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π-Acid/π-Base Carbonyloxomolybdenum(IV) Complexes and Their Oxomolybdenum(VI/IV) Precursors

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Brown Tp$^{i\mathrm{Pr}}$MoO(SR)(CO) (Tp$^{i\mathrm{Pr}}$ = hydrotris(3-isopropylpyrazol-1-yl)borate; R = Et, ^{i}Pr, Ph, *p*-tol, Bz) are formed when Tp$^{i\mathrm{Pr}}$MoO(SR)(NCMe) react with CO gas in toluene. The carbonyloxomolybdenum(IV) complexes exhibit ν(CO) and ν(Mo═O) IR bands at ca. 2025 and 935 cm^{-1}, respectively, and NMR spectra indicative of C_1 symmetry, with δ_C(CO) ca. 250. The crystal structure of Tp$^{i\mathrm{Pr}}$MoO(S^{i}Pr)(CO), the first for a mononuclear carbonyloxomolybdenum complex, revealed a distorted octahedral geometry, with d(Mo═O) = 1.683(3) Å, d(Mo–C) = 2.043(5) Å, and $\angle$(O═Mo–C) = 90.87(16)°. The blue-green acetonitrile precursors are generated by reacting *cis*-Tp$^{i\mathrm{Pr}}$MoO$_2$(SR) with PPh$_3$; they are unstable, display a single ν(Mo═O) IR band at ca. 950 cm^{-1}, and exhibit NMR spectra consistent with C_1 symmetry. Red-brown *cis*-Tp$^{i\mathrm{Pr}}$MoO$_2$(SR) (R = as above and ^{t}Bu) are formed by metathesis of Tp$^{i\mathrm{Pr}}$MoO$_2$Cl and HSR/NEt$_3$ in dichloromethane. The complexes exhibit strong ν(MoO$_2$) IR bands at ca. 925 and 895 cm^{-1}, and NMR spectra indicative of C_s symmetry; the isopropyl, *p*-tolyl, and benzyl derivatives possess distorted octahedral geometries, with d(Mo═O)$_{\mathrm{av}}$ = 1.698 Å and $\angle$(MoO$_2$)$_{\mathrm{av}}$ = 103.5°.

Introduction

Interest in carbonyloxo species is piqued by their scarcity and electronic novelty,[1,2] as well as their potential applications in green technology, catalysis, and synthesis.[3−9] Metal-induced carboxyl (CO$_2$) bond-cleavage reactions produce carbonyl, oxo, or carbonyloxo species, depending on the oxophilicity of the metal.[3,4] Carbonyl ligand displacement, redox and oxo group-transfer reactions, etc., at these species present significant opportunities for chemical synthesis and elaboration.[5−7] The conversion of CO$_2$ (and other C1 sources, including CO) into chemicals and fuels promises to enhance economic security and contribute to the reduction of atmospheric CO$_2$, a principal contributor to global warming.[8,9] Bifunctional carbonyloxo species may be envisaged as stoichiometrically efficient intermediates in the aforementioned conversions. Carbonyloxo complexes are also putative intermediates in other metal- and metal-oxide-catalyzed processes, e.g., exhaust gas conversion, methanol synthesis, and the water gas shift reaction.[10,11]

The simultaneous coordination of π-acid carbonyl and π-base oxo ligands at a single metal center creates electronic conflicts that are hard to reconcile.[1,2] As a consequence, mononuclear carbonyloxo complexes are generally unstable and few have been isolated. Ternary carbonyloxo species, e.g., *trans*-MO$_2$(CO)$_4$, MO$_2$(CO)$_3$, MO$_2$(CO)$_2$ (M = Cr, Mo, W), [OMo(CO)]$^+$, and [MoO$_2$(CO)]$^+$, are stable only in low-temperature matrixes or the gas phase.[12−15] However, carbonyloxotungsten(IV) complexes are relatively stable, and

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a number have been isolated. The first examples, viz., $WOCl_2(CO)L_2$ (L = PMe_3, $PMePh_2$), were prepared by Mayer and co-workers by ligand substitution at $WOCl_2L_3$ or oxidative addition of CO_2 to WCl_2L_4.[2,16−18] Extension of these reactions yielded Mo (vide infra) and W complexes featuring a variety of π-acid (CO, CN^tBu, $CH_2{=}CHR$, and O═CHMe) and π-base (oxo, imido, and sulfido) ligand combinations.[2,18] The crystal structure of $WOCl_2(CO)(PMePh_2)_2$ revealed a distorted octahedral structure with d(W═O) = 1.689(6) Å, d(W−C) = 2.029(9) Å, and $\angle$(O═W−C) = 89.6(3)°.[2,17] Reports of carbonyloxotungsten(IV) complexes of hydrotris(3,5-dimethylpyrazol-1-yl)borate (Tp*) followed; these described dinuclear, mixed-valence $Tp^*W^{VI}O_2(\mu\text{-}O)W^{IV}O(CO)Tp^*$,[19] formed by oxidative hydrolysis of $[Tp^*W(CO)_3]^-$, and monomeric Tp*WOX(CO) (X = I, Br)[20] and $Tp^*WO(S_2PPh_2\text{-}S)(CO)$,[21] generated by oxygen atom transfer to carbonyltungsten(II) precursors. More recently, Templeton and co-workers have described the synthesis of Tp*WO(Me)(CO), $Tp^*WO(O_3SCF_3)(CO)$, and salts of $[Tp^*WO(NCMe)(CO)]^+$ and their deployment in the preparation of alkyne, vinylidene, acylimido, carbene, and dimeric nitrile-coupled oxo complexes.[5−7] Related carbonylsulfidotungsten(IV) complexes of Tp* have also been reported.[21]

Only two carbonyloxomolybdenum(IV) complexes, viz., $MoOCl_2(CO)L_2$ (L = PMe_3, $PMePh_2$), are known.[2,18] Both were generated by Mayer and co-workers by reacting $MoOCl_2L_3$ with CO gas. Only $MoOCl_2(CO)(PMePh_2)_2$ has been isolated, and neither complex has been structurally characterized.

