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Oxidations of (R_3tach)M(CO)$_3$ Complexes [M = Cr, Mo, W; R_3tach = 1,3,5-Trialkyl-1,3,5-triazacyclohexane (R = *t*-Bu, Bn)]. Crystal Structures of (*t*-Bu_3tach)$MO_3\cdot 15H_2O$ (M = Mo, W)

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Stable Cr, Mo, and W complexes having a metal in oxidation state II, III, or VI, and possessing a facially coordinated 1,3,5-trialkyl-1,3,5-triazacyclohexane (R_3tach) ligand, can be prepared by oxidation of (R_3tach)M(CO)$_3$ with a variety of oxidizing agents. The reaction of the chromium or molybdenum complexes (R_3tach)M(CO)$_3$ (M = Cr, R = Bn (benzyl), *t*-Bu and M = Mo, R = *t*-Bu) with bromine or thionyl chloride at reflux affords a series of monomeric M(III) trihalide complexes. More controlled oxidation of (*t*-Bu_3tach)M(CO)$_3$ (M = Mo, W) with either bromine or iodine yields the 7-coordinate M(II) cations $[(t\text{-Bu}_3\text{tach})M(CO)_3X]^+$ (X = Br, I); protonation with trifluoromethanesulfonic acid affords the isolable $[(t\text{-Bu}_3\text{tach})M(CO)_3H]^+$ cations as their trifluoromethanesulfonate salts. Exhaustive oxidation of (*t*-Bu_3tach)M(CO)$_3$ (M = Mo, W) with hydrogen peroxide affords the monomeric M(VI) trioxo complexes (*t*-Bu_3tach)MO_3. The facial complexes (*t*-Bu_3tach)MO_3 (M = Mo, W) have been characterized by room-temperature single-crystal X-ray diffraction studies. The complexes both crystallize with 15 waters of hydration and lie on the 3-axes of rhombohedral *R*3*c* cells of dimensions $a = 21.026(3)$ Å and $c = 13.418(2)$ Å for M = Mo and $a = 21.011(3)$ Å and $c = 13.390(3)$ Å for M = W. The array is a superlattice on a quasi-*R*3*m* structure (*c* halved) with successive molecules along *c* slightly staggered and with a small perturbation on the molecular symmetry, degrading it from 3*m* to 3. The Mo═O (W═O) bond distances are 1.724(3) Å (1.745(4) Å), and the Mo−N (W−N) bond distances are 2.374(3) Å (2.355(6) Å). The O−Mo−O (O−W−O) angles are 107.1(2)° (106.4(3)°), and the N−Mo−N (N−W−N) angles are 58.8(1)° (59.0(3)°). The high solvent component is associated with a hydrogen-bonded array, with the substrate molecules lying in axial tunnels in an ice-like structure.

Introduction

The coordination chemistry of the group 6 metals (Cr, Mo, and W) with facially coordinating tridentate ligands has been of interest for some time. Research in this area has included, for example, the chemistry of tris(pyrazolyl)borates (Tp),[1,2] 1,4,7-triazacyclononanes (R_3tacn),[3] tris(pyrazolyl)methanes,[4] 1,5,9-triphosphacyclododecanes (tpcd),[5,6] and 1,4,7-trithiacyclononane (ttcn).[7,8] This interest is in part driven by the possibility of using these ligands to model the binding sites of certain metalloenzymes (in particular those of Mo) and therefore to probe reactivity pathways in bioinorganic chemistry.[9,10]

We recently reported the preparation of a range of group 6 metal tricarbonyl complexes using the facially tridentate 1,3,5-trialkyl-1,3,5-triazacyclohexanes (R_3tach).[11,12] The reactivity of these complexes varies greatly according to the steric bulk of the alkyl substituent R. R_3tach ligands with small substituents (R = Me, Et) are labile toward displacement by nucleophiles, and (Me_3tach)M(CO)$_3$ can be used as sources of the M(CO)$_3$ groups.[13] R_3tach ligands with larger substituents (R = *t*-Bu, Bn) are inert toward displacement and remain bound to the metal when (R_3tach)M(CO)$_3$ are subjected to, for example, oxidation reactions. Here we report the synthesis and spectroscopic properties of a range of mononuclear R_3tach complexes with Cr, Mo, and W in oxidation states 0, II, III, and VI. The crystal structures of (*t*-Bu_3tach)$MO_3\cdot 15H_2O$ (M = Mo, W) are also reported.

Experimental Section

Materials. The starting complexes (*t*-Bu_3tach)M(CO)$_3$ [M = Cr (**1a**), Mo (**1b**), W (**1c**)] and (Bn_3tach)Mo(CO)$_3$ (**2b**) were synthesized as described previously.[11,12] Thionyl chloride was redistilled prior to use.

Methods. Nuclear magnetic resonance spectra were recorded using a Bruker ARX 500 spectrometer (500.1 MHz for ^{1}H, 125.8 MHz for ^{13}C, 32.58 MHz for ^{95}Mo) at ambient temperature (ca. 22 °C) unless otherwise stated and were referenced with respect to solvent resonances or external 2 M Na_2MoO_4 solution at pH 11. Infrared spectra were recorded from KBr disks or as dichloromethane solutions using a Bio-Rad FTS-45 FTIR spectrophotometer. Mass spectra were obtained by

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Dr. A. Reeder using a VG Autospec mass spectrometer, using fast atom bombardment (FAB) with a cesium ion source and *m*-nitrobenzyl alcohol as the matrix. Electronic spectra of the complexes in solution were recorded on a GBC UV/vis 918 instrument at room temperature. Microanalyses were performed by either the Chemistry Centre of Western Australia or CMAS, Victoria, Australia. All compounds, except for **15** and **16**, were prepared under nitrogen. Manipulations of air-sensitive compounds or solutions were performed using standard Schlenk techniques or in a drybox under nitrogen. All solvents were distilled prior to use, and those involved in the preparation of air-sensitive compounds were also deoxygenated. Deoxygenation of solvents and reagents was carried out either by distillation under nitrogen or by at least three freeze−pump−thaw cycles. Benzene was dried by distillation from sodium under nitrogen.

Bn_3tach. Paraformaldehyde (6.0 g, 0.2 mol) was added portionwise with cooling (ice bath) and stirring to a solution of benzylamine (20 mL, 0.18 mol) in EtOH (100 mL). The mixture was stirred overnight at room temperature and was then filtered to remove unreacted paraformaldehyde, and the solvent was removed at reduced pressure. The resulting oil crystallized on standing and was recrystallized from hexanes to give Bn_3tach as colorless prisms (yield 16.3 g, 75%). Mp 49−50 °C (lit.[14] mp 49−50 °C).

