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Nucleophilic Reactivity and Oxo/Sulfido Substitution Reactions of $M^{VI}O_3$ Groups (M = Mo, W)

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The nucleophilic reactivity of oxo ligands in the groups $M^{VI}O_3$ in the trigonal complexes [(Me_3tacn)MO_3] (M = Mo (**1**), W (**10**)) and [(Bu^t_3tach)MO_3] (M = Mo (**5**), W (**14**)) has been investigated. Complexes **1**/**10** can be alkylated with MeOTf to give [(Me_3tacn)MO_2(OMe)]$^{1+}$ (**2**/**11**), silylated with Pr^i_3SiOTf to form [(Me_3tacn)MO_2($OSiPr^i_3$)]$^+$ (**3**/**12**), and protonated with HOTf to yield [(Me_3tacn)MoO_2(OH)]$^+$ (**4**). Similarly, complexes **5**/**14** can be silylated to [(Bu^t_3tach)MO_2($OSiPr^i_3$)]$^+$ (**6**/**15**) and protonated to [(Bu^t_3tach)MO_2(OH)]$^+$ (**7**/**16**). Products were isolated as triflate salts in yields exceeding 70%. When excess acid was used, the dinuclear μ-oxo species [(Bu^t_3tach)$_2M_2O_5$]$^{2+}$ (**8**/**17**) were obtained. X-ray structures are reported for **2**–**4**, **6**–**8**, **12**, and **15**–**17**. All mononuclear complexes have dominant trigonal symmetry with a rhombic distortion owing to a M—OR bond (R = Me, $SiPr^i_3$, H), which is longer than M═O oxo interactions; the latter exert a substantial trans influence on M—N bond lengths. Oxo ligands in **5**/**14** undergo replacement with sulfide. Lawesson's reagent effects formation of [(Bu^t_3tach)MS_3] (**9**/**18**), **14** with excess B_2S_3 yields incompletely substituted [(Bu^t_3tach)WOS_2] (**20**), and **5** with excess B_2S_3 yields [(Bu^t_3tach)$Mo^{IV}O(S_4)$] (**19**). The structures of **9**, **19**, and **20** are reported. Precedents for $M^{VI}S_3$ groups in five- and six-coordinate molecules are limited. This investigation is the first detailed study of the behavior of $M^{VI}O_3$ groups in nucleophilic and oxo/sulfido substitution reactions and should be useful in synthetic approaches to the active sites of the xanthine oxidase enzyme family and of certain tungstoenzymes. (Bu^t_3tach = 1,3,5-tri-*tert*-butyl-1,3,5-triazacyclohexane, Me_3tacn = 1,4,7-trimethyl-1,4,7-triazacyclonane; OTf = triflate).

Introduction

The pyramidal MO_3 fragment is a common structural motif in the oxo chemistry of groups 6 and 7. It may be considered a functional group[1] inasmuch as it may be transformed into other groups by oxygen atom substitution, derivatization, or elimination. However, well-defined examples of such reactivity, including structure proof of products, are not numerous. Among such studies are the demonstrations of nucleophilic reactivity of MoO_3 and WO_3 groups in protonation[2−5] and metal complexation[6,7] reactions. These groups are of interest in the context of molybdenum and tungsten hydroxylase and oxotransferase enzymes[8,9] inasmuch as they may be considered the actual or formal progenitors of portions of metal sites whose other ligand is a pyranopterindithiolate. A mutant form of sulfite oxidase is proposed to contain a MoO_3 group from Mo extended X-ray absorption fine structure (EXAFS) analysis.[10] The $Mo^{VI}OS(OH)$ portion of the site of active xanthine oxidase[11,12] is derived from the $Mo^{VI}O_3$ group by oxo/sulfido substitution and protonation. The $Mo^{VI}O_2(OH)$ portion of the inactive enzyme, obtained

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(1) Holm, R. H. *Chem. Rev.* **1987**, *87*, 1401−1449.
(2) Herrmann, W.; Wieghardt, K. *Polyhedron* **1986**, *5*, 513−520.
(3) Schreiber, P.; Wieghardt, K.; Nuber, B.; Weiss, J. *Polyhedron* **1989**, *8*, 1675−1682.
(4) Schreiber, P.; Wieghardt, K.; Nuber, B.; Weiss, J. *Z. Anorg. Allg. Chem.* **1990**, *587*, 174−192.
(5) Eagle, A. A.; George, G. N.; Tiekink, E. R. T.; Young, C. G. *Inorg. Chem.* **1997**, *36*, 472−479.
(6) Roy, P. S.; Wieghardt, K. *Inorg. Chem.* **1987**, *26*, 1885−1888.
(7) Schreiber, P.; Wieghardt, K.; Nuber, B.; Weiss, J. *Z. Naturforsch.* **1990**, *45b*, 619−628.
(8) Hille, R. *Chem. Rev.* **1996**, *96*, 2757−2816.
(9) Hille, R. *Trends Biochem. Sci.* **2002**, *27*, 360−367.
(10) George, G. N.; Garrett, R. M.; Prince, R. C.; Rajagopalan, K. V. *J. Am. Chem. Soc.* **1996**, *118*, 8588−8592.
(11) Romão, M. J.; Archer, M.; Moura, I.; Moura, J. J. G.; LeGall, J.; Engh, R.; Schneider, M.; Hof, P.; Huber, R. *Science* **1995**, *270*, 1170−1176.
(12) Huber, R.; Hof, P.; Duarte, R. O.; Moura, J. J. G.; Moura, I.; Liu, M.-Y.; LeGall, J.; Hille, R.; Archer, M.; Romão, M. J. *Proc. Natl. Acad. Sci. U. S. A.* **1996**, *93*, 8846−8851.

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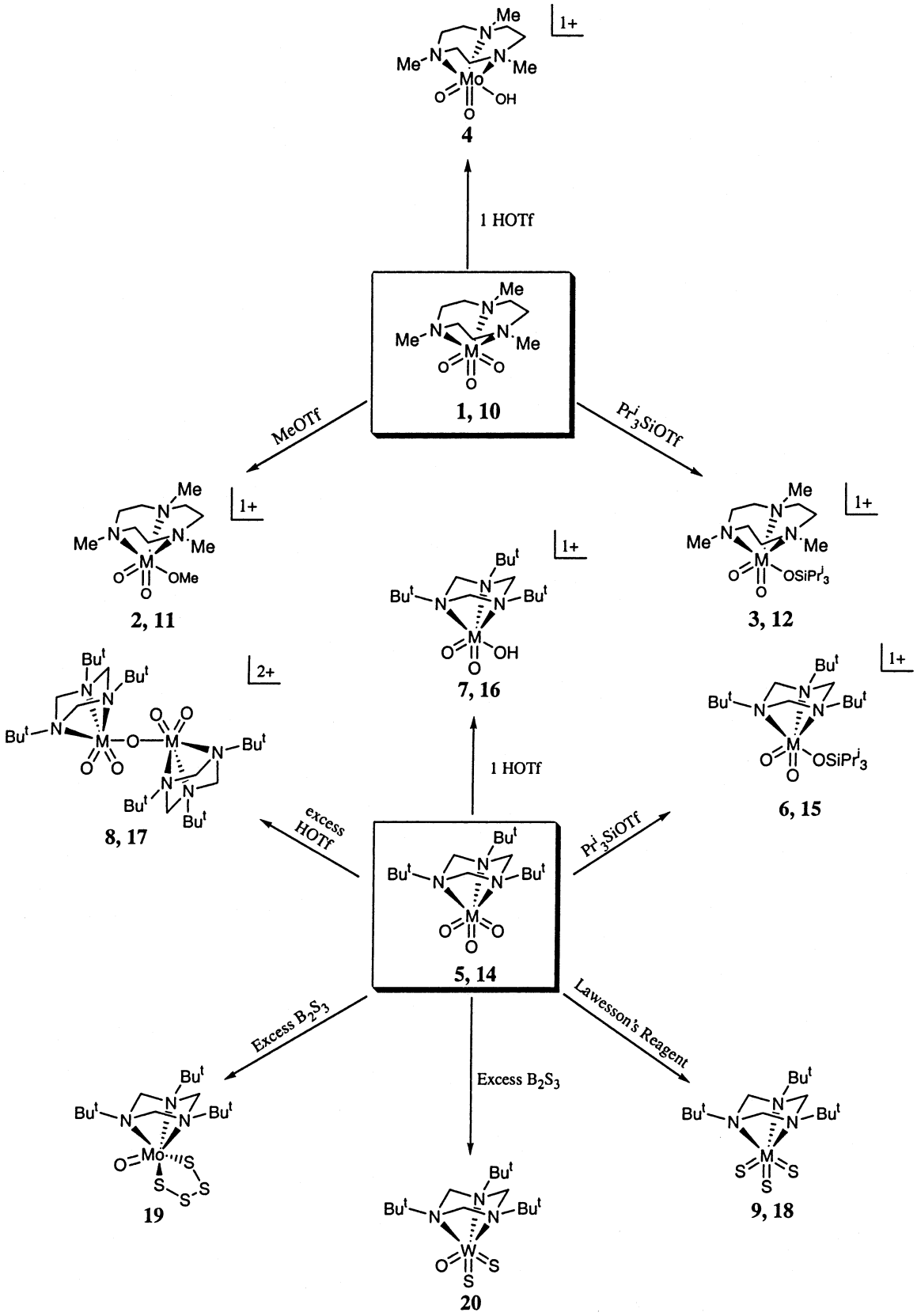