The stability of group 6 *cis*-carbonyloxometal(IV) species is vested in their structure and bonding.[1,2] In these d^2 complexes, the filled d_{xy} orbital orthogonal to the strong-field oxo ligand (along z) is uniquely positioned to back-bond to the $\pi^*_\perp$ orbital of a *cis*-CO ligand (along x). π-Donation from the oxo ligand is directed into the d_{xz} and d_{yz} orbitals. This electronic structure results in a strong triple bond to the π-base oxo ligand and back-bonding to the π-acid CO ligand, both of which stabilize the complexes. Favorable overlap of the O p_x, M d_{xz}, and CO $\pi^*_{\parallel}$ orbitals has also been discussed.[1,2]

This paper reports the synthesis of dioxo(thiolato)molybdenum(VI) complexes, *cis*-$Tp^{iPr}MoO_2(SR)$ [Tp^{iPr} = hydrotris(3-isopropylpyrazol-1-yl)borate; R = Et, ^{i}Pr, ^{t}Bu, Ph,[22] *p*-tol, Bz (benzyl)], and their conversion by oxygen atom transfer into the useful synthetic intermediates $Tp^{iPr}MoO(SR)(NCMe)$ (R = Et, ^{i}Pr, *p*-tol, Bz). The thiolate complexes, $Tp^{iPr}MoO_2(SR)$ (R = Ph, ^{n}Bu, ^{s}Bu), are known, but their chemistry is still in its infancy;[22,23] the reported crystal structures of *cis*-$Tp^{iPr}MoO_2(SR)$ (R = ^{i}Pr, *p*-tol, Bz) are the first available for dioxomolybdenum thiolate complexes of Tp^{iPr}. The acetonitrile complexes are the immediate precursors for a unique range of carbonyloxomolybdenum(IV) species, viz., $Tp^{iPr}MoO(SR)(CO)$ (R = Et, ^{i}Pr, Ph, *p*-tol, Bz). The crystal structure of $Tp^{iPr}MoO(S^iPr)(CO)$ is the first reported for any mononuclear carbonyloxomolybdenum complex. The report further affirms the accessibility and relative stability of mononuclear, group 6 heavy-metal *cis*-carbonyloxometal(IV) species.

Experimental Section

Materials and Methods. All reactions were performed under an atmosphere of dinitrogen using dried, deoxygenated solvents and standard Schlenk techniques. Samples of $Tp^*MoO_2(SPh)$,[22] $Tp^{iPr}MoO_2(SPh)$,[22] and $Tp^{iPr}MoO_2Cl$[23] were synthesized according to literature methods. Other reagents were analytical grade or better.

IR spectra were recorded on a Biorad FTS 165 FTIR spectrophotometer as pressed KBr disks. ^1H and $^{13}C\{^1H\}$ NMR spectra were obtained using Varian Unity 300 and Varian Unity Plus 400 spectrometers. The spectra of the dioxo and carbonyloxo complexes were recorded in $CDCl_3$ (referenced to residual $CHCl_3$, δ_H 7.26, or $CDCl_3$, δ_C 77.36), while those of the nitrile complexes were recorded in CD_3CN (referenced to CHD_2CN, δ_H 1.93, or CD_3CN, δ_C 1.79); apart from the dioxo complexes, samples were prepared under strictly anaerobic conditions. Mass spectra were recorded on a Bruker BioApex 47e FTMS fitted with an Analytica electrospray ionization source operating with capillary voltages of 30−120 V. Electrochemical measurements were performed using a Cypress Electrochemical System II configured with a 3-mm glassy-carbon working electrode, a platinum auxiliary electrode, and a reference electrode consisting of an $Ag/AgNO_3$ (0.01 M in CH_3CN) electrode incorporated into a salt bridge containing supporting electrolyte (to minimize Ag^+ leakage). Sample solutions were prepared in acetonitrile/0.1 M $N^nBu_4PF_6$. Potentials were referenced against internal ferrocene (Fc) and are reported relative to the saturated calomel electrode [$E_{1/2}(Fc^+/Fc)$ = 0.460 V vs SCE[24]]. Microanalyses were performed by Atlantic Microlabs, Norcross, GA. Selected spectroscopic and electrochemical data are presented in Tables 1 and 2, respectively. Complete IR and ^{13}C NMR data are included as Supporting Information.

Synthesis of Dioxomolybdenum(VI) Complexes. $Tp^{iPr}MoO_2(SR)$ (R = Et, ^{i}Pr, ^{t}Bu, *p*-tol, Bz). The following general procedure was employed: A solution of $Tp^{iPr}MoO_2Cl$ (1.50 g, 2.98 mmol) in dichloromethane (30 mL) was treated with triethylamine (1.2 mL, 7.4 mmol), followed by thiol (8.0 mmol). The yellow solution was stirred for ca. 16 h, whereupon a dark-red-brown coloration developed. The mixture was reduced to dryness, and the residue was column chromatographed on silica gel using 3:2 dichloromethane/hexane as the eluent. The first red band was collected and evaporated to dryness. The residue was then treated with hexane (5 mL), stirred, and cooled to ca. 0 °C to yield orange- or red-brown crystals. The product was collected by filtration, washed with cold hexane, and dried in vacuo. Variations that optimized yields included NEt_3 (mmol):RSH (mmol) ratios and reaction times