(Bn_3tach)Cr(CO)$_3$ (2a). A mixture of Bn_3tach (0.61 g, 1.71 mmol) and $Cr(CO)_6$ (0.25 g, 1.14 mmol) in benzene (25 mL) was heated at reflux by irradiation with a 150 W tungsten filament lamp for 5 h. The mixture was filtered while hot, and the orange precipitate was collected. The filtrate was irradiated for a further 5 h to produce more precipitate, the mixture again filtered while hot, and the filtrate irradiated once more (5 h). The orange solids obtained after the three such irradiations were combined, washed with hexane, and dried in vacuo to afford **2a** as an orange powder (yield 0.46 g, 81%). ^{1}H NMR (acetone-d_6): δ 3.74 (apparent d, splitting 8.2 Hz, 3H, NC*H*HN), 3.79 (s, 6H, benzylic CH_2), 4.66 (apparent d, splitting 8.2 Hz, 3H, NCH*H*N), 7.30−7.50 (m, 15H, Ph). ^{13}C NMR (acetone-d_6): δ 59.6 (benzylic CH_2), 79.1 (CH_2), 129.2 (C_{ortho} + C_{para}), 131.1 (C_{meta}), 133.7 (C_{ipso}), 237.2 (CO). IR (KBr): ν(CO) 1902 (vs), 1763 (vs) cm^{-1}. Anal. Calcd for $C_{24}H_{27}CrN_3O_3$: C, 65.7; H, 5.5; N, 8.5. Found: C, 65.9; H, 5.6; N, 8.3.

(Bn_3tach)Cr^{III}Cl$_3$ (3). Thionyl chloride (2 mL, 27 mmol) was added dropwise with stirring to a suspension of (Bn_3tach)Cr(CO)$_3$ (**2a**) (0.31 g, 0.63 mmol) in CCl_4 (15 mL). The mixture was refluxed for 1 h. The solid which formed was collected, washed with ether, and dried in vacuo to give (Bn_3tach)CrCl$_3$ as a purple solid (yield 0.32 g, 97%), identical (by IR and UV/vis spectroscopy) with material reported previously by Köhn et al.[15]

(*t*-Bu$_3$tach)Cr^{III}Cl$_3$ (4). This compound was prepared in the same way as **3** and was obtained as a purple solid (yield 71%). MS: *m/z* 377, 379 (M^+ − Cl). IR (KBr): 2978 (s), 2924 (s), 1464 (m), 1398 (s), 1373 (vs), 1260 (m), 1190 (s), 1140 (m), 1050 (m), 970 (s) cm^{-1}. Anal. Calcd for $C_{15}H_{33}Cl_3CrN_3$: C, 43.5; H, 8.0; N, 10.1. Found: C, 43.7; H, 8.0; N, 9.8.

(Bn_3tach)Cr^{III}Br$_3$ (5). Bromine (0.12 g, 0.77 mmol) was added to a stirred suspension of (Bn_3tach)Cr(CO)$_3$ (**2a**) (0.23 g, 0.47 mmol) in $CHCl_3$ and the mixture was heated at reflux for 1 h. The mixture was allowed to cool to room temperature and was diluted with hexanes. The resulting purple solid was collected, washed with hexanes and ether, dried in vacuo, and recrystallized from CH_2Cl_2/hexanes to give **5** as purple needles (yield 0.29 g, 71%). MS: *m/z* 646, 648, 650, 652 (M^+), 567, 569, 571 (M^+ − Br). IR (KBr): 3030 (m), 2941 (m), 1083 (s), 1006 (m), 932 (w), 753 (s), 702 (s), 668 (s) cm^{-1}. Anal. Calcd for $C_{24}H_{27}Br_3CrN_3$: C, 44.4; H, 4.2; N, 6.5. Found: C, 44.8; H, 4.3; N, 6.8.

(*t*-Bu$_3$tach)Cr^{III}Br$_3$ (6). This compound was prepared in the same way as **5** and was obtained as a purple solid, which was recrystallized from acetonitrile using a Soxhlet apparatus (yield 90%). MS: *m/z* 469, 467, 465 (M^+ − Br). IR (KBr): 2979 (m), 1471 (m), 1394 (m), 1371 (s), 1265 (m), 1185 (s), 1144 (m), 1050 (m), 998 (s), 971 (s), 923 (m) cm^{-1}. Anal. Calcd for $C_{15}H_{33}Br_3CrN_3$: C, 32.9; H, 6.1; N, 7.7. Found: C, 32.6; H, 5.8; N, 8.0.

(*t*-Bu$_3$tach)Mo^{III}Cl$_3$·SOCl$_2$ (7). Reaction of (*t*-Bu$_3$tach)Mo(CO)$_3$ (**1b**) with excess thionyl chloride according to the procedure outlined for **3** above afforded (after 10 h reflux) a yellow/brown solid which analyzed as the thionyl chloride solvate (*t*-Bu$_3$tach)MoCl$_3$·SOCl$_2$ (**7**) (yield 93%). IR (KBr): 2980 (s), 1395 (s), 1380 (vs), 1190 (s), 1140 (m), 1050 (m), 965 (s) cm^{-1}. Anal. Calcd for $C_{15}H_{33}Cl_3MoN_3\cdot SOCl_2$: C, 31.2; H, 5.8; N, 7.3. Found: C, 31.3; H, 5.7; N, 7.1.

(*t*-Bu$_3$tach)Mo^{III}Br$_3$ (8). This compound was prepared in the same way as **5**, with (*t*-Bu$_3$tach)Mo(CO)$_3$ (**1b**) as starting material and a 10 h period of reflux, and was obtained as a tan solid, which was recrystallized from acetonitrile using a Soxhlet apparatus (yield 90%). MS: *m/z* 505, 507, 508, 509, 510, 511, 512, 513, 515 (M^+ − Br). IR (KBr): 2978 (m), 2920 (w), 1260 (m), 1187 (s), 1136 (s), 1051 (s), 1000 (m), 965 (s), 925 (m), 355 (vs), 342 (vs) cm^{-1}. Anal. Calcd for $C_{15}H_{33}Br_3MoN_3$: C, 30.5; H, 5.6; N, 7.1. Found: C, 30.1; H, 5.4; N, 7.2.

[(*t*-Bu$_3$tach)Mo^{II}(CO)$_3$Br]Br$_3$ (9) and [(*t*-Bu$_3$tach)Mo^{II}(CO)$_3$Br]-Br (9a). A suspension of (*t*-Bu$_3$tach)Mo(CO)$_3$ (1.0 g, 2.3 mmol) in chloroform (30 mL) was stirred at room temperature while bromine (0.3 mL, 0.93 g, 5.8 mmol) was added. The mixture was stirred for 1 h, and the resultant tan precipitate of the tribromide salt **9** was collected in the air, washed with hexanes, and dried in vacuo before being stored under nitrogen (yield 1.55 g, 89%). ^{1}H NMR ($CDCl_3$): δ 1.52 (s, 27H, Me), 5.18 (apparent d, splitting 8.7 Hz, 3H, NC*H*HN), 5.45 (apparent d, splitting 8.7 Hz, 3H, NCH*H*N). ^{13}C NMR ($CDCl_3$): δ 26.3 (Me), 62.1 (N*C*Me$_3$), 75.3 (CH_2), 229.5 (CO). No satisfactory elemental analysis could be obtained for **9**. Use of only 1 equiv of bromine in the above procedure gave the monobromide salt **9a** as a tan powder. ^{1}H NMR (DMSO-d_6): δ 1.37 (s, 27H, Me), 5.10 (apparent d, splitting 9.1 Hz, 3H, NC*H*HN), 5.21 (apparent d, splitting 9.1 Hz, 3H, NCH*H*N). ^{13}C NMR (DMSO-d_6): δ 24.8 (Me), 61.5 (N*C*Me$_3$), 75.2 (CH_2). Poor solubility prevented acquisition of a satisfactory ^{95}Mo NMR spectrum. Anal. Calcd for $C_{18}H_{33}Br_2MoN_3O_3$: C, 36.3; H, 5.6; N, 7.1. Found: C, 36.0; H, 5.5; N, 7.1.