Figure 1. Reaction scheme summarizing nucleophilic reactions of [(Me_3tacn)MO_3] (**1, 10**) and [(Bu^t_3tach)MO_3] (**5**, **14**) and oxo/sulfido substitution reactions of the latter (M = Mo, W).

by cyanolysis of the active form, is a monoprotonation product. The diprotonated fragment $Mo^{VI}O_2(OH_2)$ has been detected crystallographically in (presumably inactive) aldehyde oxidoreductases[13,14] and it and/or the monoprotonated form is present in cyanide-deactivated carbon monoxide dehydrogenase.[15] Further, in the active CODH from *O. carboxidovorans*, the site contains the unprotonated or monoprotonated $Mo^{VI}O_2S$ group, which is implicated in a

Mo-(μ_2-S)-Cu^I bridge and in the copper-deficient form the site contains a mixture of $Mo^{VI}O_2(SH)$ and $Mo^{VI}O(OH_{(2)})$-(SH) groups.[15]

Recent research in this laboratory[16−18] has been directed toward obtaining structural and functional analogues of the active sites of the molybdenum and tungsten oxotransferases. These species are largely bis(dithiolene) complexes of the types $[M^{IV}(OR')(S_2C_2R_2)_2]^{1-}$ and $[M^{VI}O(OR')(S_2C_2R_2)_2]^{1-}$ and represent the active sites of the DMSO reductase enzyme family in the Hille classification.[8] Analogues of the sites of members of the xanthine oxidase family, which includes the foregoing enzymes, must be monodithiolene complexes with a protonated $Mo^{VI}O_2S$ fragment. In contemplating routes to such analogue species, we note above that inactive (desulfo) enzymes, lacking the apical sulfide critical to activity, have been found to have protonated $Mo^{VI}O_3$ coordination fragments. We have commenced an approach to site analogues by first examining pertinent reactions of $M^{VI}O_3$ (M = Mo, W) groups. Tungsten is included because of our ongoing practice to develop, insofar as possible, molybdenum and tungsten site analogue chemistry in parallel. In this way, tungsten coordination units, recognized and as yet undiscovered in proteins, may be realized synthetically for reactivity studies.[19,20] For this purpose, the complexes [(Me_3-tacn)MO_3] (**1**, **10**)[2,6] and [(Bu^t_3tach)MO_3] (**5**, **14**),[21] shown in Figure 1, have been selected because of their M^{VI} oxidation state and nonreducing ligand environment. Abbreviations are given in Chart 1. Our initial results in exploring the reactivity of $M^{VI}O_3$ groups are reported here.

Experimental Section

Preparation of Compounds. All operations were performed under a pure dinitrogen atmosphere using standard Schlenk techniques or an inert atmosphere box. Acetonitrile, ether, and THF were purified with an Innovative Technology solvent purification system. Hexanes were distilled over sodium benzophenone ketyl; acetonitrile-d_3 was stored over 4-Å molecular sieves. Other reagents were commercial samples used as received.

[(Me_3tacn)MoO_2(OMe)](OTf). [(Me_3tacn)MoO_3][2,6] (45 mg, 0.14 mmol) was suspended in 4 mL of acetonitrile. To the stirred suspension was added dropwise 25 mg (0.15 mmol) of methyl triflate in 1 mL of acetonitrile. Over 60 min, a pale-yellow solution formed, which was concentrated in vacuo. The residue was treated with THF and hexanes to yield the product as 55 mg (80%) of a white solid. IR (KBr): 794 (m); 907, 931 (s, ν_{MoO}) cm^{-1}. ^1H NMR (CD_3CN): δ 2.85−3.20 (m, −12), 2.99 (s, 6), 3.09 (s, 3), 4.51 (s, 3). Anal. Calcd for $C_{11}H_{24}F_3MoN_3O_6S$: C, 27.56; H, 5.05; Mo, 20.02; N, 8.77. Found: C, 27.42; H, 4.89; Mo, 20.18; N, 8.83.

[(Me_3tacn)MoO_2($OSiPr^i_3$)](OTf). To a suspension of [(Me_3-tacn)MoO_3] (110 mg, 0.349 mmol) in 5 mL of ether was added 107 mg (0.349 mmol) of Pr^i_3SiOTf. The reaction mixture was stirred for 6 h, and the ether was decanted. The residue was washed thoroughly with ether and dried to afford the product as a white solid in essentially quantitative yield. IR (KBr): 793 (s); 860 (s); 911, 943 (s, ν_{MoO}) cm^{-1}. ^1H NMR (CD_3CN): δ 1.14 (d, 18), 1.28 (sep, 3), 2.94−3.20 (m, ∼12), 3.04 (s, 6), 3.14 (s, 3). Anal. Calcd for $C_{19}H_{42}F_3MoN_3O_6SSi$: C, 36.71; H, 6.81; Mo, 15.43; N, 6.76. Found: C, 36.89; H, 6.74; Mo, 15.34; N, 6.85.

[(Me_3tacn)MoO_2(OH)](OTf). [(Me_3tacn)MoO_3] (157 mg, 0.498 mmol) was suspended in 6 mL of acetonitrile. To the stirred suspension was added dropwise 75 mg (0.500 mmol) of triflic acid in 1 mL of acetonitrile. The suspension slowly became a pale-yellow solution. The reaction mixture was stirred for 30 min and concentrated in vacuo to <1 mL. Addition of 5 mL of ether and 30 mL of hexanes caused separation of the product as 195 mg (84%) of white solid. IR (KBr): 701 (m); 913, 931 (s, ν_{MoO}) cm^{-1}. ^1H NMR (CD_3CN): δ 3.0−3.1 (m, ∼12), 3.06 (s, 9). Anal. Calcd for $C_{10}H_{22}F_3MoN_3O_6S$: C, 25.81; H, 4.76; Mo, 20.62; N, 9.03. Found: C, 25.75; H, 4.85; Mo, 20.76; N, 8.84.

[(Me_3tacn)WO_2(OMe)](OTf). To a stirred suspension of [(Me_3-tacn)WO_3][6] (82 mg, 0.20 mmol) in 4 mL of acetonitrile was added 34 mg (0.21 mmol) of methyl triflate in 1 mL of acetonitrile. The mixture was stirred for 90 min, during which a pale-yellow solution formed. The solution was filtered through Celite, and the filtrate was concentrated in vacuo. The residue was treated with THF and hexanes to give the product as 87 mg (75%) of white solid. IR (KBr): 798 (m); 905, 940 (s, ν_{WO}) cm^{-1}. ^1H NMR (CD_3CN): δ 2.95−3.52 (m, ∼12), 3.01 (s, 6), 3.20 (s, 3), 4.57 (s, 3). Anal. Calcd for $C_{11}H_{24}F_3N_3O_6SW$: C, 23.29; H, 4.26; N, 7.41; W, 32.41. Found: C, 23.36; H, 4.21; N, 7.49; W, 32.45.

[(Me_3tacn)WO_2($OSiPr^i_3$)](OTf). The procedure is analogous to that of the molybdenum analogue and afforded the product as a white solid in comparable yield. IR (KBr): 797 (s); 869 (s); 919, 962 (s, ν_{WO}) cm^{-1}. ^1H NMR (CD_3CN): δ 1.16 (d, 18), 1.28 (sep, 3), 3.04−3.38 (m, ∼12), 3.07 (s, 6), 3.25 (s, 3). Anal. Calcd for $C_{19}H_{42}F_3N_3O_6SSiW$: C, 32.16; H, 5.97; N, 5.92; W, 25.91. Found: C, 32.02; H, 5.88; N, 6.03; W, 25.83.