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Table 1. Selected Characterization Data

compd (R)	IR spectrum (KBr, cm^{-1})			^{1}H NMR spectrum, δ (multiplicity, no. of H)				
	ν(BH)	ν(MoO)	ν(CO)	Tp^{iPr} methyl^a	Tp^{iPr} methine^b	Tp^{iPr} ring^c	CH_3CN	R
				Tp^{iPr}MoO$_2$(SR) Complexes				
Et	2496, 2462	929, 896		1.21, 1.23, 1.32	3.97, 4.27 (2H)	6.08, 6.11 (2H), 7.58 (2H), 7.61		1.50 (t, 3H), 3.49 (q, 2H)
^{i}Pr	2487, 2458	923, 895		1.21, 1.23, 1.32	4.00, 4.28 (2H)	6.09, 6.11 (2H), 7.57 (2H), 7.61		1.56 (d, 6H), 3.92 (sept, 1H)
^{t}Bu	2498, 2464	925, 893		1.19, 1.24, 1.31	4.08, 4.35 (2H)	6.08 (3H), 7.56 (2H), 7.60		1.65 (s, 9H)
p-tol	2509	927, 893		1.15, 1.21. 1.30	3.97, 4.23 (2H)	6.09, 6.14 (2H), 7.61 (2H), 7.64		2.38 (s, 3H), 7.16 (d, 2H), 7.55 (d, 2H)
Bz	2487, 2455	931, 898		1.18, 1.24 (12 H)	3.97, 4.18 (2H)	6.08, 6.09 (2H), 7.56 (2H), 7.62		4.60 (s, 2H), 7.21 (t, 1H), 7.31 (t, 2H), 7.39 (d, 2H)
				Tp^{iPr}MoO(SR)(NCMe) Complexes				
Et	2488, 2453	950		1.05, 1.13, 1.19, 1.26, 1.30, 1.31	3.83, 3.95, 4.15	5.94, 6.26, 6.38, 7.36, 7.63, 7.82	3.05	1.30 (t, 3H), 2.79 and 3.05 (each m, 1H)
^{i}Pr	2487, 2453	950		1.06, 1.14, 1.21, 1.26, 1.29, 1.31	3.66, 3.83, 4.22	5.93, 6.26, 6.38, 7.36, 7.63, 7.83	3.07	1.14, 1.45 (each d, 3H), 3.96 (sept, 1H)
Ph	2497, 2455	950		0.91, 1.10, 1.15, 1.16, 1.27 (6H)	3.56, 3.87, 4.20	5.93, 6.30, 6.37, 7.39, 7.70, 7.86	2.54	7.05 (t, 1H), 7.20 (t, 2H), 7.34 (d, 2H)
p-tol	2486, 2451	952		0.91, 1.10, 1.16, 1.17, 1.27 (6H)	3.56, 3.86, 4.22	5.94, 6.29, 6.38, 7.39, 7.69, 7.85	2.54	2.30 (s, 3H), 7.03 (d, 2H), 7.23 (d, 2H)
Bz	2488, 2454	949		1.06, 1.16, 1.19, 1.26, 1.27, 1.30	3.85, 3.95, 4.18	5.96, 6.27, 6.38, 7.39, 7.66, 7.85	3.06	4.08 and 4.28 (each d, 1H), 7.14 (t, 1H), 7.26 (t, 2H), 7.34 (d, 2H)
				Tp^{iPr}MoO(SR)(CO) Complexes				
Et	2495, 2459	923	2017	1.11 (6H), 1.20, 1.25, 1.28, 1.40	3.60, 3.70, 4.10	5.83, 6.16, 6.35, 7.31, 7.56, 7.78		1.15 (t, 3H), 2.58 and 3.10 (each m, 1H)
^{i}Pr	2496, 2456	935	2031	1.11, 1.13, 1.22, 1.25, 1.29, 1.42	3.59, 3.64, 4.13	5.81, 6.15, 6.36, 7.30, 7.55, 7.77		0.8 (br, 3H), 1.45 (d, 3H), 3.47 (m, 1H).
Ph	2495, 2459	940	2031	0.94, 1.05, 1.10, 1.15, 1.26, 1.31	3.19, 3.69, 4.17	5.83, 6.21, 6.28, 7.35, 7.61, 7.77		7.02 (t, 1H), 7.12 (t, 2H), 7.23 (d, 2H)
p-tol	2486, 2458	939	2025	0.94, 1.07, 1.10, 1.16, 1.26, 1.31	3.20, 3.68, 4.19	5.82, 6.20, 6.28, 7.34, 7.60, 7.76		2.29 (s, 3H), 6.95 (d, 2H), 7.12 (d, 2H)
Bz	2488, 2458	935	2026	0.91, 1.04, 1.14, 1.26, 1.27, 1.43	3.62, 3.69, 4.07	5.80, 6.16, 6.38, 7.35, 7.57, 7.84		3.47 and 4.15 (each d, 1H), 6.88 (d, 2H), 7.05−7.13 (m, 3H)

[a] All doublet resonances integrating for 6H (dioxo complexes) or 3H (others) unless indicated. [b] All septet resonances integrating for 1H each unless indicated. [c] All doublet resonances integrating for 1H unless indicated.

Table 2. Cyclic Voltammetric Data for Tp^{iPr}MoO$_2$(SR)^a

R	$E_{1/2}$ (V)	E_{pa} (V)	E_{pc} (V)	I_{pa}/I_{pc}	ΔE_{pp} (mV)
Et	−0.781	−0.740	−0.823	0.99	83
^{i}Pr	−0.802	−0.757	−0.848	0.94	91
^{n}Bu^b	−0.781	−0.745	−0.817	1.02	73
^{s}Bu^b	−0.811	−0.772	−0.851	1.03	79
^{t}Bu	−0.846	−0.796	−0.895	0.97	99
Ph^c	−0.660	−0.625	−0.696	1.00	71
p-tol	−0.679	−0.634	−0.725	0.92	91
Bz	−0.736	−0.687	−0.785	1.01	98

[a] Measured at 100 mV s^{-1} in dry acetonitrile. [b] Data from Millar et al.,[23] run at 10 mV s^{-1}. [c] Data from Xiao et al.[22]

of 11:6 (72 h), 11:6 (1 h), and 9:9 (2 h) for the ^{t}Bu, *p*-tol, and Bz derivatives, respectively.

