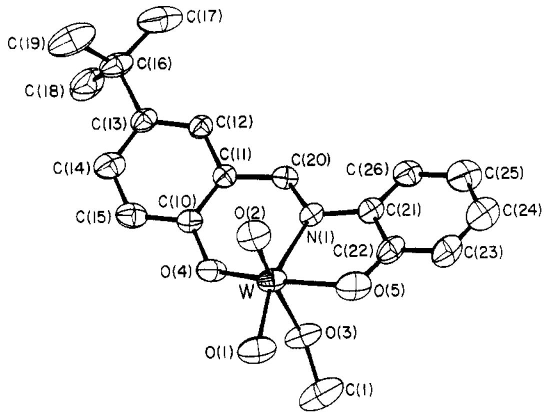

Figure 3. Structure of $WO_2(5\text{-}t\text{-}Busap)(MeOH)$ as its methanol monosolvate. The atom-labeling scheme and 50% probability ellipsoids are shown.

Table IV. Selected Interatomic Distances (Å) and Angles (deg) for $[WO_2(5\text{-}t\text{-}Busap)(MeOH)]\cdot MeOH$

W-O(1)	1.764 (8)	C(10)-O(4)	1.36 (1)
W-O(2)	1.642 (9)	C(22)-O(5)	1.35 (1)
W-O(4)	1.898 (8)	C(1)-O(3)	1.41 (2)
W-O(5)	1.982 (9)	C(20)-N(1)	1.28 (1)
W-N(1)	2.234 (8)	C(21)-N(1)	1.43 (1)
W-O(3)	2.392 (9)	C(11)-C(20)	1.44 (1)
O(1)-W-O(2)	104.4 (4)	O(2)-W-N(1)	97.9 (4)
O(1)-W-O(4)	100.0 (4)	O(4)-W-O(3)	78.2 (3)
O(1)-W-O(5)	93.8 (4)	O(4)-W-N(1)	81.8 (3)
O(1)-W-O(3)	81.7 (4)	O(5)-W-O(3)	78.7 (4)
O(2)-W-O(4)	102.3 (4)	O(5)-W-N(1)	74.9 (3)
O(2)-W-O(5)	98.8 (4)	O(3)-W-N(1)	75.8 (3)
O(1)-W-N(1)	156.4 (4)	O(2)-W-O(3)	173.6 (4)
O(4)-W-O(5)	150.4 (4)		

The reaction of $WO_2(acac)_2$ (4) with the Schiff base ligands in methanol affords the products $WO_2(sap)$ (5), $WO_2(5\text{-}t\text{-}Busap)$ (6), and $WO_2(ssp)$ (7) in yields exceeding 90%. In DMF and Me_2SO (the only common solvents in which they are appreciably soluble), these compounds exist as solvated six-coordinate species as do their Mo counterparts.[10,18,19,23a] As solids, they are readily desolvated by washing with ether or exposure to a stream of dinitrogen. As a representative of the set, the structure of compound 6 in the form of its methanol adduct was determined. The structure is shown in Figure 3, and selected metric data are compiled in Table IV.

$WO_2(5\text{-}t\text{-}Busap)(MeOH)$ is isostructural with its Mo counterpart.[10] Its structure is that of a severely distorted octahedron which is dominated by the *cis*-dioxo stereochemistry. As is always the case with $Mo^{VI}O_2$ complexes, the remaining anionic donor

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(37) See the paragraph at the end of this article concerning supplementary material available.

atoms are mutually trans and cis to the oxo atoms. The tridentate ligand assumes a *mer* orientation. The W—O single-bond distances are consistent with those in e.g. W(VI) alkoxides,[38] and ligand dimensions are unexceptional when compared to those in Mo complexes.[10] The only unusual features of this molecule are the W=O bond lengths of 1.764 (8) and 1.642 (9) Å. These differ by 0.12 Å and are the shortest and longest values yet found for the group **2** in the few cases where its structures have been determined.[24a-d,26] The O(1)-W-O(2) angle of 104.4 (4)° is normal for this group.