[(Bu^t_3tach)MoO_2($OSiPr^i_3$)](OTf). To a suspension of [(Bu^t_3-tach)MoO_3][21] (135 mg, 0.338 mmol) was added dropwise 110 mg (0.359 mmol) of Pr^i_3SiOTf in 1 mL of acetonitrile. The reaction mixture was stirred for 90 min, during which a colorless solution formed. The solvent was removed in vacuo, and the residue was dissolved in a minimal volume of acetonitrile. Addition of 20 mL of ether and 40 mL of hexanes caused separation of the product as 179 mg (75%) of white solid. IR (KBr): 851 (vs); 926, 952 (s, ν_{MoO}) cm^{-1}. ^1H NMR (CD_3CN): δ 1.13 (d, 18), 1.31 (sep, 3), 1.39 (s, 9), 1.43 (s, 18), 4.11 (d, 1), 4.20 (d, 2), 4.75 (d, 1), 4.97 (d, 2). Anal. Calcd for $C_{25}H_{54}F_3MoN_3O_6SSi$: C, 42.54; H, 7.71; N, 5.95; Mo, 13.59. Found: C, 42.36; H, 7.35; N, 5.96; Mo, 13.74.

[(Bu^t_3tach)MoO_2(OH)](OTf). To a stirred suspension of [(Bu^t_3-tach)MoO_3] (110 mg, 0.16 mmol) in 6 mL of acetonitrile was added 41 mg (0.16 mmol) of triflic acid in 1 mL of acetonitrile. The suspension formed a pale-yellow solution, which was immediately concentrated in vacuo to ca. 1 mL. Addition of 20 mL of ether and 20 mL of hexanes afforded the product as 113 mg (75%) of white solid. IR (KBr): 714 (vs); 919, 970 (s, ν_{MoO}) cm^{-1}. ^1H NMR (CD_3CN): δ 1.40 (27), 4.12 (d, 3), 4.87 (d, 3). Anal. Calcd for $C_{16}H_{34}F_3MoN_3O_6S$: C, 34.97; H, 6.24; Mo, 17.46; N, 7.65. Found: C, 34.90; H, 6.38; Mo, 17.38; N, 7.73.

(13) Rebelo, J. M.; Dias, J. M.; Huber, R.; Moura, J. J. G.; Romão, M. J. *J. Biol. Inorg. Chem.* **2001**, *6*, 791−800.
(14) Rebelo, J.; Maceira, S.; Dias, J. M.; Huber, R.; Ascenso, C. S.; Rusnak, F.; Moura, J. J. G.; Moura, I.; Romão, M. J. *J. Mol. Biol.* **2000**, *297*, 135−146.
(15) Dobbek, H.; Gremer, L.; Kiefersauer, R.; Huber, R.; Meyer, O. *Proc. Natl. Acad. Sci. U. S. A.* **2002**, *99*, 15971−15976.
(16) Lim, B. S.; Holm, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 1920−1930.
(17) Sung, K.-M.; Holm, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 1931−1943.
(18) Sung, K.-M.; Holm, R. H. *J. Am. Chem. Soc.* **2002**, *124*, 4312−4320.
(19) Sung, K.-M.; Holm, R. H. *Inorg. Chem.* **2000**, *39*, 1275−1281.
(20) Sung, K.-M.; Holm, R. H. *Inorg. Chem.* **2001**, *40*, 4518−4525.
(21) Baker, M. V.; North, M. R.; Skelton, B. W.; White, A. H. *Inorg. Chem.* **1999**, *38*, 4515−4521.

[((Bu^t$_3$tach)MoO$_2$)$_2$(μ-O)](OTf)$_2$. This compound was prepared by the reaction of an acetonitrile suspension of [(Bu^t$_3$tach)MoO$_3$] (0.94 mg, 0.23 mmol) with a solution of 172 mg (1.15 mmol) of triflic acid, followed by vapor diffusion of ether into the concentrated reaction solution. The product was obtained as a colorless crystalline solid together with a small amount of other contaminants. It was confirmed by an X-ray structure determination. IR (KBr): 749, 782 (vs, ν_{MoOMo}); 931, 967 (s, ν_{MoO}) cm^{-1}. ^{1}H NMR (CD$_3$CN): δ 1.38 (s, 18), 1.44 (s, 36), 4.25 (d, 2), 4.33 (d, 4), 4.69 (d, 2), 5.05 (d, 4).

[(Bu^t$_3$tach)WO$_2$(OSiPr^i$_3$)](OTf). To a stirred suspension of [(Bu^t$_3$tach)WO$_3$][21] (151 mg, 0.310 mmol) was added 104 mg (0.341 mmol) of Pr^i$_3$SiOTf in 1 mL of acetonitrile. The mixture was stirred for 2 h during which a colorless solution formed. The volume was reduced in vacuo to 1 mL; ether and hexanes were added sequentially, causing separation of the product as 174 mg (71%) of white solid. IR (KBr): 861 (vs); 931, 972 (s, ν_{WO}) cm^{-1}. ^{1}H NMR (CD$_3$CN): δ 1.14 (d, 18), 1.30 (sep, 3), 1.40 (s, 9), 1.41 (s, 18), 4.81 (m, 2), 4.87 (d, 2), 5.08 (d, 2). Anal. Calcd for C$_{25}$H$_{54}$F$_3$N$_3$O$_6$SSiW: C, 37.83; H, 6.86; N, 5.29; W, 23.16. Found: C, 37.69; H, 6.72; N, 5.36; W, 23.23.

[(Bu^t$_3$tach)WO$_2$(OH)](OTf). To a stirred suspension of [(Bu^t$_3$tach)WO$_3$] (192 mg, 0.394 mmol) in 6 mL of acetonitrile was added dropwise 59 mg (0.393 mmol) of triflic acid. The suspension was stirred for 10 min, concentrated in vacuo to about 1 mL, and treated with 25 mL of ether and 15 mL of hexanes. The product was isolated as 190 mg (76%) of white solid. IR (KBr): 921, 971 (s, ν_{WO}) cm^{-1}. ^{1}H NMR (CD$_3$CN): δ 1.40 (s, 27), 4.67 (d, 3), 4.93 (d, 3). Anal. Calcd for C$_{16}$H$_{34}$F$_3$N$_3$O$_6$SW: C, 30.15; H, 5.38; N, 6.59; W, 28.84. Found: C, 30.25; H, 5.46; N, 6.43; W, 28.68.

[((Bu^t$_3$tach)WO$_2$)$_2$(μ-O)](OTf)$_2$. To a stirred suspension of [(Bu^t$_3$tach)WO$_3$] (118 mg, 0.242 mmol) was added 363 mg (2.42 mmol) of triflic acid in 1 mL of acetonitrile. The suspension became a solution almost immediately. The reaction mixture was stirred for 15 min and concentrated to ca. 1 mL. Diffusion of ether afforded the product as 57 mg (37%) of colorless crystals. IR (KBr): 814 (s, ν_{WOW}); 935, 970 (s, ν_{WO}) cm^{-1}. ^{1}H NMR (CD$_3$CN): δ 1.42 (s, 18), 1.43 (s, 36), 4.79 (d, 2), 4.96 (d, 2), 4.98 (d, 4), 5.16 (d, 4).

[(Bu^t$_3$tach)MoS$_3$]. To a suspension of 100 mg (0.229 mmol) of [(Bu^t$_3$tach)MoO$_3$] in 10 mL of acetonitrile was added 152 mg (0.376 mmol) of Lawesson's reagent ([*p*-MeOC$_6$H$_4$P(S)S]$_2$). The reaction mixture immediately formed a brown solution that was stirred for 5 min and chromatographed on a silica column. (In this and the following preparations, the silica was pretreated with triethylamine and washed with eluant prior to use on the column. This procedure was found necessary to prevent decomposition during chromatography.) Elution with dichloromethane gave first a green-brown band that was collected and concentrated to dryness. The residue was suspended in 5 mL of acetonitrile and precipitated with ether. The product was collected as 58 mg (52%) of a red-brown microcrystalline solid. IR (KBr): 473, 483 (s, ν_{MoS}) cm^{-1}. ^{1}H NMR (CD$_3$CN): δ 1.48 (s, 27), 3.72 (d, 3), 4.67 (d, 3). Absorption spectrum (DMF): λ_{max} (ϵ_M) 312 (4330), 406 (8420), 487 (684), 582 (323) nm. Anal. Calcd for C$_{15}$H$_{33}$MoN$_3$S$_3$: C, 40.25; H, 7.43; Mo, 21.43; N, 9.39. Found: C, 40.10; H, 7.48; Mo, 21.58; N, 9.31.