For R = Et. Yield: 750 mg (48%). Anal. Calcd for $C_{20}H_{33}BMoN_6O_2S$: C, 45.47; H, 6.30; N, 15.91; S, 6.07. Found: C, 45.34; H, 6.30; N, 15.80; S, 5.79. MS: *m*/*z* 531.2 [M + H]$^+$.

For R = ^{i}Pr. Yield: 1.07 g (66%). Anal. Calcd for $C_{21}H_{35}BMoN_6O_2S$: C, 46.51; H, 6.50; N, 15.50; S, 5.91. Found: C, 46.81; H, 6.66; N, 15.32; S, 5.66. MS: *m*/*z* 545.2 [M + H]$^+$.

For R = ^{t}Bu. Yield: 640 mg (39%). Anal. Calcd for $C_{22}H_{37}BMoN_6O_2S$: C, 47.49; H, 6.70; N, 15.11; S, 5.76. Found: C, 47.81; H, 6.71; N, 15.12; S, 5.47. MS: *m*/*z* 559.2 [M + H]$^+$.

For R = *p*-tol. Yield: 1.14 g (64%). Anal. Calcd for $C_{25}H_{35}BMoN_6O_2S$: C, 50.86; H, 5.97; N, 14.23; S, 5.43. Found: C, 51.07; H, 6.01; N, 14.06; S, 5.70. MS: *m*/*z* 593.2 [M + H]$^+$.

For R = Bz. Yield: 1.61 g (91%). Anal. Calcd for $C_{25}H_{35}BMoN_6O_2S$: C, 50.86; H, 5.97; N, 14.23; S, 5.43. Found: C, 50.84; H, 6.05; N, 14.09; S, 5.59. MS: *m*/*z* 593.2 [M + H]$^+$.

Synthesis of Oxo(acetonitrile)molybdenum(IV) Complexes. Tp*MoO(SPh)(NCMe). A mixture of Tp*MoO$_2$(SPh) (0.95 g, 1.8 mmol) and PPh$_3$ (0.56 g, 2.1 mmol) in acetonitrile (20 mL) was stirred overnight to form a blue solution. The volume of the solution was reduced to 10 mL, and methanol (10 mL) was added to precipitate green-blue crystals. These were filtered, washed with methanol (2 × 5 mL), and dried under vacuum. Yield: 0.74 g (74%). Anal. Calcd for $C_{23}H_{30}BMoN_7OS$: C, 49.38; H, 5.41; N, 17.53; S, 5.73. Found: C, 49.25; H, 5.36; N, 17.47; S, 5.62. IR (KBr): ν(BH) 2531 br, w, ν(CN) 1545 s, ν(Mo=O) 948 s cm^{-1}. ^{1}H NMR (CD_3CN): δ 2.20, 2.24, 2.40, 2.52, 2.60 (6H) (s, 6 CH_3 of Tp*); 2.52 (s, CH_3CN); 5.59, 5.98, 6.07 (s, 3 CH of Tp*); 7.00 (t, 1H), 7.15 (t, 2H), 7.36 (d, 2H) (Ph).

Tp^{iPr}MoOCl(NCMe). A mixture of Tp^{iPr}MoO$_2$Cl (300 mg, 0.597 mmol) and PPh$_3$ (290 mg, 1.11 mmol) in acetonitrile (20 mL) was stirred for 16 h to form a green solution. The solvent was removed in vacuo, and dry hexane (15 mL) was added. The resulting suspension was stirred overnight and then cooled to ca. 0

°C. The bright-green solid precipitated was collected by filtration, washed with hexane (2 × 5 mL) and 2-propanol (2 × 5 mL), and dried in vacuo. Yield: ∼200 mg. Characterization data are included as Supporting Information.

Tp^{iPr}MoO(SR)(NCMe) (R = Et, ^{i}Pr, Ph, *p*-tol, Bz). The following general procedure was employed: A mixture of Tp^{iPr}MoO$_2$(SR) (500 mg) and PPh$_3$ (2.0 mol equiv) in acetonitrile (30 mL) was stirred for 12 h to produce a green-blue solution. The solvent was removed in vacuo, and dry hexane (20 mL) was added. Stirring overnight, followed by cooling to ca. 0 °C, produced a blue solid that was collected by filtration, washed with hexane (2 × 5 mL) and 2-propanol (2 × 5 mL), and dried in vacuo. The approximate yields obtained were as follows: R = Et, 320 mg; R = ^{i}Pr, 460 mg; R = Ph, 360 mg (70%); R = *p*-tol, 395 mg; R = Bz, 230 mg.

Microanalysis for Tp^{iPr}MoO(SPh)(NCMe). Anal. Calcd for $C_{26}H_{36}BMoN_7OS$: C, 51.92; H, 6.03; N, 16.30; S, 5.33. Found: C, 52.18; H, 5.97; N, 16.49; S, 5.48. Characterization data can be found in Table 1 and the Supporting Information.