(b) Reactivity. The oxo transfer propensity of tungsten complexes **5**-**7** was examined by using tertiary phosphines. In earlier work,[10,15,18,19] both $MoO_2(sap)(solv)$ and $MoO_2(ssp)(solv)$ were shown to be inert to Ph_3P but to react with more basic X = Ph_2RP (R = Me, Et) in reaction 1. Convenient rates of reaction of these complexes are achieved at elevated temperatures ($\gtrsim$60 °C). The instantaneous $Mo^{IV}O$ product has not been detected because it is immediately consumed in μ-oxo dimer formation reaction 2. None of the tungsten complexes reacted by oxo transfer with R_3P (R = Ph, Et, Me, OMe, and 2,4,6-$C_6H_2(OMe)_3$) at ambient or elevated temperatures. For example, a solution of $WO_2(ssp)$ in DMF was treated with a 5-fold excess of $P(OMe)_3$, and the system was heated at 100 °C for 24 h. The absorption spectrum of complex **7** (Figure 2) was undiminished. The lack of reaction toward tris(2,4,6-trimethoxyphenyl)phosphine is noteworthy inasmuch as this compound has been described as probably the most basic phosphine,[39] and we have shown earlier that the rates of reduction of one $Mo^{VI}O_2$ complex parallel phosphine basicity.[3]

While complexes **5**-**7** do not yield to reductive oxo transfer, they readily undergo oxo substitution. Thus, reaction 3 proceeds

$$WO_2L(solv) + 2(Me_3Si)_2S \rightarrow WS_2L(solv) + 2(Me_3Si)_2O \quad (3)$$

smoothly with a 1-2-fold excess of sulfiding reagent to afford $WS_2(sap)$ (**10**), WS_2(5-*t*-Busap)(DMF) (**8**), and $WS_2(ssp)$ (**9**) in good to excellent yields. The use of $(Me_3Si)_2S$ for O/S substitution of M=O groups in this laboratory has been described earlier.[40] When a deficiency of the sulfide reagent was used, the formation of WOSL(solv) compounds was detected in the azomethine proton shifts. These compounds were not isolated. Compared to their dioxo analogues, complexes **8**-**10** show red-shifted absorption spectra (Figure 2). They are completely stable in the absence of moisture and air and are freely soluble in solvents such as chloroform, dichloromethane, DMF, and Me_2SO. Upon exposure to water they are immediately hydrolyzed to the corresponding dioxo species. These complexes are expected to have the *cis*-disulfido stereochemistry that may apply to $[WS_2Cl_4]^{2-}$.[41] Other than substituted tetrahedral variants of $[MoS_4]^{2-}$ (e.g., $[MoO_2S_2]^{2-}$), compounds containing the $Mo^{VI}S_2$ group are unknown, presumably because, if they can be formed at all, they are unstable to autoreduction. In contrast, even the trioxo group **3** can be completely substituted. The stable anion $[WS_3(CH_2CMe_3)]^-$ has been prepared from the corresponding trioxo compound by reaction with $(Me_3Si)_2S$.[26]

Dithiocarbamate Complexes. (a) Preparation. Despite the large number of $MoO_2(R_2dtc)_2$ complexes that have been synthesized, only three tungsten species $WO_2(R_2dtc)_2$ (R = Me, Et, *n*-Pr) have been reported, with little characterization data.[21] These compounds were prepared by the intermetal oxo transfer reaction[1] between $W(CO)_2(PPh_3)(R_2dtc)_2$ and $Mo_2O_3(Et_2dtp)_4$ (**14**). As indicated in Figure 1, μ-oxo dimer **14** exists in labile equilibrium (reaction 4) with $MoO(Et_2dtp)_2$ (**15**) and $MoO_2(Et_2dtp)_2$ (**16**),[42]

$$MoO_2(Et_2dtp)_2 + MoO(Et_2dtp)_2 \rightleftharpoons Mo_2O_3(Et_2dtp)_4 \quad (4)$$

$$W(CO)_3(R_2dtc)_2 + 2MoO_2(Et_2dtp)_2 \rightarrow WO_2(R_2dtc)_2 + 3CO + 2MoO(Et_2dtp)_2 \quad (5)$$