[(Bu^t$_3$tach)MoO(S$_4$)]. To a suspension of 150 mg (0.376 mmol) of [(Bu^t$_3$tach)MoO$_3$] in 15 mL of acetonitrile was added 210 mg (1.78 mmol) of B$_2$S$_3$. The suspension began to turn orange and was stirred at 40 °C for 6 h. The reaction mixture was chromatographed on silica gel with 1:4 v/v acetonitrile/ether eluant. The initial red band was collected, dried, and extracted into a minimum volume of DMF. The solution was filtered, and ca. 50 mL of dichloromethane was added. The solution was extracted with water, and the organic phase was separated and dried (MgSO$_4$). It was reduced in volume and ether was added, causing the compound to separate as a red microcrystalline solid in ca. 25% yield. IR (KBr): 917 (s, ν_{MoO}) cm^{-1}. ^{1}H NMR (CD$_3$CN): δ 0.73 (s, 9), 1.66 (s, 18), 3.59 (d, 2), 4.21 (d, 2), 4.81 (d, 1), 6.45 (d, 1). The compound was identified by an X-ray structure determination.

Chart 1. Designation of Compounds and Abbreviations[a]

[(Me$_3$tacn)MO$_3$]	M = Mo (**1**),[2,6] W (**10**)[6]
[(Me$_3$tacn)MO$_2$(OMe)]$^{1+}$	M = Mo (**2**), W (**11**)
[(Me$_3$tacn)MO$_2$(OSiPr^i$_3$)]$^{1+}$	M = Mo (**3**), W (**12**)
[(Me$_3$tacn)MO$_2$(OH)]$^{1+}$	M = Mo (**4**), W (**13**)[3]
[(Bu^t$_3$tach)MO$_3$]	M = Mo (**5**),[21] W (**14**)[21]
[(Bu^t$_3$tach)MO$_2$(OSiPr^i$_3$)]$^{1+}$	M = Mo (**6**), W (**15**)
[(Bu^t$_3$tach)MO$_2$(OH)]$^{1+}$	M = Mo (**7**), W (**16**)
[((Bu^t$_3$tach)MO$_2$)$_2$(μ-O)]$^{2+}$	M = Mo (**8**), W (**17**)
[(Bu^t$_3$tach)MS$_3$]	M = Mo (**9**), W (**18**)
[(Bu^t$_3$tach)Mo(O)(S$_4$)]	(**19**)
[(Bu^t$_3$tach)WOS$_2$]	(**20**)

[a] Key: bdt, 1,2-benzenedithiolate(2−); Bu^t$_3$tach, 1,3,5-tri-*tert*-butyl-1,3,5-triazacyclohexane; CODH, carbon monoxide dehydrogenase; Me$_3$tacn, 1,4,7-trimethyl-1,4,7-triazacyclononane; OTf, triflate(1−); tacn, 1,4,7-triazacyclononane; Tp*, tris(3,5-dimethylpyrazolyl)hydroborate(1−).

[(Bu^t$_3$tach)WS$_3$]. To a suspension of 101 mg (0.207 mmol) of [(Bu^t$_3$tach)WO$_3$] in 10 mL was added 167 mg (0.413 mmol) of Lawesson's reagent. The suspension immediately began to change from colorless to orange and was stirred for 5 min. It was chromatographed on silica gel with dichloromethane as the eluant. The orange band was collected and reduced to dryness, and the residue was suspended in 5 mL of acetonitrile followed by the addition of ether. The suspension was agitated vigorously several times. The product was collected by filtration as 57 mg (51%) of an orange microcrystalline solid. IR (KBr): 466, 484 (s, ν_{WS}) cm^{-1}. ^{1}H NMR (CD$_3$CN): δ 1.49 (s, 27), 4.76 (d, 3), 4.94 (d, 3). Absorption spectrum (DMF): λ_{max} (ϵ_M) 350 (7060), 398 (1070) nm. Mass spectrum: 534.2, 536.2, 538.2 (P$^+$). Anal. Calcd for C$_{15}$H$_{33}$N$_3$S$_3$W: C, 33.64; H, 6.21; N, 7.85. Found: C, 33.67; H, 6.18; N, 7.78.

[(Bu^t$_3$tach)WOS$_2$]. To a suspension of 75 mg (0.154 mmol) of [(Bu^t$_3$tach)WO$_3$] in 7 mL of acetonitrile was added 100 mg (0.849 mmol) of B$_2$S$_3$. The colorless suspension quickly turned to yellow and then slowly to orange; it was stirred for 4 days and the solvent was removed. The solid was extracted into DMF (leaving some residue) and chromatographed on silica gel with dichloromethane as the eluant. The initial yellow band was collected; workup thereafter followed that in the preceding preparation. The product was obtained as 52 mg (65%) of a yellow solid. IR (KBr): 477 (br, ν_{WS}), 890, 895 (s, ν_{WO}) cm^{-1}. ^{1}H NMR (CD$_3$CN): δ 1.40 (s, 18), 1.60 (s, 9), 4.56 (d, 2), 4.67 (d, 1), 4.81 (d, 2), 4.91 (d, 1). Absorption spectrum (DMF): λ_{max} (ϵ_M) 298 (2860), 376 (530), 454 (252), 376 (530), 454 (252) nm. Anal. Calcd for C$_{15}$H$_{33}$N$_3$OS$_2$W: C, 34.68; H, 6.40; N, 8.09; W, 35.39. Found: C, 35.04; H, 6.52; N, 8.05; W, 35.45.

In the following sections, complexes are numerically designated according to Chart 1.

X-ray Structure Determinations. Crystals of [**2**](OTf) were grown by vapor diffusion of ether into a 1:1 acetone/acetonitrile (v/v) solution. Crystals of the triflate salts of **3**, **4**, **6**, **8**, **12**, **16**, and **17** were obtained by vapor diffusion of ether into concentrated acetonitrile solutions. Crystals of [**7**](OTf) and [**15**](OTf) were grown by vapor diffusion of 2−3 volume equiv of ether into

Table 1. Crystallographic Data[a] for Oxo-Me_3tacn Complexes

	[**2**](OTf)	[**3**](OTf)	[**4**](OTf)	[**12**](OTf)
formula	$C_{11}H_{24}F_3MoN_3O_6S$	$C_{19}H_{42}F_3MoN_3O_6SSi$	$C_{10}H_{22}F_3MoN_3O_6S$	$C_{19}H_{42}F_3N_3O_6SSiW$
fw	479.33	621.65	465.31	709.56
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1$	$P2_1/c$
Z	4	4	4	4
a, Å	7.912(2)	8.322(2)	7.701(2)	8.297(2)
b, Å	21.469(4)	30.128(6)	15.198(3)	30.09(1)
c, Å	10.974(2)	11.041(2)	14.866(3)	11.006(2)
β, deg	93.67(3)	93.91(1)	94.03(3)	93.82(3)
V, Å^3	1860.3(6)	2762.0(1)	1735.6(6)	2741.6(1)
R^b ($R_w{}^c$): %	4.92 (10.56)	5.72 (11.28)	3.11 (7.53)	2.65 (7.01)

[a] Obtained with graphite-monochromatized Mo Kα ($\lambda = 0.71073$ Å) radiation at 213 K. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w = \{\sum[w(|F_o| - |F_c|)^2]/\sum[w|F_o|^2]\}^{1/2}$.