Synthesis of Carbonyloxomolybdenum(IV) Complexes. Tp*MoO(SPh)(CO). Carbon monoxide gas was bubbled through a solution of Tp*MoO(SPh)(NCMe) (100 mg, 0.542 mmol) in dry toluene (15 mL) for 30 min at room temperature. The vessel was then sealed and stirred overnight. The solvent was removed in vacuo to yield a red-purple solid. Attempted purification resulted in decomposition. Data for the crude solid (with tentative assignments) include the following. IR (KBr): ν(BH) 2549 w, ν(CO) 2020 s, ν(CN) 1545 m, ν(Mo=O) 933 cm^{-1}. ^{1}H NMR (C_6D_6): δ 1.87, 2.02, 2.06, 2.16, 2.47, 2.82 (s, 6 CH$_3$ of Tp*); 5.17, 5.52, 5.57 (s, 3 CH of Tp*); 7.05 (t, 1H, Ph-4); 7.18 (t, 2H, Ph-3,5); 7.30 (d, 2H, Ph-2,6).

Tp^{iPr}MoO(SR)(CO) (R = Et, ^{i}Pr, Ph, *p*-tol, Bz). The following general procedure was employed: A solution of Tp^{iPr}MoO(SR)(NCMe) (300 mg) in toluene (30 mL) contained in a 100-mL Schlenk flask was treated with bubbling CO gas for 30 min at room temperature. The Schlenk flask was then closed and the solution stirred for 12−16 h under an atmosphere of CO. The solvent was removed from the red-brown mixture (in vacuo), and the residue was treated with hexane (5 mL). The mixture was stirred for 2 h before storage at −4 °C overnight to produce gold- or red-brown crystals. The product was collected by filtration, washed with cold hexane (1 mL), and dried in vacuo.

For R = Et. Yield: 135 mg (46%). Anal. Calcd for $C_{21}H_{33}BMoN_6O_2S$: C, 46.68; H, 6.16; N, 15.55; S, 5.93. Found: C, 46.64; H, 6.21; N, 15.29; S, 5.68.

For R = ^{i}Pr. Yield: 130 mg (44%). Anal. Calcd for $C_{22}H_{35}BMoN_6O_2S$: C, 47.66; H, 6.36; N, 15.16; S, 5.78. Found: C, 47.58; H, 6.38; N, 14.97; S, 5.52.

For R = Ph. Yield: 200 mg (65%). Anal. Calcd for $C_{25}H_{34}BMoN_6O_2S$: C, 51.03; H, 5.65; N, 14.28; S, 5.44. Found: C, 51.48; H, 5.67; N, 14.47; S, 5.37.

For R = *p*-tol. Yield: 160 mg (54%). Anal. Calcd for $C_{26}H_{35}BMoN_6O_2S$: C, 51.84; H, 5.86; N, 13.95; S, 5.32. Found: C, 51.82; H, 5.86; N, 13.83; S, 5.24.

For R = Bz. Yield: 103 mg (50%). Anal. Calcd for $C_{26}H_{35}BMoN_6O_2S$: C, 51.84; H, 5.86; N, 13.95; S, 5.32. Found: C, 51.69; H, 5.93; N, 13.59; S, 5.07.

X-ray Crystallography. Red-brown crystals of Tp^{iPr}MoO$_2$(SR) (R = ^{i}Pr, *p*-tol, Bz) were grown by diffusion of hexane into saturated dichloromethane solutions of the complexes. Crystals of Tp^{iPr}MoO(S^{i}Pr)(CO) were grown by cooling a saturated solution in hexane under a dinitrogen atmosphere to 4 °C.

X-ray diffraction data were collected at 293(2) K (dioxo species) or 130(2) K (carbonyloxo) using a Bruker SMART Apex CCD detector using Mo Kα radiation (graphite crystal monochromator, λ = 0.710 73 Å).[25] Accurate cell parameters and crystal orientation were obtained by least-squares refinement of 6861, 6646, 8037, and 1293 reflections with θ values between 2.3 and 27.5°, 2.4 and 27.1°, 2.3 and 27.5°, and 2.4 and 21.6° for Tp^{iPr}MoO$_2$(SR) (R = ^{i}Pr, *p*-tol, Bz) and Tp^{iPr}MoO(S^{i}Pr)(CO), respectively. Data were reduced using the program *SAINT* and corrected for absorption (ratio of max/min transmission of 0.60, 0.62, 0.57, and 0.60, respectively).[25]

The structures were solved by direct methods and difference Fourier synthesis.[25] Hydrogen atoms were included in calculated positions. Full-matrix least-squares refinements on F^2, using all data, were carried out with anisotropic displacement parameters applied to all non-hydrogen atoms. Weighting schemes of the type $w = [\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}$, where $P = (F_o^2 + 2F_c^2)/3$, were applied. In the final refinement, the maximum shift/error ratios were less than 0.001 in all cases. In the final difference maps, the maximum (near Mo)/minimum peak heights were 0.457/−0.276, 0.412/−0.241, 0.427/−0.183, and 0.988/−0.492 e Å^{-3} for Tp^{iPr}MoO$_2$(SR) (R = ^{i}Pr, *p*-tol, Bz) and Tp^{iPr}MoO(S^{i}Pr)(CO), respectively. The structures were refined to conventional *R* factors of 0.0309, 0.0281, 0.0251, and 0.0607, respectively.

Crystallographic data are presented in Table 3, and selected bond distances and angles are given in Table 4. Figures 1−4 were prepared using ORTEP 3.[26]

Results and Discussion

Synthesis and Characterization of Tp^{iPr}MoO$_2$(SR). Red-brown, diamagnetic Tp^{iPr}MoO$_2$(SR) were produced in the reactions of yellow Tp^{iPr}MoO$_2$Cl with thiols and triethylamine in dichloromethane at room temperature. The reactions and workup procedures closely parallel those reported for related thiolate complexes;[22,23] reaction times varied from hours (*p*-tol) to days (*t*-Bu). The air-stable complexes are soluble and stable in chlorinated solvents, benzene, and toluene, slightly soluble in hexane, and insoluble in alcohols (N.B.: The benzyl derivative decomposed over a period of weeks in air).