[(*t*-Bu$_3$tach)Mo^{II}(CO)$_3$I]I$_3$ (10). Iodine (0.58 g, 2.3 mmol) was added to a stirred suspension of (*t*-Bu$_3$tach)Mo(CO)$_3$ (0.5 g, 1.15 mmol) in chloroform (30 mL). The addition caused gradual dissolution of (*t*-Bu$_3$tach)Mo(CO)$_3$, and after a further 30 min at room temperature a red/brown precipitate of **10** had formed. The precipitate was collected in the air, washed with hexanes, and dried in vacuo before being stored under an inert atmosphere (yield 0.75 g, 95%). ^{1}H NMR (acetone-d_6): δ 1.58 (s, 27H, Me), 5.34 (apparent d, splitting 9.3 Hz, 3H, NC*H*HN), 5.58 (apparent d, splitting 9.3 Hz, 3H, NCH*H*N). ^{13}C NMR (acetone-d_6): δ 25.3 (Me), 62.7 (N*C*Me$_3$), 76.3 (CH_2), 209.8 (CO). ^{95}Mo NMR (acetone-d_6): δ −737 ($W_{1/2}$ < 5 Hz). Anal. Calcd for $C_{18}H_{33}I_4MoN_3O_3$: C, 22.9; H, 3.5; N, 4.5. Found: C, 22.8; H, 3.5; N, 4.4.

[(*t*-Bu$_3$tach)W^{II}(CO)$_3$Br]Br$_3$ (11) and [(*t*-Bu$_3$tach)W^{II}(CO)$_3$Br]Br (11a). The tribromide salt **11** was prepared in the same way as **9** and was obtained as an orange powder (yield 92%). ^{1}H NMR ($CDCl_3$): δ 1.50 (s, 27H, Me), 5.25 (apparent d, splitting 8.4 Hz, 3H, NC*H*HN), 6.24 (apparent d, splitting 8.4 Hz, 3H, NCH*H*N). ^{13}C NMR ($CDCl_3$): δ 26.2 (Me), 63.2 (N*C*Me$_3$), 75.0 (CH_2). No satisfactory elemental analysis could be obtained. The monobromide salt **11a** was prepared in the same way as **9a** and was obtained as an orange powder. ^{1}H NMR (DMSO-d_6): δ 1.37 (s, 27H, Me), 5.31 (apparent d, splitting 9.2 Hz, 3H, NC*H*HN), 5.86 (apparent d, splitting 9.2 Hz, 3H, NCH*H*N). ^{13}C NMR (DMSO-d_6): δ 24.7 (Me), 62.7 (N*C*Me$_3$), 75.2 (CH_2). Anal. Calcd for $C_{18}H_{33}Br_2N_3O_3W$: C, 31.6; H, 4.9; N, 6.2. Found: C, 31.2; H, 4.8; N, 6.2.

[(*t*-Bu$_3$tach)W^{II}(CO)$_3$I]I$_3$ (12) and [(*t*-Bu$_3$tach)W^{II}(CO)$_3$I]I (12a). The triiodide salt **12** was prepared in the same way as **10** and was obtained as a brown/red solid (yield 95%). ^{1}H NMR (acetone-d_6): δ 1.58 (s, 27H, Me), 5.71 (apparent d, splitting 8.7 Hz, 3H, NC*H*HN), 6.19 (apparent d, splitting 8.7 Hz, 3H, NCH*H*N). ^{13}C NMR (acetone-d_6, 25 °C): δ 25.5 (Me), 64.2 (N*C*Me$_3$), 76.5 (CH_2). ^{13}C NMR (acetone-d_6, −22 °C): δ 25.5 (Me), 64.2 (N*C*Me$_3$), 76.5 (CH_2), 221.2 and 244.7 (CO, ratio 2:1 respectively). No satisfactory elemental analysis could be obtained. The monoiodide salt **12a** was prepared in the same way

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as **10a** and was obtained as a brown solid (yield 78%). Anal. Calcd for $C_{18}H_{33}I_2N_3O_3W$: C, 27.8; H, 4.3; N, 5.4. Found: C, 27.8; H, 4.1; N, 5.3.

[(*t*-Bu$_3$tach)Mo^{II}(CO)$_3$H](CF$_3$SO$_3$) (13). A suspension of (*t*-Bu$_3$tach)Mo(CO)$_3$ (**1b**) (0.2 g, 0.46 mmol) in dry ether (20 mL) was cooled and stirred in an ice bath. Trifluoromethanesulfonic acid (0.2 mL) was added, and the suspension was stirred at room temperature for 8 h. The resulting pale yellow solid was collected, washed with ether, and dried in vacuo (yield 0.23 g, 85%). ^{1}H NMR (CDCl$_3$): δ −4.18 (s, 1H, Mo−H), 1.35 (s, 27H, Me), 4.98 (apparent d, splitting 8.6 Hz, 3H, NC*H*HN), 5.05 (apparent d, splitting 8.6 Hz, 3H, NCH*H*N). ^{13}C NMR (CDCl$_3$): δ 25.4 (Me), 58.2 (N*C*Me$_3$), 73.6 (CH$_2$), 220.1 (CO). Anal. Calcd for $C_{19}H_{34}F_3MoN_3O_6S$: C, 39.0; H, 5.8; N, 7.2. Found: C, 38.7; H, 5.9; N, 7.1.

[(*t*-Bu$_3$tach)W^{II}(CO)$_3$H] (CF$_3$SO$_3$) (14). This compound was prepared in the same way as the Mo analogue **13** and was obtained as a pale yellow powder (yield 83%). ^{1}H NMR (CDCl$_3$): δ −3.26 (s, 1H, W−H, ^{183}W satellites, J_{W-H} = 18.5 Hz), 1.36 (s, 27H, Me), 5.09 (apparent d, splitting 8.7 Hz, 3H, NC*H*HN), 5.91 (apparent d, splitting 8.7 Hz, 3H, NCH*H*N). ^{13}C NMR (CDCl$_3$): δ 25.2 (Me), 59.2 (N*C*Me$_3$), 73.4 (CH$_2$), 215.6 (CO). Anal. Calcd for $C_{19}H_{34}F_3N_3O_6SW$: C, 33.9; H, 5.1; N, 6.2. Found: C, 34.0; H, 5.0; N, 6.0.