Table 2. Crystallographic Data[a] for Oxo-Bu^t_3tach Complexes

	[**6**](OTf)	[**7**](OTf)	[**8**](OTf)$_2$	[**15**](Bu^tNH_3)(OTf)$_2$	[**16**](OTf)	[**17**](OTf)$_2$
formula	$C_{25}H_{54}F_3MoN_3O_6SSi$	$C_{16}H_{34}F_3MoN_3O_6S$	$C_{32}H_{66}F_6Mo_2N_6O_{11}S_2$	$C_{30}H_{66}F_6N_4O_9S_2SiW$	$C_{16}H_{34}F_3N_3O_6SW$	$C_{32}H_{66}F_6N_6O_{11}S_2W_2$
fw	705.80	549.46	1080.91	1016.93	637.37	1256.73
cryst syst	monoclinic	orthorhombic	triclinic	orthorhombic	orthorhombic	triclinic
space group	$P2_1/n$	$Pna2_1$	$P\bar{1}$	$Pna2_1$	$Pna2_1$	$P\bar{1}$
Z	4	4	1	4	4	1
a, Å	17.126(3)	13.214(3)	10.071(2)	14.432(3)	13.183(1)	10.089(2)
b, Å	9.438(2)	15.653(3)	10.541(2)	25.788(5)	15.616(2)	10.534(2)
c, Å	22.930(5)	11.290(2)	11.868(2)	12.065(2)	11.317(1)	11.855(2)
α, deg			70.98(3)			71.09(3)
β, deg	111.91(3)		74.29)3)			74.05(3)
γ, deg			88.13(3)			88.16(3)
V, Å^3	3438.6(1)	2335.3(8)	1144.5(4)	4490.3(2)	2329.8(4)	1143.7(4)
R^b($R_w{}^c$): %	5.71(15.08)	4.97(11.08)	5.41(12.30)	2.61(5.69)	4.16(7.74)	4.21(10.49)

[a] Obtained with graphitic-monochromatized Mo Kα ($\lambda = 0.71073$ Å) radiation at 213 K. [b] $R = \{\sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w = \{\sum[w(|F_o| - |F_c|)^2]/\sum[w|F_o|^2]\}^{1/2}$.

acetonitrile solutions followed by layering the solutions with hexanes. Crystals of **9** were produced by slow vapor diffusion of benzene into saturated *N*,*N*-dimethylacetamide solutions; those of **19** were grown by vapor diffusion of ether into a saturated DMF solution. Crystals of **20** were formed in the eluant solutions. All samples were coated in paratone oil and mounted by means of glass capillary fibers on a Bruker CCD area detector instrument operated by the SMART software package. For each crystal, a hemisphere of data was collected at 213 K in 30 s frames and ω scans of 0.3 deg/frame. Data reduction was performed with SAINT, which corrects for Lorentz polarization and decay. Absorption corrections were applied using SADABS, and space groups were assigned using XPREP.

Structures were solved by Patterson methods with SHELXTL and refined against all data by full-matrix least squares on F^2. All structures contained one formula unit in the asymmetric unit, with the exceptions of [**4**](OTf), [**8**](OTf)$_2$, and [**17**](OTf)$_2$; in the latter two cases, one-half formula unit was generated by an inversion center. For [**1**](OTf), the fluorine atoms of the anion were disordered over two positions; the anions in [**7**](OTf) and [**16**](OTf) were highly disordered; in addition, these structures were refined with the program TWIN. The compound [**15**](OTf) crystallized with one (Bu^tNH_3)(OTf) formula unit in the asymmetric unit; the cation was presumably a result of ligand decomposition. The structure of **9** was solved in space group $P6_3/mc$ by analysis of systematic absences. The refinement was performed by modeling disorder in the sulfur and molybdenum atoms. The disorder was treated to allow for refinement of the occupancy value of one molecular orientation vs the other, with thermal values of the sulfur and molybdenum atoms restrained to be the same for the disordered partner. This refinement gave an occupancy value of almost 0.3. Refinement of the racemic twin component gave occupancy values of about 0.3. No new or twinned cell systems were located using software designed for this purpose. Final refinement gave the final occupancy values of 0.276 and 0.304 for the racemic twin. A disordered solvent molecule was also located, and its identity assigned as acetonitrile carried over from the original synthesis. The crystal used showed no decomposition during data collection. Hydrogen atoms in all structures were attached at idealized positions on carbon atoms and were refined as riding atoms with uniform isotropic thermal parameters. All structures converged in the final stages of refinement, showing no movement in atom positions. Use of the checking program PLATON did not identify any missing or higher symmetry. Crystal data and agreement factors are presented in Tables 1−3.[22]

Table 3. Crystallographic Data[a] for Sulfido-Bu^t_3tach Complexes

	9·($^1/_2$MeCN)	**19**	**20**
formula	$C_{16}H_{34.5}MoN_{3.5}S_3$	$C_{15}H_{33}MoN_3OS_4$	$C_{15}H_{33}N_3OS_2W$
fw	468.09	495.64	519.41
cryst syst	hexagonal	monoclinic	monoclinic
space group	$P6_3/mc$	$P2_1/c$	$Pnma$
Z	2	4	4
a, Å	13.549(2)	10.360(2)	12.644(3)
b, Å	13.549(2)	9.498(2)	16.067(3)
c, Å	7.227(2)	22.348(5)	9.906(2)
β, deg		90.84(3)	
V, Å^3	1148.9(4)	2198.7(8)	2012.5(7)
R^b($R_w{}^c$): %	5.10(11.42)	6.55(15.20)	3.63(7.67)

[a] Obtained with graphite-monochromatized Mo Kα ($\lambda = 0.71073$ Å) radiation at 213 K. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w = \{\sum[w(|F_o| - |F_c|)^2]/\sum[w|F_o|^2]\}^{1/2}$.

Other Physical Measurements. ^{1}H NMR spectra were obtained with Bruker AM400N/500N/600N spectrometers. FT-IR spectra were taken on recrystallized solid samples in KBr on a Nicolet Nexus 470 FT-IR spectrometer. Electrospray mass spectra were determined with Micromass LCT spectrometer.

(22) See paragraph at the end of this article for Supporting Information available.

Table 4. Selected (Mean) Bond Lengths (Å) and Angles (deg) of $M^{VI}O_3$ and $M^{VI}O_2(OR)$ Complexes (M = Mo, W)

complex	M═O	M−OR[a]	O−M−O	O−M−OR[a]
[(tacn)Mo/WO_3][b]	1.75(1)/1.79(5)[c]		106.6(4)/107(1)	
2	1.705(1)	1.881(3)	105.7(1)	105.0(7)
3/12	1.700(1)/1.719(1)	1.891(2)/1.888(2)	105.9(1)/105.7(1)	105.0(7)/104.3(9)
4/13[d]	1.700(1)/1.78(2)	1.873(3)/1.89(1)	106.5(2)/110.6(9)	105.8(9)/103(3)
5/14[e]	1.724(3)/1.745(4)		107.1(2)/106.4(3)	
6/15	1.693(4)/1.717(6)	1.869(2)/1.865(3)	106.3(1)/106.1(2)	106.4(0)/105.7(7)
7/16	1.71(1)/1.70(2)	1.802(7)/1.84(2)	110.0(5)/107.9(9)	105.1(4)/105.2(6)
8/17	1.688(3)/1.705(7)	1.896(1)/1.895(7)	106.1(2)/105.8(3)	105(1)/104(1)

[a] R = H, Me, $SiPr^i_3$, Mo, W. [b] References 4 and 20. [c] One long bond (1.851(8) Å) attributed to hydrogen bonding with water.[4] [d] Reference 4. [e] Reference 20.

Results and Discussion

The Me_3tacn complexes **1** and **10**[2,6] and the Bu^t_3tach complexes **5** and **14**[21] present MO_3 groups (M = Mo, W) in trigonally symmetric, nonreducing environments that are suited to investigation of reactivity with retention of the M^{VI} oxidation state. The structures of **1** and **10** have not been reported but are doubtless highly similar to those of [(tacn)MoO_3][23] and [(tacn)WO_3].[4] The reactivity of these groups in nucleophilic and sulfidation reactions has been examined in this work, with emphasis on product isolation and structure proof by X-ray diffraction. Reactions were performed in acetonitrile at room temperature and are summarized in Figure 1. All cationic products were isolated as triflate salts. Principal structural parameters, limited to those of the MO_3 or $MO_2(OR)$ (R = H, Me, $SiPr^i_3$) groups, are contained in Table 4. Because of the high degree of similarity of (Me_3-tacn)M and (Bu^t_3tach)M fragments in their respective complexes, only representative structural results for several complexes are described. In general, complexes of hexahydrotriazines have been much less thoroughly investigated than those of triazacyclononanes. The advantage of the Bu^t_3-tach ligand used here is the ready solubility of its complexes in acetonitrile. Some of the other attributes of this ligand class are revealed, for example, by the recent work of the Australian group.[21,24−28]