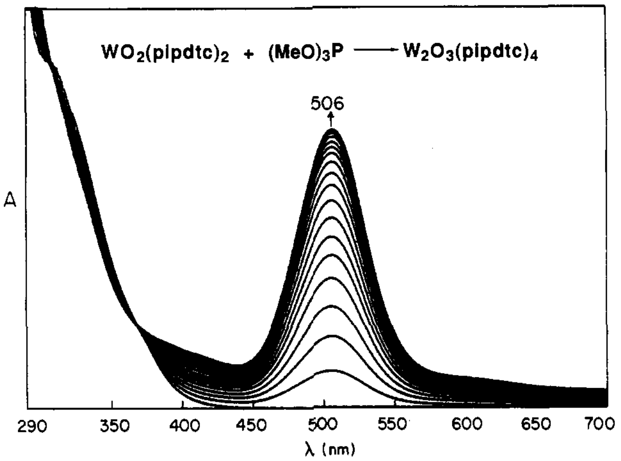

Figure 4. Spectrophotometric time course of the reaction between $WO_2(pipdtc)_2$ (initial concentration 9.7 mM) and 0.5 equiv of $(MeO)_3P$ in 1,2-dichloroethane solution at 6 °C. The spectra were recorded every 5 min over 90 min. In this and the following figure, band maxima and the direction of absorbance change are indicated.

for which K_{eq} = 256 (1,2-dichloroethane, 298 K).[13b] While **16** has never been isolated, it is the likely oxo donor to W(II). Accordingly, we formulate the present preparations of $WO_2(Me_2dtc)_2$ and $WO_2(pipdtc)_2$ (**11**) in terms of the similar reaction 5, which affords the products in high yield. As reported by Chen et al.,[21] the W(VI) dithiocarbamates are unstable compounds, being decidedly water and dioxygen sensitive, and also prone to decomposition even in dry solvents. For this reason, workup of the reaction mixture should proceed immediately after the reaction has been completed. $MoO(Et_2dtp)_2$ was identified as a product after being extracted with ether from the reaction mixture. Of the derivatives we have examined, which include those prepared earlier, $WO_2(pipdtc)_2$ is the most stable and was used in the reaction systems that follow. The compound is soluble in solvents such as dichloromethane and 1,2-dichloroethane, forming light yellow solutions, and is stable for short periods; it is unstable in DMF and Me_2SO.

(b) Oxo-Transfer Reactions. In 1,2-dichloroethane solution, $WO_2(pipdtc)_2$ (**11**) did not react with excess Ph_3P and reacted slowly with Me_3P and Et_3P at 50 °C. The reaction with $(MeO)_3P$ at ambient temperature is relatively rapid and affords a purple chromophore. As shown in Figure 4, the reaction is sufficiently slow at 6 °C that it can be monitored spectrophotometrically. The initial spectrum with a band at 307 nm is progressively replaced with a spectrum whose principal feature is at 506 nm. The maximum intensity was developed with 0.5 equiv of $(MeO)_3P$. The analogous reaction with $MoO_2(pipdtc)_2$ also affords a purple chromophore with λ_{max} = 514 nm. Bands in this region are characteristic of the products of reaction 2, viz., $Mo_2O_3(R_2dtc)_4$. When the reaction was conducted in CD_2Cl_2, the ^1H NMR doublet of $(MeO)_3P$ at δ 3.48 was replaced by that of $(MeO)_3PO$ at δ 3.73. A product of composition $W_2O_3(pipdtc)_4$ (**13**) was obtained in 85% yield from this reaction system when the procedure was carried out on a preparative scale. The observations are consistent with the occurrence of reactions 6 and 7. The

$$WO_2(pipdtc)_2 + (MeO)_3P \rightarrow WO(pipdtc)_2 + (MeO)_3PO \quad (6)$$

$$WO_2(pipdtc)_2 + WO(pipdtc)_2 \rightleftharpoons W_2O_3(pipdtc)_4 \quad (7)$$

production of $WO(pipdtc)_2$ (**17**) in reaction 6 is inferred from the formation of μ-oxo dimer **13**, there being no evident pathway other than reaction 7 for its formation.