Microanalytical and mass spectrometric data were consistent with the proposed formulations. IR spectra (Table 1) exhibited bands assigned to ν(MoO$_2$) vibrational modes, at ca. 925 and 895 cm^{-1}, respectively, in accordance with the IR spectra of related complexes.[22,23,27] ^{1}H NMR spectral data (Table 1) were indicative of molecular C_s symmetry, with each complex displaying three doublet isopropyl methyl resonances (6:6:6 integrated ratio) and pairs of septet isopropyl methine, doublet ring 4-H, and doublet ring 5-H resonances (each with 2:1 integrated ratios). Appropriate coligand resonances were also observed. ^{13}C NMR spectra (see the Supporting Information) were also indicative of C_s symmetry.

cis-Dioxo hydrotris(3-isopropylpyrazol-1-yl)borate complexes generally undergo a reversible one-electron reduction,

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[25] *SMART, SAINT, and SADABS*; Siemens Analytical X-ray Instruments Inc.: Madison, WI, 1999.

[26] Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 565.

[27] Doonan, C. J.; Millar, A. J.; Nielsen, D. J.; Young, C. G. *Inorg. Chem.* **2005**, *44*, 4506−4514.

Table 3. Crystallographic Data

compd	$Tp^{iPr}MoO_2(S^iPr)$	$Tp^{iPr}MoO_2(S\text{-}p\text{-}tol)$	$Tp^{iPr}MoO_2(SBz)$	$Tp^{iPr}MoO(S^iPr)(CO)$
formula	$C_{21}H_{35}BMoN_6O_2S$	$C_{25}H_{35}BMoN_6O_2S$	$C_{25}H_{35}BMoN_6O_2S$	$C_{22}H_{35}BMoN_6O_2S$
fw	542.36	590.40	590.40	554.37
space group	$P2_1/c$	$P\bar{4}2_1c$	$P2_1/c$	$P\bar{1}$
a, Å	15.2105(7)	19.3498(4)	15.2064(8)	9.0180(11)
b, Å	10.9957(5)	19.3498(4)	10.1692(5)	12.6643(15)
c, Å	15.9661(8)	15.6532(8)	19.0274(9)	13.3832(16)
α, deg	90	90	90	68.919(2)
β, deg	95.3550(10)	90	103.8370(10)	72.315(2)
γ, deg	90	90	90	74.808(2)
V, Å^3	2658.7(2)	5860.8(3)	2857.0(2)	1338.5(3)
Z	4	8	4	2
ρ, g cm^{-3}	1.355	1.338	1.373	1.375
μ, cm^{-1}	5.99	5.50	5.64	5.97
data/param	6028/301	6724/336	4097/335	5951/310
GOF (on F^2)	0.963	0.968	1.036	1.032
R_{int}	0.0319	0.0651	0.0183	0.0350
R^a	0.0309	0.0281	0.0251	0.0607
$R_w{}^a$	0.0816	0.0621	0.0687	0.1302

[a] $R = \sum(|F_o| - |F_c|)/\sum|F_o|$ for data with $I > 2\sigma(I)$; $R_w = \{\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2\}^{1/2}$ for all data.

Table 4. Selected Bond Distances (Å) and Angles (deg)

distance/angle[a]	$Tp^{iPr}MoO_2(S^iPr)$	$Tp^{iPr}MoO_2(S\text{-}p\text{-}tol)$	$Tp^{iPr}MoO_2(SBz)$	$Tp^{iPr}MoO(S^iPr)(CO)$
Mo−O1	1.6946(15)	1.6930(17)	1.7065(16)	1.683(3)
Mo−O/C	1.6896(15)	1.7029(17)	1.6990(16)	2.043(5)
Mo−S1	2.3893(6)	2.4134(6)	2.3994(6)	2.3738(12)
Mo−N11	2.3248(15)	2.3236(19)	2.3846(18)	2.367(3)
Mo−N21	2.3617(16)	2.339(2)	2.3171(18)	2.187(3)
Mo−N31	2.1936(17)	2.1870(18)	2.2005(18)	2.241(3)
S1−C	1.815(2)	1.787(2)	1.843(3)	1.829(5)
O1−Mo-O/C	103.13(7)	103.66(9)	103.63(8)	90.87(16)
O1−Mo−S1	98.26(6)	98.05(5)	101.91(6)	103.74(11)
O1−Mo−N11	168.25(7)	169.28(7)	165.85(7)	167.02(13)
O1−Mo−N21	87.62(6)	88.46(8)	88.42(7)	99.67(14)
O1−Mo−N31	98.81(7)	97.03(7)	91.54(7)	90.48(13)
O/C−Mo−S1	102.13(5)	102.42(6)	95.50(6)	95.31(13)
O/C−Mo−N11	88.45(7)	86.90(8)	87.27(7)	83.87(15)
O/C−Mo−N21	167.14(7)	164.59(7)	167.95(7)	169.24(15)
O/C−Mo−N31	93.11(7)	91.84(8)	98.99(7)	94.70(15)
S1−Mo−N11	80.96(4)	81.23(5)	85.72(5)	88.60(9)
S1−Mo−N21	82.98(4)	84.94(5)	81.76(5)	84.39(10)
S1−Mo−N31	153.84(5)	156.12(6)	157.32(5)	162.44(9)
N11−Mo−N21	80.65(6)	80.82(6)	80.83(6)	85.37(12)
N11−Mo−N31	78.30(6)	80.52(7)	77.68(6)	78.18(12)
N21−Mo−N31	78.09(6)	77.05(7)	80.43(7)	83.09(13)
C−S1−Mo	105.63(9)	106.11(8)	105.39(9)	116.99(16)

[a] O/C refers to either O2 in the dioxo complexes or C1 in the carbonyloxo complex.