Alkylation and Silylation Reactions. Treatment of Me_3-tacn complexes **1** and **10** with 1 equiv of methyl triflate results in immediate reaction and formation of **2** (80%) and **11** (75%), respectively, in the indicated yields. The structure of **2**, depicted in Figure 2, demonstrates the alkylated product, as does the ^{1}H NMR spectrum which shows two N-Me signals at δ 2.99 and 3.09 in a 2:1 intensity ratio and an OMe resonance at δ 4.51; the spectrum is consistent with C_s symmetry in solution. The corresponding signals of **11** are at δ 3.01, 3.20, and 4.57. The shape of the coordination sphere is influenced by the constraints of the Me_3tacn ligand and is dominantly trigonal but with a rhombic component owing to an idealized mirror plane bisecting the O(2)−Mo−O(3) angle. The range of N−Mo−N bite angles is 73.7(1)−75.3(1)° and trans O−Mo−N angles are 157.0(1)−158.4(1)°. The six cis O−Mo−N angles occur in the interval 87.2-(1)−89.7(1)°. An obvious but notable feature in alkylated and silylated complexes is the much longer M−OR than M═O bond, the difference being 0.17 Å in **2**. Of the three Mo−N bonds, Mo−N(1) (2.273(3) Å) is the shortest because it is not subject to the trans influence of an oxo ligand. The other two Mo−N bonds (Mo−N(3) 2.337(3) Å, Mo−N(2) 2.356(3) Å) are 0.07−0.09 Å longer, owing to the oxo trans influence. In [(tacn)MoO_3], where this factor is absent, the variation in Mo−N distances is much smaller (0.029 Å).[23]

Reaction of **1** and **10** with 1 equiv of Pr^i_3SiOTf rapidly forms silyloxide complexes **3** and **12**, respectively, in essentially quantitative yield. With the same reagent, Bu^t_3-tach complexes **5** and **14** afford **6** (75%) and **15** (71%), respectively. ^{1}H NMR spectra are consistent with C_s symmetry; for example, **6** displays Bu^t signals in a 2:1 intensity ratio at δ 1.39 and 1.43. Members of the pairs **3** and **12** (Figure 2) and **6** and **15** (Figure 3) are isostructural and nearly isometric and possess the essential stereochemistry of methoxide complex **2**. The oxo trans influence amounts to 0.08−0.12 Å in **3** and **12**.

The shape of the coordination spheres of **6** and **15** is dominated by the characteristically small bite angle of the hexahydrotriazine ligands. In **6**, N−Mo−N angles are 58.20-(8)−59.63(9)°. Trans and cis O−Mo−N angles define the ranges 145.4(1)−149.4(1)° and 91.1(1)−94.2(1)°, respectively. The shortest Mo−N distance (2.283(3) Å) is opposite the Mo−OSi bond; the other two bonds (2.391(3), 2.393(3) Å) are lengthened by the trans influence. In comparison, mean values for the trigonally symmetric trioxo complex **5** are Mo−O 1.724(3) Å, Mo−N 2.374(3) Å, N−Mo−N 58.8-(1)°, trans O−Mo−N 146.2(1)°, and cis O−Mo−N 93°. In this and the foregoing cases, monofunctionalization of the trioxo group degrades the idealized trigonal symmetry with the only important dimensional change being the longer M−OR bond. We are unaware of prior reactions leading to alkylation or silylation of the $M^{VI}O_3$ group. Methoxide complex **2** has been previously prepared[29] but not by an alkylation reaction.

Protonation Reactions. Treatment of **1** with 1 equiv of triflic acid led to formation and isolation of the monopro-

(23) McGowan, P. C.; Podesta, T. J.; Thornton-Pett, M. *Inorg. Chem.* **2001**, *40*, 1445−1453.
(24) Baker, M. V.; Brown, D. H.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1999**, 1483−1490.
(25) Baker, M. V.; Palermo, M. C.; Skelton, B. W.; White, A. H. *Austr. J. Chem.* **1999**, *52*, 179−184.
(26) Baker, M. V.; Brown, D. H.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **2000**, 763−768.
(27) Armanasco, N. L.; Baker, M. V.; North, M. R.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1998**, 1145−1149.
(28) Armanasco, N. L.; Baker, M. V.; North, M. R.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1997**, 1363−1368.
(29) Bürger, K. S.; Haselhorst, G.; Stötzel, S.; Weyhermüller, T.; Wieghardt, K.; Nuber, B. *J. Chem. Soc., Dalton Trans.* **1993**, 1987−1997.

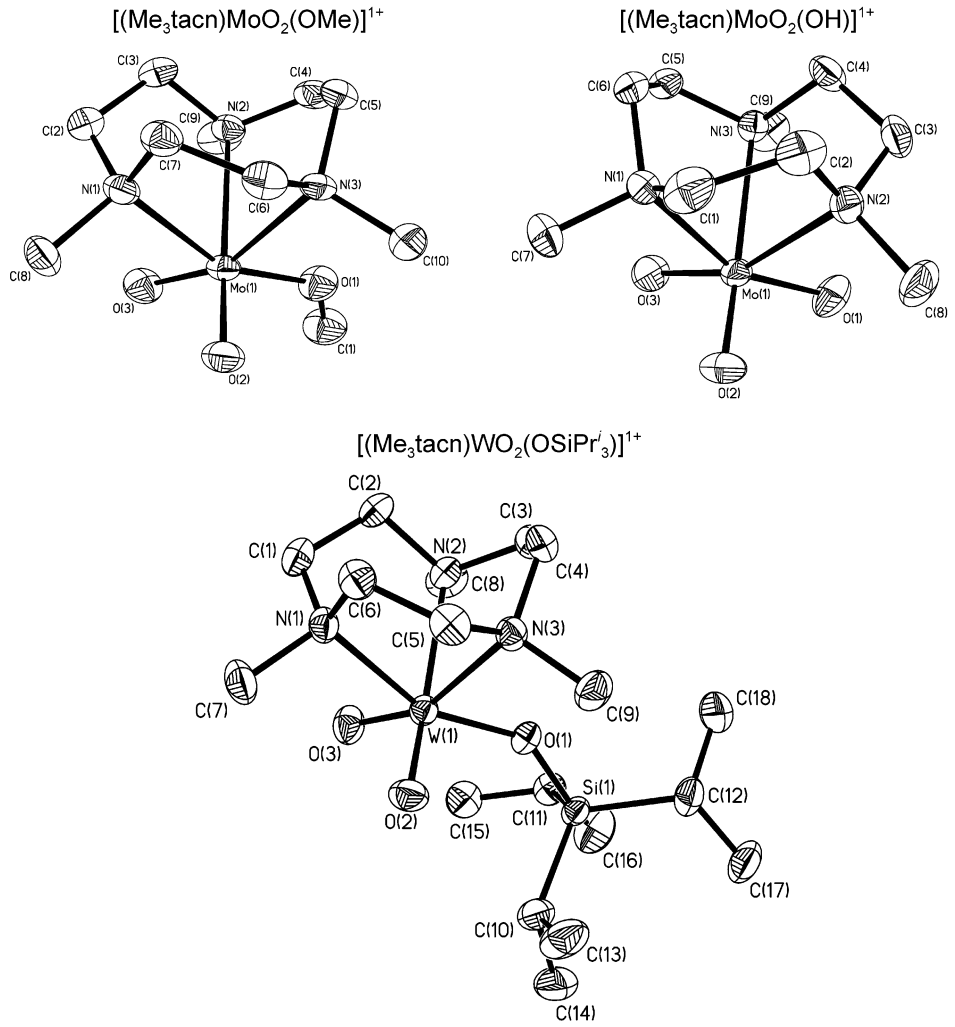

Figure 2. Structures of $[(Me_3tacn)MoO_2(OMe)]^+$ (**2**), $[(Me_3tacn)MoO_2(OH)]^+$ (**4**), and $[(Me_3tacn)WO_2(OSiPr^i_3)]^+$ (**12**) showing 50% probability ellipsoids and atom numbering schemes. Bond angles: Mo−O(1)−C(1) 131.2(3)° (**2**), W−O(1)−Si(1) 144.7(1)° (**12**).

tonated Me_3tacn complex **4** (84%). Its tungsten analogue **13** had been obtained earlier by the reaction of **10** with aqueous HBr.[4,30] The presence of coordinated hydroxide in these complexes is recognized by longer bond lengths (Table 4). Unexpectedly, the W═O bond distances are apparently 0.08 Å longer than the Mo═O bond lengths. The structure of **4** is entirely similar to that of **2**; in the former, the oxo trans influence on Mo−N bond lengths is 0.05−0.06 Å. Similar reactions of complexes **5** and **14** afford the monoprotonated Bu^t_3tach complexes **7** (75%) and **16** (76%). The structures of **7** (Figure 3) and **16** follow the now-standard structural pattern of rhombically distorted trigonal stereochemistry with easily detectable M−OH groups and oxo trans influences of 0.05−0.09 Å. Protonated complexes show a single methyl or Bu^t NMR signal, as would be expected from rapid site exchange.