Attempts to obtain diffraction-quality crystals of **11** and **13** have not been successful. The composition of **13** is readily distinguished from that of $W_2O_4(pipdtc)_2$, another but less likely reduction product of **11**. Compounds of the type $W_2O_3(R_2dtc)_4$ and

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[38] (a) Chisholm, M. H.; Hoffman, D. M.; Huffman, J. C. *Inorg. Chem.* **1983**, *22*, 2903. (b) Chisholm, M. H.; Folting, K.; Heppert, J. A.; Hoffman, D. M.; Huffman, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 1234.

[39] Wada, M.; Higashizaki, S. *J. Chem. Soc., Chem. Commun.* **1984**, 482.

[40] Do, Y.; Simhon, E. D.; Holm, R. H. *Inorg. Chem.* **1983**, *22*, 3809.

[41] Klingelhöfer, P.; Müller, U. *Z. Anorg. Allg. Chem.* **1988**, *556*, 70. The anion shows S/Cl disorder.

[42] Chen, G. J.-J.; McDonald, J. W.; Newton, W. E. *Inorg. Nucl. Chem. Lett.* **1976**, *12*, 697.

Table V. Selected Thermodynamic Data for the Reactions $X + {}^{1}/_{2}O_2(g) \rightarrow XO$

X	XO	ΔH, kcal/mol
PhCH=NPh(g)	PhCN=N(O)Ph(g)	-4^{a}
$C_5H_5N(g)$	$C_5H_5NO(g)$	-13^{b}
PhN=NPh(g)	PhN=N(O)Ph(g)	-17^{a}
$Me_2S(g)$	$Me_2SO(g)$	-27^{c}
$MoO(Et_2dtc)_2$	$MoO_2(Et_2dtc)_2$	$-35^{d,e}$
$2MoO(Et_2dtc)_2$	$Mo_2O_3(Et_2dtc)_4$	$-42^{d,e}$
Ph_3P	Ph_3PO	$-67,^{c-e}$ -70^{f}
n-Bu_3P	*n*-Bu_3PO	-80^{c}
$Me_3P(g)$	$Me_3PO(g)$	-80^{g}
$(EtO)_3P(l)$	$(EtO)_3PO(l)$	$-93^{f,h}$

[a] Reference 47. [b] Reference 48. [c] Reference 1; gas phase. [d] Reference 49. [e] 1,2-Dichloroethane solution. [f] Reference 50; solid state. [g] Reference 51. [h] Reference 52.

$W_2O_4(R_2dtc)_2$ have been reported to be formed by the reduction of tungstate in aqueous solution in the presence of $R_2NCS_2^-$ and are described as dark violet.[43,44] In 1,2-dichloroethane solution, $W_2O_3(pipdtc)_4$ at 0.1–10 mM and ambient temperature shows small deviations from Beer's law, consistent with the presence of equilibrium 7 and the lack of a perfect isosbestic point (at 370 nm) in the spectra of reaction 6 (Figure 4) and/or with a small amount of decomposition. Spectral measurement of **11** and reaction 6 at the same total W concentration gave an apparent 88% yield of the μ-oxo compound. The yield in the analogous Mo system was 100%; the difference may be due to some decomposition in the W system.[46]