forming the corresponding dioxomolybdenum(V) anions.[22,23,27] Halide complexes have the most positive reduction potentials, followed by thiophenolates, phenolates, alkylthiolates, and alkoxides (with some overlap). The cyclic voltammograms of the title complexes each revealed a reversible one-electron reduction at a potential in the range of −0.679 to −0.802 V vs SCE (Table 2). No other processes were observed. Consistent with the trend noted above, the *p*-tolyl derivative was reduced at a potential significantly more positive than the alkyl derivatives, with the order of the reduction potentials being: Ph > *p*-tol > Bz > Et, ^{n}Bu > ^{i}Pr > ^{s}Bu > ^{t}Bu (including earlier derivatives). The effect of the coligand on the reduction potential has been discussed elsewhere.[22,23,27] All processes were characterized by peak current ratios (I_{pa}/I_{pc}) close to unity at all scan rates. $E_{1/2}$ values were independent of the scan rate, while ΔE_{pp} values were close to the values recorded for ferrocene under the same conditions. Such behavior is indicative of electrochemically reversible processes.[28] These results indicate that $Tp^{iPr}Mo^{VI}O_2(SR)$ are reduced to $[Tp^{iPr}Mo^{V}O_2(SR)]^-$ species that are stable on the cyclic voltammetric time scale. The behavior is consistent with previous electrochemical studies (vide supra)[22,23,27] and the isolation of salts such as $CoCp_2[Tp^{iPr}MoO_2(SPh)]$.[29]

Crystal Structures of Dioxo Complexes. The crystal structures of $Tp^{iPr}MoO_2(SR)$ (R = ^{i}Pr, *p*-tol, Bz) were determined, and views of the molecules are given in Figures 1−3; selected distances and angles are presented in Table 4. In the discussion that follows, the parameters quoted pertain to the complexes in the order above.

All three complexes exhibit six-coordinate, distorted octahedral geometries, with coordination spheres comprised of *fac*-tridentate Tp^{iPr} and mutually cis thiolate and terminal

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(28) Christensen, P. A.; Hamnett, A. *Techniques and Mechanisms in Electrochemistry*; Chapman and Hall: Oxford, U.K., 1994.

(29) Xiao, Z.; Gable, R. W.; Wedd, A. G.; Young, C. G. *J. Am. Chem. Soc.* **1996**, *118*, 2912−2921.

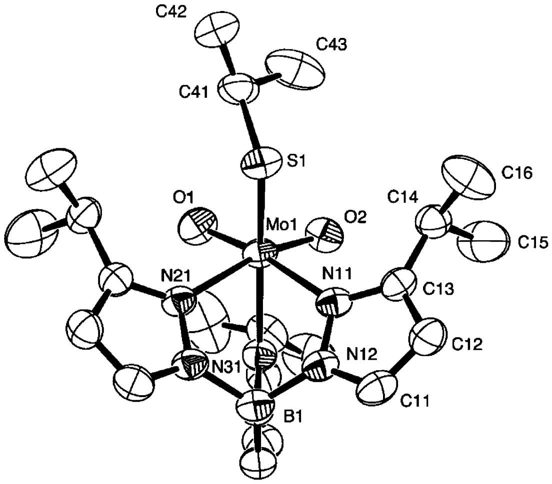

Figure 1. Structure of Tp^{iPr}MoO$_2$(S^{i}Pr). The numbering schemes for the pyrazolyl rings containing N21 and N31 parallel that shown for the ring containing N11. Thermal ellipsoids are drawn at the 30% probability level, and H atoms are excluded for clarity.

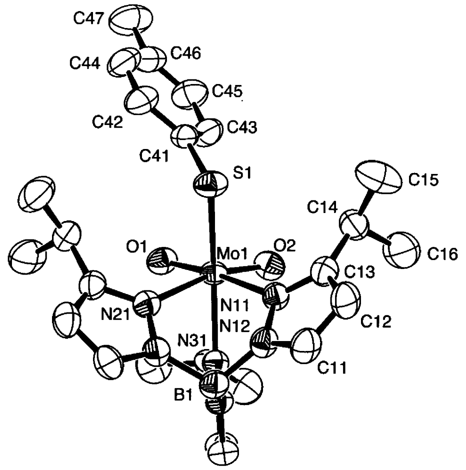

Figure 2. Structure of Tp^{iPr}MoO$_2$(S-*p*-tol). See Figure 1 for comments.

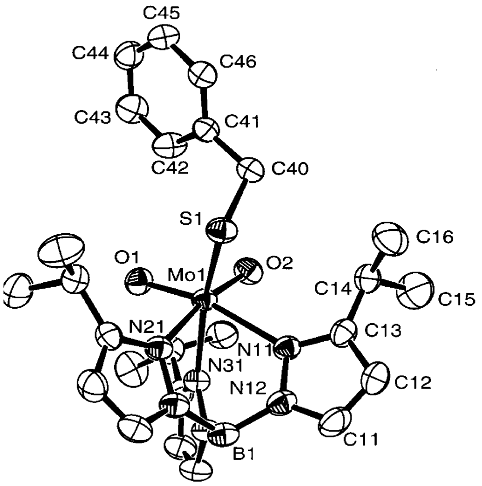

Figure 3. Structure of Tp^{iPr}MoO$_2$(SBz). See Figure 1 for comments.

oxo ligands. The largest angular deviations from ideal octahedral geometry are the obtuse O=Mo=O (average 103.5°) and O=Mo−S1 (average 99.7°) angles and the acute N−Mo−N (average 79.4°) angles associated with the Tp^{iPr} ligand. These lead to trans O/S−Mo−N angles that deviate considerably from 180°, exemplified by S1−Mo−N31 angles as low as 153.84(5)°. The Mo atom in each complex lies much closer to the O$_2$S face of the "octahedron" (0.839, 0.838, and 0.861 Å) than the N$_3$ face (1.555, 1.538, and 1.545 Å). The methine protons of the Tp^{iPr} isopropyl groups are directed toward the pseudo-3-fold axis through Mo and B. Similar distortions are observed for related complexes,[30] including Tp*MoO$_2$(SPh).[22]