When excess triflic acid is employed, μ-oxo species **8** (Figure 3) and **17** were obtained in low nonoptimized yields. The minimal reaction is $2[MO_3] + 2H^+ \rightarrow [M_2O_5]^{2+} + H_2O$, as has been observed in the formation of $[(tacn)W_2O_5]^{2+}$.[4,30] The complexes are centrosymmetric with linear bridges and unexceptional structural parameters. They are precedented structurally by $[(Tp^*)_2M_2O_5]$ (M = Mo,[31] W[5]) and $[(Cp^*)_2Mo_2O_5]$.[32]

Related protonation results include the apparent equilibrium $[(H_2O)_3MoO_3] + H^+ \rightleftarrows [(H_2O)_3MoO_2(OH)]^+$ in strongly acidic dilute solution, with molybdate formulated as a triaquo species,[33,34] and the formation of $[(Me_3tacn)Mo^{IV}O(OH_2)_2]^{2+}$, proposed from the pH dependence of the first quasi-reversible reduction step of **1**. The complex $[(Tp^*)WO_2(OH)]$ has been isolated and structurally characterized by tungsten EXAFS analysis.[5] The bond distances of 1.736(4) Å (W═O) and 1.90(1) Å (W−OH) are somewhat similar to those of **16**, but the difference (0.16 Å) is the same. The pK_a in acetonitrile has been estimated as 4.6−4.8. Last, the dissociation constant of $[Cp^*MoO_2(OH)]$ has been determined as pK_a = 3.65 in 20% methanol−water.[35] The compound was not isolated.

(30) Schreiber, P.; Wieghardt, K.; Nuber, B.; Weiss, J. *Polyhedron* **1989**, *8*, 1675−1682.
(31) Barnhart, K. M.; Enemark, J. H. *Acta Crystallogr.* **1984**, *C40*, 1362−1364.
(32) Rheingold, A. L.; Harper, J. R. *J. Organomet. Chem.* **1991**, *403*, 335−344.
(33) Paffett, M. A.; Anson, F. C. *Inorg. Chem.* **1981**, *20*, 3967−3972.
(34) Cruywagen, J. J. *Adv. Inorg. Chem.* **1999**, *49*, 127−182.

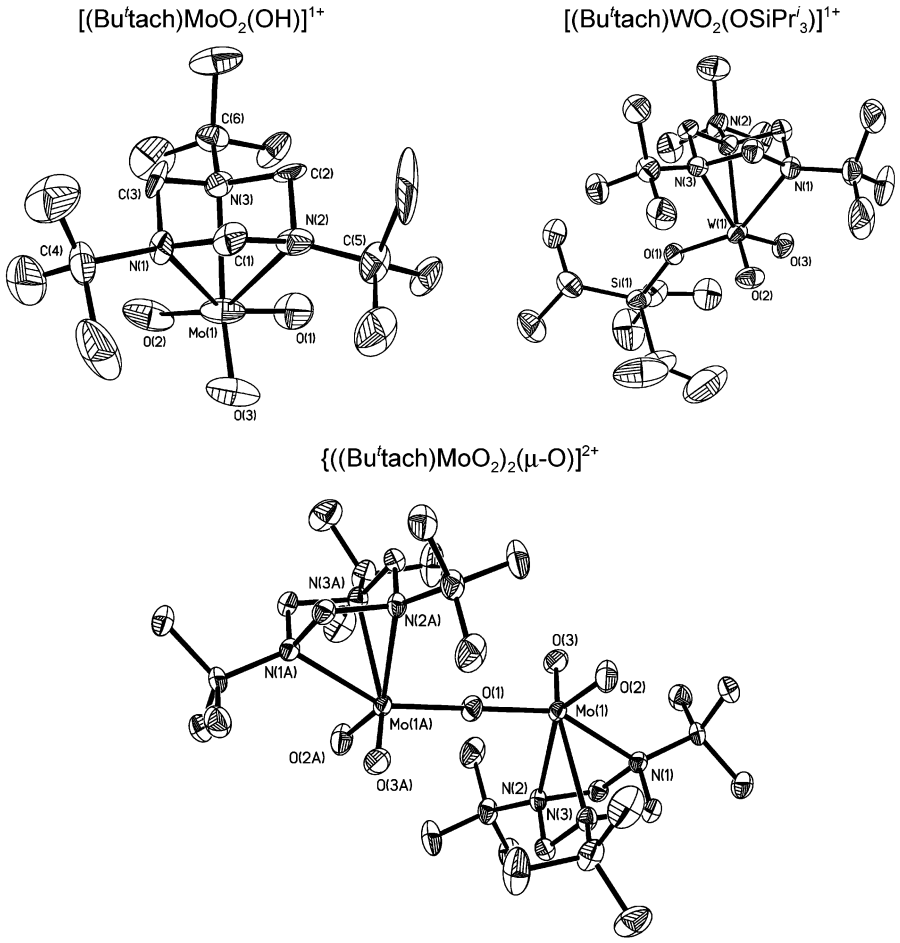

Figure 3. Structures of [(Bu$^t_3$tach)MoO$_2$(OH)]$^+$ (**7**), [(Bu$^t_3$tach)WO$_2$(OSiPr$^i_3$)]$^+$ (**15**), and [((Bu$^t_3$tach)MoO$_2$)$_2$(μ-O)]$^{2+}$ (**8**, crystallographically imposed centrosymmetry). Bond angle: W−O(1)−Si(1) 149.3(2)° (**15**).

Sulfidation Reactions. Because of the presence of terminal sulfide in the active site of enzymes in the xanthine oxidase family, the replacement of oxo by sulfido in complexes **5** and **14** has been examined (Figure 1). Structures of reaction products are collected in Figure 4, together with leading metric parameters. The transformation M═O → M═S for multiply bound terminal ligands does not have a general solution. The most significant reagents for this purpose are H_2S/HS^-,[36−38] B_2S_3,[39−42] P_4S_{10},[42,43] and $(Me_3Si)_2S$.[44−48] Treatment with 1.6−2.0:1 mol ratio of Lawesson's reagent (a derivatized form of P_4S_{10}) resulted in rapid reactions, which, followed by silica gel chromatography, afforded the trisulfido complexes red-brown **9** (52%) and orange **18** (51%). The two compounds are isomorphous and severely disordered; trigonal symmetry is crystallographically imposed. They contain the $M^{VI}S_3$ group, which with M = Mo is precedented only by $[Cp^*MoS_3]^-$ [49] in five- and six-coordinate complexes. (Two non-oxo tetrahedral species containing the $Mo^{VI}S_3$ group have also been described.[45,50]) Complex **18** is most closely related to $[(Tp^*)WS_3]^-$;[51] several other examples of the $W^{VI}S_3$ group have been reported.[49,50,52,53] None of these compounds were prepared by oxo/sulfido substitution. A heterogeneous reaction between **14** and excess (5.5:1 mol ratio) of B_2S_3 in acetonitrile for 4 days followed by chromatography afforded the yellow oxodisulfido com-