(*t*-Bu$_3$tach)Mo^{VI}O$_3$ (15). Hydrogen peroxide solution (30%, 7 mL) was added dropwise to a stirred suspension of (*t*-Bu$_3$tach)Mo(CO)$_3$ (**1b**) (0.2 g, 0.46 mmol) in THF (7 mL). Following the addition, the mixture was either stirred overnight at room temperature or heated gently to 60 °C for 1 h to complete the reaction. Removal of the THF under reduced pressure gave colorless, microcrystalline needles, which were collected, washed with water, and dried in vacuo over CaCl$_2$ (yield 0.16 g, 87%). Small samples for microanalysis were recrystallized from water, and slightly larger needles of (*t*-Bu$_3$tach)MoO$_3$·15H$_2$O, suitable for X-ray structure analysis, were grown (after many attempts) by slow cooling of aqueous solutions to room temperature. ^{1}H NMR (methanol-*d*$_4$): δ 1.45 (s, 27H, Me), 3.78 (apparent d, splitting 8.9 Hz, 3H, NC*H*HN), 4.74 (apparent d, splitting 8.7 Hz, 3H, NCH*H*N). ^{13}C NMR (methanol-*d*$_4$): δ 29.3 (Me), 62.3 (N*C*Me$_3$), 70.7 (CH$_2$). ^{95}Mo NMR (methanol-*d*$_4$): δ −13 ($W_{1/2}$ = 45 Hz). MS: *m*/*z* 399 (^{96}Mo M$^+$), 401 (^{98}Mo M$^+$). IR (KBr): 2971 (m), 1370 (m), 1257 (w), 1200 (m), 1146 (m), 981 (s), 899 (s), 870 (vs), 838 (w) cm^{-1}. Anal. Calcd for $C_{15}H_{33}MoN_3O_3$: C, 45.1; H, 8.3; N, 10.5. Found: C, 44.9; H, 8.6; N, 10.6 (recrystallized sample, dried in vacuo at room temperature).

(*t*-Bu$_3$tach)W^{VI}O$_3$ (16). This compound was prepared in the same way as **15** and was obtained as a white microcrystalline solid (yield 97%). Samples for microanalysis and X-ray structure determination were recrystallized from water. ^{1}H NMR (methanol-*d*$_4$): δ 1.45 (s, 27H, Me), 4.54 (apparent d, splitting 8.5 Hz, 3H, NC*H*HN), 4.93 (apparent d, splitting 8.5 Hz, 3H, NCH*H*N). ^{13}C NMR (methanol-*d*$_4$): δ 26.7 (Me), 60.5 (N*C*Me$_3$), 68.4 (CH$_2$). MS: *m*/*z* 487 (^{184}W M$^+$), 489 (^{186}W M$^+$). IR (KBr): 2974 (m), 1373 (m), 1260 (w), 1197 (s), 1151 (m), 978 (s), 920 (s), 866 (vs), 835 (w) cm^{-1}. Anal. Calcd for $C_{15}H_{33}N_3O_3W$: C, 37.0; H, 6.8; N, 8.6. Found: C, 36.6; H, 6.5; N, 9.0 (recrystallized sample, dried in vacuo at room temperature).

Structure Determinations (15, 16). (Crystals desolvated immediately on exposure to the atmosphere and were mounted in capillaries for the X-ray work.) Full spheres of diffraction data were measured at room temperature within the limit $2\theta_{max} = 58°$ (Bruker AXS CCD instrument; graphite-monochromated Mo Kα radiation, λ = 0.710 73 Å; *T* ca. 300 K) yielding, after processing using the proprietary software SAINT, 17 704 (M = Mo) (16 134 (M = W)) reflections merging to 10 700 (5655) independent, then 1494 (1489) unique data (R_{int} = 0.030 (0.024)) after "empirical absorption correction" using the proprietary software SADABS; 1159 (997) with $|F| > 4\sigma|F|$) considered "observed" were used in the full-matrix least-squares refinements, anisotropic thermal parameters being refined for the non-hydrogen atoms, $(x, y, z, U_{iso})_H$ for the substrate molecule being constrained at estimated values. Conventional residuals R, R_w (statistical weights) at convergence were 0.027 (0.022) (0.031 (0.019)), respectively, the absolute structure parameter x_{abs} being 0.05(7) (−0.02(1)), both specimens having the same chirality. Neutral atom complex scattering factors were employed, computation using the Xtal 3.4 program system.[16] Difference map residues were modeled as water molecule oxygen atoms in each case; site occupancies were set at unity after trial refinement. Associated hydrogen atoms were located in difference maps for O(03,5) only (M = Mo only).

Results and Discussion

In a manner similar to the preparation of the Mo analogue **2b**,[12] (Bn$_3$tach)Cr(CO)$_3$ (**2a**) was easily prepared in good yield from Bn$_3$tach (81%), by a photolytic reaction with Cr(CO)$_6$ in benzene. When toluene was used in place of benzene, the reaction mixture became orange, but no product precipitated, and on cooling of the reaction mixture only unreacted Cr(CO)$_6$ crystallized. When the reaction was conducted in toluene for longer periods (many days), brown and black decomposition products were obtained. The compound **2a**, which is a bright orange color, is air-stable for several days in the solid state; prolonged storage, however, should be under an inert atmosphere. The stability of the Bn$_3$tach complex **2b** thus lies between that of (Me$_3$tach)Cr(CO)$_3$ (decomposes within minutes of exposure to air) and (*t*-Bu$_3$tach)Cr(CO)$_3$ **1a** (stable indefinitely in air).

Oxidative Decarbonylation with SOCl$_2$ and Br$_2$. Reagents such as Br$_2$, I$_2$, and SOCl$_2$ can effect oxidative decarbonylation of group 6 metal carbonyl complexes.[17−19] Reaction of the chromium complexes (R$_3$tach)Cr(CO)$_3$ (R = Bn, *t*-Bu) with an excess of either thionyl chloride or elemental bromine in CHCl$_3$ or CCl$_4$ at reflux gave the monomeric chromium(III) trihalides **3**−**6** (Scheme 1). By similar oxidative decarbonylations of (tpcd)Cr(CO)$_3$, Edwards et al.[5] synthesized 16-electron Cr(II) complexes attributed the structure [(tpcd)CrX(CO)$_2$]$^+$ (X = Cl, Br). Although [(R$_3$tach)CrX(CO)$_2$]$^+$ may be formed during the syntheses of **3**−**6**, we have obtained no evidence of these possible intermediates, and the low solubility of the (R$_3$tach)Cr(CO)$_3$ complexes and the trihalide adducts **3**−**6** made investigation of the oxidative decarbonylation reactions difficult. Complexes **3**−**6** are air-stable and soluble to varying degrees in organic solvents such as dichloromethane, chloroform, acetonitrile, and DMSO (DMSO = dimethyl sulfoxide). The bromine complexes are generally more soluble than the corresponding chlorine adducts, with (Bn$_3$tach)CrBr$_3$ being very soluble in dichloromethane and chloroform.

(Bn$_3$tach)CrCl$_3$ (**3**) has previously been synthesized by Köhn et al. by reaction of Bn$_3$tach with CrCl$_3$(THF)$_3$ in tetrahydrofuran (THF).[15] Oxidative removal of the carbonyl ligands from the chromium(0) and molybdenum(0) tricarbonyl complexes provides an alternative to Köhn's method and has the advantage that it can be extended to the chloride and bromide adducts of both chromium and molybdenum (see below).