Thermodynamic Considerations. We have previously introduced a thermodynamic reaction scale for oxo transfer.[1,5] It consists of a series of reactions (couples) of the general type (8), which

$$X + {}^{1}/_{2}O_2(g) = XO \qquad (8)$$

are ranked in the order of decreasing ΔH. A partial series containing couples of interest in this work is presented in Table V; a more extensive series is given elsewhere.[1] Reaction enthalpies were obtained from thermochemical data.[1,47-52] Some of these have been determined by calorimetry,[49] and the majority of the rest have been obtained from heats of formation. With use of exothermicity as the criterion, the reduced member of a given couple can reduce the oxidized member of another couple with a larger ΔH, and conversely. The occurrence of reaction 5 and a closely similar reaction,[21] in which complex **16** acts as an oxo donor, raises the question as to the position of the $MoO(Et_2dtp)_2/MoO_2(Et_2dtp)_2$ couple (a) in the reactivity series.

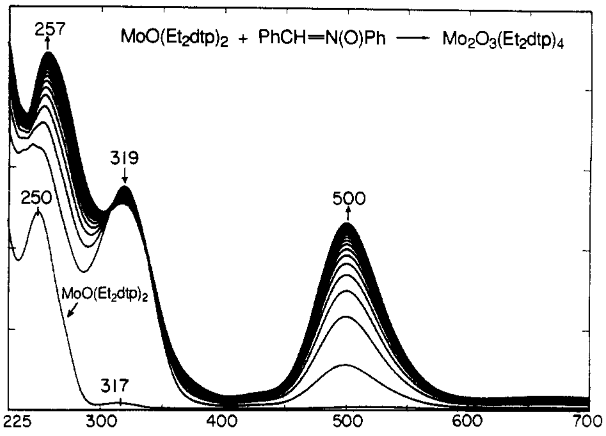

Figure 5. Spectrophotometric time course of the reaction between $MoO(Et_2dtp)_2$ (initial concentration 7.9 mM) and 0.5 equiv of PhCH=N(O)Ph in 1,2-dichloroethane solution at 6 °C. The spectra were recorded every 1.6 min over 32 min. Also shown is the spectrum of $MoO(Et_2dtp)_2$ recorded separately.

In 1,2-dichloroethane solution, complex **15** undergoes reaction 9 with oxo donors XO = PhCH=N(O)Ph and pyO. The reaction

$$2MoO(Et_2dtp)_2 + XO \rightarrow Mo_2O_3(Et_2dtp)_4 + X \qquad (9)$$

with *N*-phenylbenzaldimine *N*-oxide was monitored spectrophotometrically at 6 °C, as shown in Figure 5. The characteristic intense band of $Mo_2O_3(Et_2dtp)_4$ at 500 mm grew in with time. On the assumption that $MoO_2(Et_2dtp)_2$ and $MoO(Et_2dtp)_2$ (ϵ_M = 72) absorb negligibly at 500 nm and with use of the equilibrium constant of reaction 4, ϵ_M = 24 600 for $Mo_2O_3(Et_2dtp)_4$ at this wavelength was obtained. From this value, the in situ yield of the μ-oxo Mo(V) complex **14**, whose spectrum has not been previously published, was determined to be 98%. Under the same conditions with pyridine *N*-oxide, a rapid reaction was observed that at the maximum absorbance at 500 nm corresponded to an 85% yield of the μ-oxo product. Thereafter, the violet color of the solution faded to near-colorless, indicating decomposition.

For reaction 9, $\Delta H_9 = \Delta H_a + \Delta H_4 - \Delta H_8$. This requires $\Delta H_a \lesssim 0.5$ kcal/mol from the reaction with XO = pyO.[53] For the couple $2MoO(Et_2dtp)_2/Mo_2O_3(Et_2dtp)_4$ (b), $\Delta H_b \lesssim -13$ kcal/mol as an upper limit. On the basis of the results for dithiocarbamate complexes (Table V), the latter couple is expected to be the stronger oxo acceptor system. In 1,2-dichloromethane at ambient temperature, $MoO(Et_2dtp)_2$ did not react with PhN=N(O)Ph, Me_2SO, and Ph_3AsO ($\lesssim$-35 kcal/mol[1]). Further, under the same conditions, solutions containing $Mo_2O_3(Et_2dtp)_4$ did not react with PhN=NPh, $(PhCH_2)_2S$, or Ph_3As or with the first two reagents at 50 °C. Upon treatment with 1 equiv of Ph_3P, the purple solution of the μ-oxo dimer changed to a yellowish color. Because of the weak spectrum of $MoO(Et_2dtp)_2$ (Figure 5), 1 equiv of PhCH=N(O)Ph was added, resulting in an 80% recovery of the initial intensity of the 500-nm band of the μ-oxo complex. This indicates the occurrence of overall reaction 10 and therewith the