(35) Collange, E.; Garcia, J. A.; Poli, R. *New J. Chem.* **2002**, *26*, 1249−1256.
(36) Wieghardt, K.; Hahn, M.; Weiss, J.; Swiridoff, W. *Z. Anorg. Allg. Chem.* **1982**, *492*, 164−174.
(37) McDonald, J. W.; Friesen, G. D.; Rosenhein, L. D.; Newton, W. E. *Inorg. Chim. Acta* **1983**, *72*, 205−210.
(38) Faller, J. W.; Ma, Y. *Organometallics* **1989**, *8*, 609−612.
(39) Callahan, K. P.; Durand, P. J. *Inorg. Chem.* **1980**, *19*, 3211−3217.
(40) Bristow, S.; Collison, D.; Garner, C. D.; Clegg, W. *J. Chem. Soc., Dalton Trans.* **1983**, 2495−2499.
(41) Barnard, K. R.; Gable, R. W.; Wedd, A. G. *J. Biol. Inorg. Chem.* **1997**, *2*, 623−633.
(42) Eagle, A. A.; Tiekink, E. R. T.; George, G. N.; Young, C. G. *Inorg. Chem.* **2001**, *40*, 4563−4573.
(43) Jacob, J.; Guzei, I. A.; Espenson, J. H. *Inorg. Chem.* **1999**, *38*, 3266−3267.
(44) Do, Y.; Simhon, E. D.; Holm, R. H. *Inorg. Chem.* **1983**, *22*, 3809−3812.
(45) Do, Y.; Simhon, E. D.; Holm, R. H. *Inorg. Chem.* **1985**, *24*, 1831−1838.
(46) Feinstein-Jaffe, I.; Dewan, J. C.; Schrock, R. R. *Organometallics* **1985**, *4*, 1189−1193.
(47) Klemperer, W. G.; Schwartz, C. *Inorg. Chem.* **1985**, *24*, 4459−4461.
(48) Yu, S.-B.; Holm, R. H. *Inorg. Chem.* **1989**, *28*, 4385−4391.
(49) Kawaguchi, H.; Yamada, K.; Lang, J.-P.; Tatsumi, K. *J. Am. Chem. Soc.* **1997**, *119*, 10346−10358.
(50) Kruhlak, N. L.; Wang, M.; Boorman, P. M.; Parvez, M.; McDonald, R. *Inorg. Chem.* **2001**, *40*, 3141−3148.
(51) Seino, H.; Arai, Y.; Iwata, N.; Nagao, S.; Mizobe, Y.; Hidai, M. *Inorg. Chem.* **2001**, *40*, 1677−1682.
(52) Rau, M. S.; Kretz, C. M.; Geoffroy, G. N. *Organometallics* **1993**, *12*, 3447−3460.
(53) Arikawa, Y.; Kawaguchi, H.; Kashiwabara, K.; Tatsumi, K. *Inorg. Chem.* **2002**, *41*, 513−520.

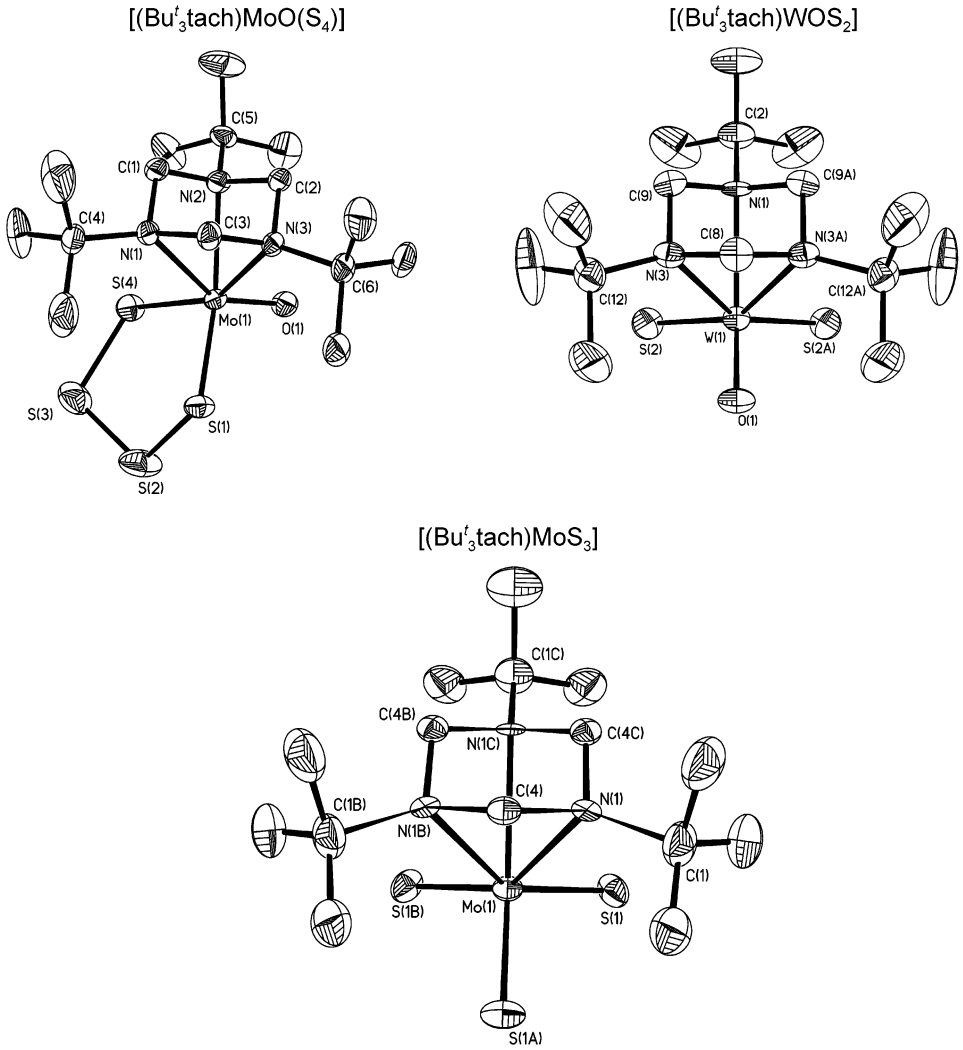

Figure 4. Structures of [(Bu$^t_3$tach)MoO(S$_4$)] (**19**), [(Bu$^t_3$tach)WOS$_2$] (**20**), and [(Bu$^t_3$tach)MoS$_3$] (**9**) showing 50% probability ellipsoids and atom numbering schemes. Metric parameters: Mo−O(1) 1.694(4) Å, Mo−S(1) 2.275(2) Å, Mo−S(4) 2.274(2) Å, S(1)−Mo−S(4) 94.06(6)°, O(1)−Mo−S(1) 105.9(2)°, O(1)−Mo−S(4) 107.5(2)° (**19**); W−O(1) 1.738(5) Å, W−S(2) 2.175(1) Å, O(1)−W−S(2) 106.35(9)° (**20**); Mo−S 2.173(6) Å, S−Mo−S 106.0(2)° (**9**).

plex **20**. ^{1}H NMR spectra indicated the stepwise substitution of sulfide in these systems; the monosulfido complex was not sought by isolation.

Reactions between **5** and B_2S_3 proved less amenable to the isolation of a pure product. In the most thoroughly studied case, reaction of a 4.7:1 mol ratio of the sulfide followed by chromatography and an extraction step gave the oxotetrasulfido complex **19**. The formation of this Mo^{IV} complex is another example of the relative tendency of Mo^{VI} vs W^{VI} toward reduction. The inverse tendency toward oxidation is illustrated in the system [(Tp*)Mo(CO)$_3$]/S$_8$ in DMF, which yields [(Tp*)Mo(S)S$_4$]$^-$ and some [(Tp*)Mo(O)S$_4$]$^-$, whose oxo ligand apparently derives from water present in the solvent. In the corresponding tungsten system, only W^{VI} products are isolated.[51]

Summary

The present results demonstrate the nucleophilic nature of oxo ligands in groups $Mo^{VI}O_3$ and $W^{VI}O_3$ as manifested in alkylation, silylation, and protonation reactions. Among the isolated and structurally characterized products are three examples of the monoprotonated groups $M^{VI}O_2(OH)$ (**4**, **7**, **16**). Previously, only two molecules with such groups had been isolated, both with tungsten.[4,5] Attempts to ascertain the site of further protonation led instead to dinuclear μ-oxo M_2O_5 species in the Bu^{t}tach series (**8**, **17**), anticipated to an extent by [(tacn)W$_2$O$_5$]$^{2+}$.[4] Oxo ligands are subject to replacement with sulfide, here with the use of Lawesson's reagent (**9**, **18**) or B_2S_3 (**19**, **20**). The present findings lend some credence to the possibility of stabilizing unprotonated and monoprotonated $M^{VI}O_3$ and $Mo^{VI}O_2S$ groups in five- or six-coordinate complexes, as in the xanthine oxidase family (M = Mo) and in corresponding tungsten complexes that may ultimately be related to enzyme sites. However, these units require stability in the potentially reducing monodithiolene (molybdenum) or bis(dithiolene) (tungsten) environment, a matter currently under investigation. In this context, we note that the complexes [$Mo^{VI}O_2$(bdt)(SR)]$^-$ [54] and

(54) Lim, B. S.; Willer, M. W.; Miao, M.; Holm, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 8343−8349.

$[WQ(SR)(S_2C_2Me_2)_2]^-$ (Q = O, S),[55] with reducing ligand environments, are sufficiently stable to be isolated.

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(55) Jiang, J.; Holm, R. H. Results to be published.

Supporting Information Available: X-ray crystallographic data in CIF format for the 13 compounds in Tables 1−3. This material is available free of charge via the Internet at http://pubs.acs.org.

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