Oxidative decarbonylations of the molybdenum complexes (R$_3$tach)Mo(CO)$_3$ (R = Bn, *t*-Bu) were more complicated than those of the chromium analogues. (*t*-Bu$_3$tach)Mo(CO)$_3$ reacted with excess bromine to form (*t*-Bu$_3$tach)MoBr$_3$ as a brown solid, which could be recrystallized from acetonitrile. The corresponding reaction with excess SOCl$_2$ gave a product which (although dried in vacuo) had apparent stoichiometry (*t*-Bu$_3$tach)MoCl$_3$·SOCl$_2$. The material was mildly air-sensitive and decomposed

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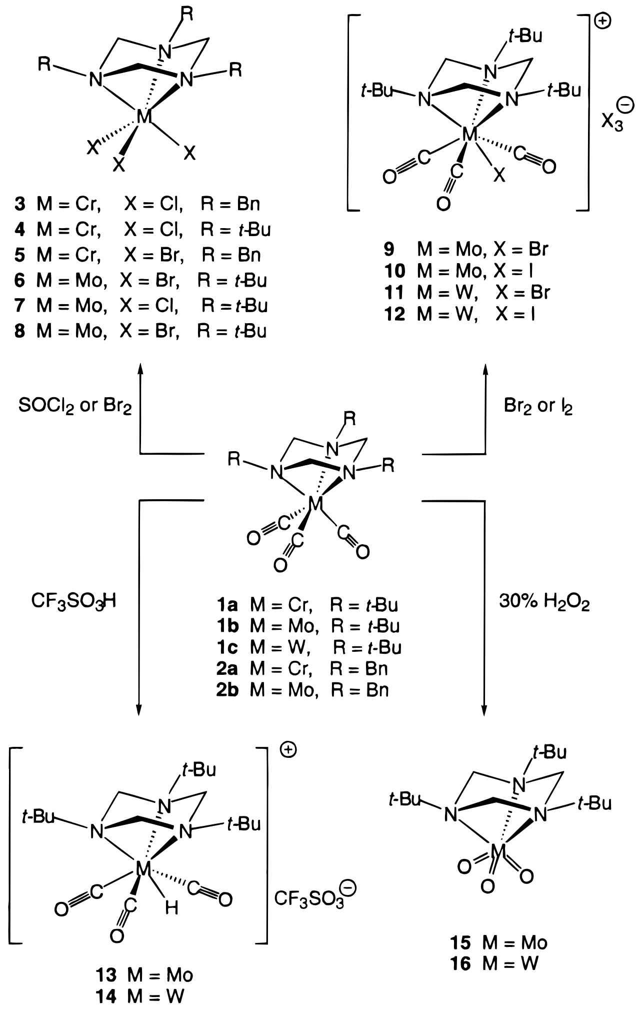
(18) Backes-Dahmann, G.; Herrmann, W.; Wieghardt, K.; Weiss, J. *Inorg. Chem.* **1985**, *24*, 485.

(19) Chaudhuri, P.; Wieghardt, K.; Tsai, Y.-H.; Krüger, C. *Inorg. Chem.* **1984**, *23*, 427.

Scheme 1



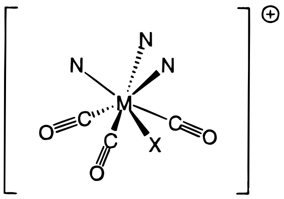
slowly to give blue/green solids. Attempts to recrystallize the product were unsuccessful. The formulation of this product as a thionyl chloride solvate of the octahedral d^3 t-Bu$_3$tach molybdenum trichloride complex **7** is supported by the similarity of its IR and UV/vis spectra with those of the tribromide complex **6** and other analogous complexes.[4,18,20]

The reaction of (Bn$_3$tach)Mo(CO)$_3$ with bromine in refluxing chloroform in the same fashion as the above preparations did not give the desired Mo(III) tribromide. The only product identified from this reaction was benzylammonium bromide, isolated as a white solid from the reaction mixture. This result may arise by dissociation of the Bn$_3$tach unit from the Mo center and subsequent destruction of the Bn$_3$tach unit under the reaction conditions; in separate experiments we found that treatment of Bn$_3$tach with bromine in refluxing chloroform also gives benzylammonium bromide, and the susceptibility of (Bn$_3$tach)-Mo(CO)$_3$ to dissociation of the Bn$_3$tach group has been noted previously.[12] The reaction of (Bn$_3$tach)Mo(CO)$_3$ with thionyl chloride in refluxing chloroform also failed to produce the desired trichloride complex, but instead resulted in a mixture of unidentified products.

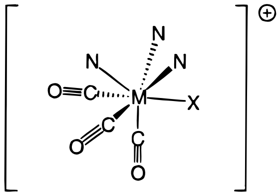
The electronic absorption spectra of the tach metal(III) complexes and the related tacn derivatives, along with derived estimates[21] for the ligand field parameters 10 Dq and B', are presented in Table 1. The values for the ligand field splitting energy, 10 Dq, for the tach complexes are consistently lower than for the corresponding tacn analogues, both ligands behaving as pure σ donors. This difference, a result of the poorer overlap of the electrons of the nitrogen lone pairs with the metal bonding orbitals in the tach complexes, has been noted previously by Köhn et al. for the chromium complex **3**.[15] As expected due to the larger size of molybdenum and consequent better overlap of the metal−tach orbitals, the relative difference in the values for 10 Dq for tach vs tacn is less than that for chromium. The lower ligand field strength for tach complexes in comparison to tacn complexes is also manifested in the ν(CO) data for the metal(0) tricarbonyl compounds (t-Bu$_3$tach)M(CO)$_3$ (M = Cr, Mo, W)[12] and the lower basicity of the Mo and W centers in (t-Bu$_3$tach)Mo(CO)$_3$ **1b** and (t-Bu$_3$tach)W(CO)$_3$ **1c** (see below).

Preparation of [(t-Bu$_3$tach)M(CO)$_3$X]$^+$ (M = Mo or W, X = Br or I). Controlled oxidation of the molybdenum(0) and tungsten(0) tricarbonyls with either bromine or iodine gives the 7-coordinate cations [(t-Bu$_3$tach)M^{II}(CO)$_3$X]$^+$ (M = Mo or W, X = Br, I) (**9**−**12**) (Scheme 1). These species can be prepared either as the trihalide (Br$_3^-$ or I$_3^-$) salt, by addition of an excess of the halogen, or as the monohalide salt (Br$^-$ or I$^-$) by careful addition of 1 equiv of the halogen. Although the trihalides were sufficiently stable for spectroscopic characterization, they gave poor elemental analysis results, so that elemental analysis was instead performed on the more stable monohalides.

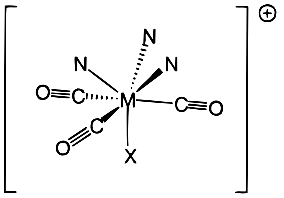
The infrared spectra of these 7-coordinate complexes show three carbonyl stretching bands (Table 2), whether measured in the solid state or in solution, consistent with either a 4:3 "piano stool" structure **I**[8,19,22] or a 3:3:1 structure **II**[2] (both C_s symmetry, 2A′ + A″ vibrational modes) rather than the alternative 3:3:1 structure **III** (C_{3v} symmetry). The CO bands are shifted to higher frequencies compared with those of the starting metal(0) tricarbonyl complexes, which reflects the decrease in electron density at the central metal atom as a result of the oxidation (Table 2).



I



II



III

The room temperature ^{13}C NMR of the molybdenum complexes **9** and **10** both display only one peak in the carbonyl region (δ 229.5 and 209.8, respectively). Since two nonequivalent carbonyl environments are expected for complexes of either the 4:3 structure **I** or the 3:3:1 structure **II**, the ^{13}C NMR data indicate that **9** and **10** are fluxional on the NMR time scale.

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(20) Mohammed, A. K.; Isovitsch, R. A.; Maverick, A. W. *Inorg. Chem.* **1998**, *37*, 2779.