$$Mo_2O_3(Et_2dtp)_4 + Ph_3P \rightarrow 2MoO(Et_2dtp)_2 + Ph_3PO \qquad (10)$$

limiting values $\Delta H_a \gtrsim -54$ kcal/mol and $\Delta H_b \gtrsim -67$ kcal/mol. The limits established for these couples, based on observed re-

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(43) (a) Lozano, R.; Doadrio, A. L.; Alarcon, E.; Roman, J.; Doadrio, A. *Rev. Chim. Mineral.* **1983**, *20*, 109. (b) Lozano, R.; Alarcon, E.; Doadrio, A. L.; Doadrio, A. *Polyhedron* **1983**, *2*, 435. (c) Lozano, R.; Alarcon, E.; Doadrio, A. L.; Doadrio, A. *Polyhedron* **1984**, *3*, 25.

(44) The absorption spectra in Me_2SO of compounds described as $W_2O_3(R_2dtc)_4$ have been tabulated.[43] They do not include an intense band at ca. 500 nm (Figure 4). The first intense band in these spectra is usually near 475 nm with $\epsilon_M \approx$ 2000–4000. In our hands $W_2O_3(pipdtc)_4$ dissolves in dry, anaerobic Me_2SO with a purple color and λ_{max} = 510 nm. Within minutes the visible band is diminished in intensity and at longer times the solution becomes light yellow. Because the observed band is clearly the 506-nm feature observed in 1,2-dichloroethane, it is not certain that the spectra of pure $W_2O_3(R_2dtc)_4$ complexes were observed.[43] No actual spectrum of such a complex has been previously published. Other reported oxotungsten dithiocarbamate complexes that have been claimed are green $W_2O_3(Et_2dtc)_2$ and dark brown $WO(Et_2dtc)_3$.[45] No structural or absorption spectral data were provided; the formula of the first of these and the suggested four-coordinate structure are highly improbable for a binuclear W(IV) complex.

(45) Brown, D. A.; Glass, W. K.; Toma, H. J.; Waghorne, W. E. *J. Chem. Soc., Dalton Trans.* **1987**, 2531.

(46) The equilibrium constant of reaction 7 was not determined, owing to indications of instability of the complexes in solution at ambient temperature. For reaction 2 with L = Et_2dtc and n = 1, K_{eq} = 500 (1,2-$C_2H_4Cl_2$, 298 K).[13a]

(47) Kirschner, J. J.; Acree, W. E., Jr.; Pilcher, G.; Li, S. *J. Chem. Thermodyn.* **1986**, *18*, 793.

(48) Li, S.; Pilcher, G. *J. Chem. Thermodyn.* **1988**, *20*, 463.

(49) Watt, G. D.; McDonald, J. W.; Newton, W. E. *J. Less-Common Met.* **1977**, *54*, 415.

(50) Bedford, A. F.; Mortimer, C. T. *J. Chem. Soc.* **1960**, 1622.

(51) (a) Long, L. H.; Sackman, J. F. *Trans. Faraday Soc.* **1957**, *53*, 1606. (b) Claydon, A. P.; Fowell, P. A.; Mortimer, C. T. *J. Chem. Soc.* **1960**, 3284.

(52) Chernick, C. L.; Skinner, H. A.; Mortimer, C. T. *J. Chem. Soc.* **1955**, 3936.

(53) The upper limit depends on the value ΔH_4 = −13.5 (8) kcal/mol taken from the work of Tanaka et al.[13b] in 1,2-dichloroethane solution. This value is quite comparable to −12.1 (6) kcal/mol for reaction 2 with L = Et_2dtc. Both values were obtained from the temperature dependencies of equilibrium constants.[13b] By calorimetry, Watt et al.[48] have obtained ΔH = −6.65 (5) kcal/mol for reaction 2. If the value of ΔH_4 used here is too negative, the upper limit will be too high.

actions, are quite broad. Inasmuch as the Mo(IV) complexes $MoO(Et_2dtc)_2$[3] and $MoO(L\text{-}NS_2)(DMF)$[4] react cleanly and completely with Me_2SO, we suspect that the failure of $MoO(Et_2dtp)_2$ to react is thermodynamic and not kinetic, in which case $\Delta H_a \lesssim -13$ kcal/mol[53] and $\Delta H_b \lesssim -27$ kcal/mol. Among the oxo donors we have investigated, only the reagent prepared from $Mo_2O_3(Et_2dtp)_4$ afforded a clean, high-yield route to $WO_2(R_2dtc)_2$ complexes. It has also been employed to prepare W(IV)–oxo–acetylene complexes from W(II) precursors.[27b]

Of all types of $Mo^{VI}O_2L_n$ complexes studied in reaction 1,[1,2] $MoO_2(R_2dtc)_2$ is reduced the most rapidly by Ph_3P in the strongly exothermic reaction 11 in 1,2-dichloroethane. This reflects the

$$MoO_2(Et_2dtc) + Ph_3P \rightarrow MoO(Et_2dtc)_2 + Ph_3PO \quad (11)$$

$$k = 0.071\ M^{-1}\ s^{-1\,3} \qquad \Delta H = -29\ \text{kcal/mol}^{49}$$

stabilization of the $Mo^{IV}O$ level by sulfur ligands[5] and the marked oxophilicity of P(III). The ΔH value of −67 kcal/mol for the couple Ph_3P/Ph_3PO shows the phosphine to be a strong oxo acceptor.[1] Given the facility of reaction 11, it is perhaps somewhat surprising that $WO_2(pipdtc)_2$ did not react with excess Ph_3P under moderately forcing conditions. This suggests that the $WO(R_2dtc)/WO_2(R_2dtc)$ couple has a large negative ΔH value, perhaps near or below −67 kcal/mol. We do not assign any value on the basis of the absence of reaction. A reaction system containing 10 mM $W_2O_3(pipdtc)_4$ and 1 equiv of Ph_3PO in 1,2-dichloroethane bleached at 6 and 25 °C and formed a white precipitate. There was no clear evidence of the formation of $WO_2(pipdtc)_2$. The enthalpy value for the couple $(MeO)_3P/(MeO)_3PO$ is unknown, but that for $(EtO)_3P/(EtO)_3PO$ (−93 kcal/mol, Table V) must be closely similar, marking these two phosphites as being among the strongest oxo acceptors known.

Summary. The foregoing results indicate that complexes of dithiocarbamates and presumably certain other ligands undergo the generalized reactions 12 and 13, whose sum is reaction 14.

$$W^{VI}O_2L_n + X \rightleftharpoons W^{IV}OL_n + XO \quad (12)$$

$$W^{VI}O_2L_n + W^{IV}OL_n \rightleftharpoons W^{V}{}_2O_3L_{2n} \quad (13)$$

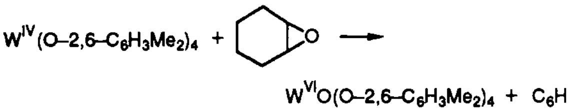
$$2W^{VI}O_2L_n + X \rightarrow W^{V}{}_2O_3L_{2n} + XO \quad (14)$$