(21) The ligand field parameters 10 Dq and B' were estimated from the energies of the spin-allowed d−d transition bands ν_1, ν_2, and ν_3 as follows: 10 $Dq = \nu_1$; $B' = (\nu_2 + \nu_3 - 3\nu_1)/15$. See: König, E. *Inorg. Chem.* **1971**, *10*, 2632.

(22) Curtis, M. D.; Shiu, K.-B. *Inorg. Chem.* **1985**, *24*, 1213.

Table 1. UV−Visible Spectral Data for the Metal(III) Trihalides

complex	color	λ_{max}, nm (ϵ, L mol^{-1} cm^{-1})	10 *Dq*, *B*′ (cm^{-1})	ref
$(Bn_3tach)CrCl_3$ **3**[a]	purple	334 (br sh), 508 (350), 715 (180)	13 989, 507	this work and 15
$(t\text{-}Bu_3tach)CrCl_3$ **4**[b]	purple	525 (120), 743 (50)	13 459, —	this work
$(Bn_3tach)CrBr_3$ **5**[a]	purple	334 (br sh), 531 (340), 741 (160)	13 495, 551	this work
$(t\text{-}Bu_3tach)CrBr_3$ **6**[c]	purple	244 (10 500), 263 (sh, 7620), 284 (sh, 5830), 351 (1740), 552 (240), 768 (br, 110)	13 020, 503	this work
$(tacn)CrBr_3$[b]	green	460, 614	16 287, —	34
$(i\text{-}Pr_3tacn)CrBr_3$[c]	green	455 (90), 642 (70)	15 576, —	35
$(t\text{-}Bu_3tach)MoCl_3$ **7**[c]	yellow	238 (3890), 314 (1800), 409 (280), 700 (140)	14 286, 896	this work
$(t\text{-}Bu_3tach)MoBr_3$ **8**[c]	tan	230 (sh, 8120), 290 (4460), 435 (300), 719 (40)	13 908, 1050	this work
$(Me_3tacn)MoCl_3$[d]	yellow	315 (410), 355 (246), 421 (130), 684 (16)	14 620, 537	18
$(Me_3tacn)MoBr_3$[d]	orange	245 (1000), 279 (1300), 426 (324), 698 (19)	14 327, 1089	18
$(i\text{-}Pr_3tacn)MoCl_3$[c]	yellow	252 (4600), 380 (220), 447 (130), 673 (7)	14 859, 274	35
$(i\text{-}Pr_3tacn)MoBr_3$[c]	orange	389 (180), 461 (80), 691 (18)	14 472, 266	35

[a] Solvent is CH_2Cl_2. [b] Solvent is DMSO. [c] Solvent is acetonitrile. [d] Solvent is DMF.

Table 2. IR Data for the Tricarbonyl Complexes (KBr Disk)

complex	ν(CO) (cm^{-1})
$(t\text{-}Bu_3tach)Mo(CO)_3$ **1b**	1903, 1766
$(t\text{-}Bu_3tach)W(CO)_3$ **1c**	1890, 1760
$[(t\text{-}Bu_3tach)Mo(CO)_3Br]Br_3$ **9**	2055, 1980, 1935
$[(t\text{-}Bu_3tach)Mo(CO)_3I]I_3$ **10**	2035, 1955, 1915
$[(t\text{-}Bu_3tach)Mo(CO)_3H]CF_3SO_3$ **13**	2020, 1940, 1905
$[(t\text{-}Bu_3tach)W(CO)_3Br]Br_3$ **11**	2045, 1955, 1930
$[(t\text{-}Bu_3tach)W(CO)_3I]I_3$ **12**	2030, 1945, 1900
$[(t\text{-}Bu_3tach)W(CO)_3H]CF_3SO_3$ **14**	2015, 1935, 1885

Table 3. Crystal Data for $(C_{15}H_{33}N_3)MO_3{\cdot}15H_2O$[a]

	M = Mo	M = W
formula	$C_{15}H_{63}N_3MoO_{18}$	$C_{15}H_{63}N_3O_{18}W$
M_r	669.6	757.5
a (Å)	21.026(2)	21.011(3)
c (Å)	13.418(2)	13.390(3)
V (Å^3)	5137	5119
D_c (g cm^{-3})	1.43_1	1.47_4
μ_{Mo} (cm^{-1})	5.0	34.5
“$T_{min,max}$”	0.56, 0.80	0.30, 0.43
specimen, mm	0.18 × 0.15 × 1.20	0.11 × 0.11 × 0.25

[a] The space group for the two isomorphous structures was rhombohedral $R3c$ (C_{3v}^6, No. 161; hexagonal setting). $R = \sum\Delta/\sum|F_o|$ and $R_w = (\sum w(\Delta)^2/\sum(w|F_o|^2))^{1/2}$. $Z = 6$.

Table 4. Selected Molecular Geometries

atoms	parameter[a]
Distances (Å)	
M−O(0)	1.724(3), 1.745(4)
M−N(1)	2.374(3), 2.355(6)
Angles (deg)	
O(0)−M−O(0^i)	107.1(2), 106.4(3)
N(1)−M−N(1^i)	58.8(1), 59.0(3)
O(0)−M−N(1)	93.9(2), 94.8(3)
O(0)−M−N(1^i)	91.1(1), 91.0(2)
O(0)−M−N(1^{ii})	146.2(1), 146.9(2)

[a] The two values in each entry are for M = Mo and W respectively. Transformations of the asymmetric unit (i; ii): $\bar{y}, x - y, z; y - x, \bar{x}, z$.

Fluxionality of other 7-coordinate molybdenum(II) and tungsten(II) complexes is well-known.[2,22−24] Curtis and Shiu have interpreted fluxionality in the analogous $TpMo(CO)_3Br$ as a rapid interconversion between isomers of the 4:3 piano stool geometry (structure **I**), possibly via the 3:3:1 geometry (structure **III**).[22]

In the ^{13}C NMR spectra of the tungsten complexes **11** and **12** in either $CDCl_3$ or acetone-d_6 at room temperature, the carbonyl resonances were exchange broadened and therefore not detected. When a sample of **12** in acetone-d_6 was cooled to −22 °C, the exchange was slowed and the ^{13}C NMR spectrum showed, as expected, two carbonyl resonances at δ 244.7 and 221.2 (intensity ratio 1:2, respectively). The cyclopentadienyl complexes $CpMo(CO)_3X$ (X = Cl, Br, I), which possess the 4:3 piano stool geometry, show two peaks (ratio 1:2) in their room temperature ^{13}C NMR spectra.[25]

Recently, 7-coordinate molybdenum(II) and tungsten(II) complexes $[(ttcn)M(CO)_3I]^+$ were prepared by reaction of ttcn with the reactive starting materials $[MI_2(CO)_3(NCMe)_2]$ (M = Mo, W).[8] Our attempts to synthesize compounds **10** and **12** using the complexes $[MI_2(CO)_3(NCMe)_2]$ (M = Mo, W) as precursors were unsuccessful and resulted only in material of unknown composition but lacking any evidence of coordinated t-Bu$_3$tach.