Reaction 12 is irreversible, and reaction 13 may be an equilibrium. The failure of reaction 12 to occur at all when L = sap and ssp and X is a highly basic tertiary phosphine, and when L = R_2dtc and X = Ph_3P, is a manifestation of the greater thermodynamic barrier to the reduction of W(VI) vs that of Mo(VI). A quantitative assessment of this point ideally could be made from the potentials of the half-reactions $MO_2L_n + 2H^+ + 2e^- = MOL_n + H_2O$ or from the calorimetric enthalpies of the reactions $MO_2L_n + X = MOL_n + XO$ (M = Mo, W), but such data are unavailable. In their absence, the potential differences $E_W - E_{Mo}$ in dichloromethane solution for series 15, from the work of Heath

$$[MCl_6]^0 \overset{-0.61\ V}{\leftrightarrow} [MCl_6]^- \overset{-0.65\ V}{\leftrightarrow} [MCl_6]^{2-} \overset{-0.87\ V}{\leftrightarrow} [MCl_6]^{3-} \quad (15)$$

et al.,[54] provide the best quantitative measurement of the relative reducibilities of the two metals at parity of ligand. Note also the always larger values of the stretching frequencies of W═O vs Mo═O groups in analogous complexes (Table I). As we have observed elsewhere,[1,2,7] catalytic cycles involving W(VI) are unpromising owing to the difficulty of reducing this oxidation state, one example being the lack of activity of W-substituted sulfite oxidase.[55]

Given the difficulty of W(VI) reduction, W(IV) complexes have the potential of being avid oxo acceptors in the reverse of reaction 12. $WO(PMe_3)(Me_2dtc)_2$[28a] and $WO(PhC{\equiv}CH)(Me_2dtc)_2$,[27b] when treated with the donors PhCH═N(O)Ph, $(PhCH_2)_3NO$, or Me_2SO, yielded unidentified products. Indeed, the first well-defined W(IV) → W(VI) oxo transfer processes (reactions 16[56] and 17[57]) have only just been reported. Given ΔH = −25 kcal/mol for the couple C_2H_4/C_2H_4O,[1] the enthalpy change of the W(IV)/W(VI) couple must be more negative than this value.



(16)

$$[W^{IV}O_5(OH_2)] + XO \rightarrow [W^{VI}(O)O_5] + X \quad (17)$$

$W(O\text{-}2,6\text{-}C_6H_3Me_2)_4$ is then an oxo acceptor of moderate to perhaps considerable strength. In reaction 17, the indicated tungsten coordination units are octahedral fragments of W_{12} heteropolyanions. A reaction is observed with XO = Me_2SO and Ph_3AsO, but not with $(MeO)_2SO_2$ (−49 kcal/mol[1]) and other less strong donors, including Ph_3PO. Consequently, ΔH for this W(IV)/W(VI) couple is more negative than −35 kcal/mol, and its actual value may be in the approximate interval −35 to −50 kcal/mol. These considerations, and similar ones given elsewhere,[1,2] make evident for a far more extensive oxo transfer reactivity scale could be produced were more calorimetrically determined reaction enthalpies available.

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Supplementary Material Available: Listings of crystallographic data for $[WO_2(5\text{-}t\text{-}Busap)(MeOH)]\cdot MeOH$, including details of the data collection, positional and thermal parameters, calculated hydrogen atom positions, and bond distances and angles (5 pages); a listing of calculated and observed structure factors (24 pages). Ordering information is given on any current masthead page.

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(54) Heath, G. A.; Moock, K. A.; Sharp, D. W. A.; Yellowlees, L. J. *J. Chem. Soc., Chem. Commun.* **1985**, 1503.

(55) (a) Johnson, J. L.; Cohen, H.; Rajagopalan, K. V. *J. Biol. Chem.* **1974**, *249*, 5046. (b) Johnson, J. L.; Rajagopalan, K. V. *J. Biol. Chem.* **1976**, *251*, 5505.

(56) Listemann, M. L.; Schrock, R. R.; Dewan, J. C.; Kolodziej, R. M. *Inorg. Chem.* **1988**, *27*, 264.

(57) Piepgrass, K.; Pope, M. T. *J. Am. Chem. Soc.* **1989**, *111*, 753.