Reaction of $(t\text{-}Bu_3tach)M(CO)_3$ (M = Mo or W) with Trifluoromethanesulfonic Acid. The zerovalent metal tricarbonyls were readily protonated with trifluoromethanesulfonic acid in dry ether to give good yields of the divalent 7-coordinate hydrido species **13** and **14** (Scheme 1). The complexes were isolated as analytically pure pale yellow/cream powders which were mildly air-sensitive as solids and quite air-sensitive in solution. In contrast with reports of preparation of the analogous complexes $[(tacn)M(CO)_3H]^+$[19] and $TpM(CO)_3H$[22,26] (M = Mo, W), attempts to prepare the $[(t\text{-}Bu_3tach)M(CO)_3H]^+$ cations using milder acids (HCl, HBF_4) were unsuccessful. This result is probably a consequence of lower electron density (basicity) at the metal center in the t-Bu$_3$tach complexes due to poorer σ donation by the tach ligand.[12] The $[(t\text{-}Bu_3tach)M(CO)_3H](CF_3SO_3)$ complexes undergo deprotonation in aqueous solution to regenerate the $(t\text{-}Bu_3tach)M(CO)_3$ complexes **1b** and **1c**.

The 7-coordinate nature of these complexes is indicated by the presence of three carbonyl stretching absorptions in the IR spectrum (Table 2), similar to those seen for the carbonyl halide complexes **9**−**12** and other analogous hydrido complexes involving a facially coordinating ligand.[19,22,26,27] There is a decrease in the ν(CO) values for the $[(t\text{-}Bu_3tach)M^{II}(CO)_3X]^+$ complexes (X = Br, I, H) in the order Br > I > H for both the

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(23) Kepert, D. L. *Inorganic Stereochemistry*; Springer-Verlag: Berlin, 1982.

(24) Drew, M. G. B.; Baker, P. K.; Armstrong, E. M.; Fraser, S. G.; Muldoon, D. J.; Lavery, A. J.; Shawcross, A. *Polyhedron* **1995**, *14*, 617.

(25) Todd, L. J.; Wilkinson, J. R.; Hickey, J. P.; Beach, D. L.; Barnett, K. W. *J. Organomet. Chem.* **1978**, *154*, 151.

(26) Caffyn, A. J. M.; Feng, S. G.; Dierdorf, A.; Gamble, A. S.; Eldredge, P. A.; Vossen, M. R.; White, P. S.; Templeton, J. L. *Organometallics* **1991**, *10*, 2842.

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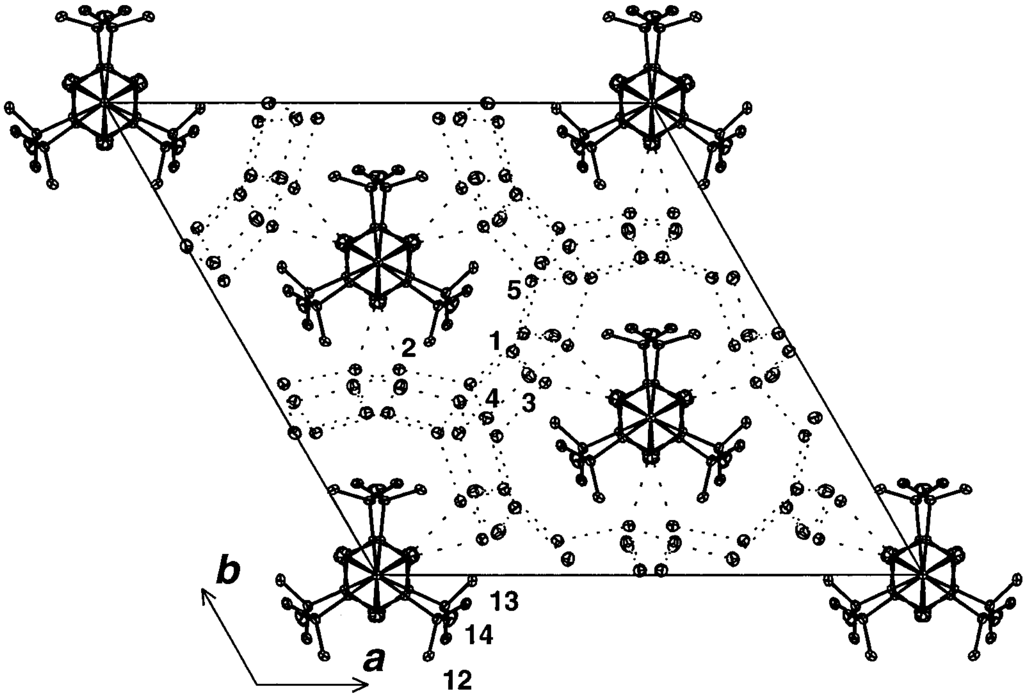

Figure 1. Projection of the unit cell contents of the molybdenum adduct **15** down rhombohedral(111)/hexagonal *c*. 20% thermal ellipsoids are shown for the non-hydrogen atoms (hydrogen atoms, shown in Figure 2, have arbitrary radii of 0.1 Å). Note the slight staggering of the alternate members of the pairs of successive molecules up *c*, breaking the symmetry from symmorphic *R*3*m* (with *c* halved) to *R*3*c* (present cell). Water molecule oxygens O(0*n*) and substituent carbon atoms C(l*m*) are indicated by number (*n*/*lm*) only.

Mo and W complexes. This trend reflects the decrease in the relative electronegativity of the substituent X along the series Br, I, H and the subsequent strength of the carbonyl bond in these complexes. The ^1H NMR spectra ($CDCl_3$) of these complexes show the hydridic proton at δ −4.18 for the molybdenum complex **13** and at δ −3.26 for the tungsten complex **14**. These chemical shifts are within the range of values reported for $[(Me_3tacn)M(CO)_3H]^+$ and $TpM(CO)_3H$ (M = Mo, W).[19,22,26,27] Complex **14** also shows a $^{183}W-{}^1H$ coupling of 18.5 Hz which is midway between the observed coupling constants for $CpW(CO)_3H$[28] (37.5 Hz) and those for $TpW(CO)_3H$[26] (9 Hz), and arguments have been made that the magnitude of this coupling constant is inversely proportional to the W−H bond distance.[26] The room temperature ^{13}C NMR spectra of both **13** and **14** show only one carbonyl resonance, indicating a very rapid interconversion of isomers; we observed no change in the signal when a sample of **14** was cooled to −60 °C.

Reaction of (R_3tach)$M(CO)_3$ (M = Mo, R = *t*-Bu, Bn and M = W, R = *t*-Bu) with Hydrogen Peroxide. Suspensions of (*t*-Bu_3tach)$M(CO)_3$ (M = Mo, W) in THF react with 30% hydrogen peroxide solution, gradually dissolving and then forming white microcrystalline needles of the respective facial trioxo complexes (*t*-Bu_3tach)MO_3 (**15** and **16**, Scheme 1) in very good yield (87−97%). These diamagnetic, metal(VI) complexes are only sparingly soluble in cold water but moderately soluble in hot water, from which they can be recrystallized as fine needles; the complexes are also soluble in methanol and to a lesser degree ethanol.

The results of the room temperature single-crystal X-ray studies (Table 3) are consistent in terms of stoichiometry, connectivity, and stereochemistry, with the representation of **15** and **16** as discrete molecules of (*t*-Bu_3tach)MO_3 (M = Mo, W) (Table 4), solvated with 15 water molecules of crystallization.

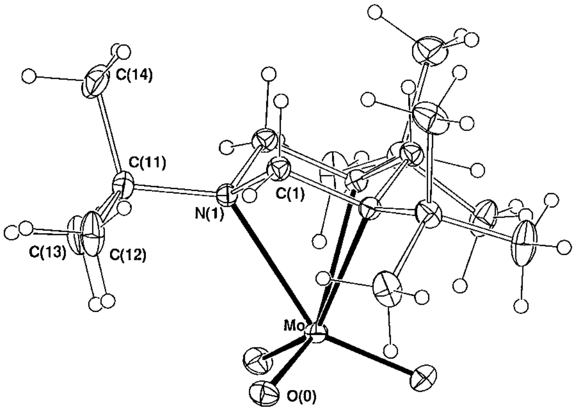

Figure 2. A single molecule of the molybdenum adduct **15** projected approximately normal to the 3-fold axis (*c*).

The complexes crystallize as fine needles in rhombohedral space group *R*3*c*, each molecule lying on a crystallographic 3-axis, with six molecules in the unit cell (hexagonal setting). Figure 1 shows the cell in projection; alternate molecules stacked up *c* are seen to be slightly displaced in alternate directions from the 3*m* site symmetry of a *R*3*m* subcell; molecular symmetry is accordingly downgraded from 3*m* to 3, the associated slight distortion being visible in Figure 1; *cis*-O−M−N angles, Figure 2, equivalent in 3*m* symmetry, now differ by 2.5−3.0°. Also evident from Figure 1 is the manner in which the columns of substrate molecules are contained in tunnels in a hydrogen-bonded ice-like matrix made up of the water molecules which comprise the unusually large hydration component.

The observation of two apparent doublets for the tach methylene protons in the ^1H NMR spectra of **15** and **16** in methanol-d_4 confirms the facial coordination of the *t*-Bu_3tach ligand, indicating that the triaza ligand remains firmly affixed, despite a change of 0 to VI in the oxidation state of these complexes. As with the (R_3tach)$M(CO)_3$ complexes (M = Cr,

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(28) Keppie, S. A.; Lappert, M. F. *J. Chem. Soc. A* **1971**, 3216.

Table 5. IR and Crystallographic Data for Known Facial N_3MO_3 Compounds

complex	ν(M═O) (cm^{-1})	M−O(av), (Å)	M−N(av) (Å)	OMO(av) (deg)	NMN(av), (deg)	ref
15	899, 870	1.724(3)	2.374(3)	107.1(2)	58.8(1)	this work
$(Me_3tach)MoO_3$	899					31
$(dien)MoO_3$	878, 839	1.75(1)	2.32(1)	106(1)	77(4)	36
$(tacn)MoO_3$	850, 820					30
$(Me_3tacn)MoO_3$	862, 851					30
$(i\text{-}Pr_3tacn)MoO_3$	904, 861, 846	1.737(3)	2.438(3)	105.5(1)	73.3(1)	35
$[TpMoO_3]^-$	897, 845	1.731(7)	2.335(8)	105.1(6)	75.4(9)	37
$[Tp^*MoO_3]^{-\,a}$	924, 898					37
$L^*MoO_3{}^b$	898, 863, 840					4
16	920, 866	1.745(4)	2.355(6)	106.4(3)	59.0(3)	this work
$(dien)WO_3$	903, 833					32
$(tacn)WO_3$	830, 800	1.79(5)	2.31(1)	107.0(5)	72.2(4)	30, 38, 39
$(Me_3tacn)WO_3$	864, 838					30
$[Tp^*WO_3]^-$	920, 840	1.75(1)	2.33(2)	104.4(5)	77(1)	40
	852, 832					41

[a] Tp* = hydrotris(3,5-dimethylpyrazolyl)borate. [b] L* = tris(3,5-dimethylpyrazolyl)methane.

Mo, W),[11,12] the ^{1}H NMR signals due to tach methylene protons in **15** and **16** contain incompletely resolved fine structure due to long-range "*W*" coupling between the equatorial tach ring protons.[29] The infrared spectra (Table 5) of **15** and **16** show two distinctive metal−oxo stretching bands, indicative of a facial MO_3 unit. The ^{95}Mo NMR spectrum of **15** in MeOH-d_4 shows a single line at δ −13. By comparison, Wieghardt reported values of δ 86 for $(tacn)MoO_3$ and δ 98 for $(Me_3tacn)MoO_3$ (in D_2O).[30] The high-field ^{95}Mo chemical shift for **15** compared to the tacn complexes suggests a lower electron density at the Mo center in the *t*-Bu$_3$tach complex, in accord with the tach system being a poorer σ-donor than the tacn system.

Recently, Schumann reported the preparation of $(Me_3tach)MoO_3$ by a procedure similar to that outlined above for the preparation of **15** and **16**.[31] However, for the ^{1}H NMR spectrum of $(Me_3tach)MoO_3$, Schumann reported a singlet for the tach methylene hydrogens rather than the pair of doublets (due to the nonequivalent axial and equatorial methylene protons) expected for a facially coordinated Me_3tach ligand. It is possible that $(Me_3tach)MoO_3$ undergoes hydrolysis in D_2O to produce a solution containing molybdate ions ($MoO_4{}^{2-}$). Similar observations were reported for the hydrolysis of the related $(dien)MO_3$ (M = Mo, W) complexes.[32] Consistent with this possibility, the ^{95}Mo and ^{17}O NMR chemical shifts[31] for $(Me_3tach)MoO_3$ in D_2O solution (δ −2 and 536, respectively) are very close to those for Na_2MoO_4 in D_2O (δ 0 and 532[33]).

Attempts to prepare $(Bn_3tach)MoO_3$ from the corresponding tricarbonyl, **2b**, using hydrogen peroxide according to the above procedure, were unsuccessful. The major organic products isolated from this reaction were benzaldehyde and benzoic acid, indicating attack and oxidation at the reactive benzylic position, probably along with the breakdown of the tach ring. This observation is also analogous to the reaction of **2b** with bromine to produce benzylammonium bromide (see above).

Table 5 summarizes the IR and crystallographic data for the few known compounds possessing a *fac*-N_3MO_3 (M = Mo, W) core. The M═O stretching frequencies for **15** and **16** fall toward the higher end of the range observed for the MO_3 complexes, while the M═O bond lengths in **15** and **16** are comparatively short, consistent with our understanding that the *t*-Bu$_3$tach ligand is a fairly poor σ-donor when compared to tacn and related systems. An intriguing feature of these systems is the increase in M−O bond lengths, paralleled by a decrease in M−N bond lengths, on passing from M = Mo to M = W in the present complexes. The O−M−O angles are splayed, but, perhaps surprisingly, no more than usually, despite the substantial closing of the N−M−N angles.

Wieghardt et al.[19] have reported that reaction of $(tacn)M(CO)_3$ (M = Mo, W) with nitric acid leads to yellow-green solutions from which, by addition of $NaClO_4$, the dimeric M(VI) cation $[(tacn)_2M_2O_5]^+$ can be isolated. Reaction of **1b** and **1c** with nitric acid leads to the formation of persistent green solutions, but as yet we have been unable to isolate any dimeric species; the only products we have isolated thus far from these reactions have been the mononuclear trioxo complexes **15** and **16**. It is possible that the large steric bulk of the *tert*-butyl groups may prevent any appreciable amount of dimer formation.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structures of **15** and **16**. This material is available free of charge via the Internet at http://pubs.acs.org.

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