The Mo=O distances of 1.6896(15)−1.7065(16) Å and O=Mo=O angles of 103.13(7)−103.66(9)° are as expected for *cis*-dioxomolybdenum(VI) species,[30−32] with the parameters being close to those of structurally characterized Tp^{iPr}MoO$_2$(OR/Ar) complexes [d(Mo=O) = 1.684(3)−1.705(3) Å; ∠(O=Mo=O) = 102.44(1)−103.92(16)°].[22,27] The Mo−S1 distances of 2.3893(6)−2.4134(6) Å are characteristic of Mo−thiolate single bonds.[32] The angle O1−Mo−S1 ranges from 98.05(5)−101.91(6)°. The O2−Mo−S1 angles are 102.13(5) and 102.42(6)° for Tp^{iPr}MoO$_2$(S^{i}Pr) and Tp^{iPr}MoO$_2$(S-*p*-tol), respectively, but it is only 95.50(6)° for Tp^{iPr}MoO$_2$(SBz); the latter value reflects increased steric interactions between the phenyl and ^{i}Pr groups, which force S1 toward the oxo ligand O2. The Mo−N11 and Mo−N21 distances trans to the oxo ligands are more than 0.12 Å longer than the Mo−N31 distances because of the strong trans influence of the oxo ligand.[30,31,33]

Synthesis and Charaterization of Tp^{iPr}MoO(SR)(NCMe). The reactions of Tp^{iPr}MoO$_2$(SR) with excess PPh$_3$ in acetonitrile yielded nitrile adducts, Tp^{iPr}MoO(SR)(NCMe), and byproduct OPPh$_3$. The isolation of analytically and spectroscopically pure complexes required copious washing to remove OPPh$_3$, with an attendant sacrifice of yield. However, the presence of residual PPh$_3$/OPPh$_3$ (typically ca. 5% by NMR) in routinely washed samples did not adversely affect the generation of carbonyloxo complexes (vide infra). The *tert*-butylthiolate derivative failed to react with PPh$_3$, presumably for steric reasons. The chloro complex, Tp^{iPr}MoOCl(NCMe), was also prepared, along with Tp*MoO(SPh)(NCMe), the immediate precursor to unstable Tp*MoO(SPh)(CO) (vide infra).

Aqua-blue, diamagnetic Tp^{iPr}MoO(SR)(NCMe) are soluble in chlorinated solvents, benzene, and toluene and insoluble in hexane and alcohols. They persist for a few hours in deoxygenated acetonitrile but rapidly decompose in chlorinated solvents. As solids, they can be stored for extended periods under dinitrogen at low temperatures (ca. −30 °C).

Parent ions, [Tp^{iPr}MoO(SR)(NCMe)]$^+$, were observed by mass spectrometry, but correct microanalyses were difficult to obtain because of persistent OPPh$_3$ contamination and general instability. The correct microanalysis obtained for Tp^{iPr}MoO(SPh)(NCMe) supports the proposed formulations.

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(30) Young, C. G. In *Comprehensive Coordination Chemistry II*; McCleverty, J. A., Meyer, T. J., Eds.; Elsevier-Pergamon: Amsterdam, The Netherlands, 2004; Vol. 4, Chapter 4.7, pp 415−527.

(31) Stiefel, E. I. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon: Oxford, U.K., 1987; Chapter 36.5, pp 1375−1420.

(32) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1−S83.

(33) Nugent, W. A.; Mayer, J. M. *Metal−Ligand Multiple Bonds*; Wiley: New York, 1988.

The IR spectra of the complexes (Table 1) exhibited a single ν(Mo=O) band at around 950 cm^{-1}, in the region expected for oxomolybdenum(IV) complexes.[30,33] The characteristic bands of Tp$^{i\mathrm{Pr}}$ were present, but a nitrile ν(C≡N) band was not observed; the latter are notoriously difficult to observe because of their low intensity.[34]

All ^{1}H NMR spectra (Table 1) were consistent with molecular C_1 symmetry, i.e., complete inequivalence of all protonic groups. Resonances in the regions δ 7.35−7.90 (three doublets), 5.90−6.40 (three doublets), 3.55−4.25 (three septets), and 1.35−0.95 (six doublets) were assigned to the 5-H, 4-H, and ^{i}Pr methine and methyl groups of Tp$^{i\mathrm{Pr}}$, respectively. A singlet resonance at ca. δ 2.5−3.0 was assigned to the methyl group of the acetonitrile ligand, which slowly exchanged with solvent CD_3CN. Expected coligand resonances were also observed, with the diastereotopic groups in the ethyl (CH_AH_B, δ 2.79 and 3.05), isopropyl (CMe_AMe_B, δ 1.14 and 1.45), and benzyl (CH_AH_B, δ 4.08 and 4.28) derivatives producing complex resonance patterns.

^{13}C NMR spectra consisted of a total of nine isopropyl methyl (δ 23−25) and methine (δ 27−30) resonances and sets of three pyrazolyl ring carbon resonances in the regions δ 102−105 (4-C), 135−140 (5-C), and 164−166 (3-C). The acetonitrile ligand was associated with resonances at ca. δ 5−6 and 165−168, assigned to the methyl and nitrile carbon atoms, respectively. Appropriate thiolate coligand resonances were also observed. For example, the isopropylthiolato ligand of Tp$^{i\mathrm{Pr}}$MoO(S^{i}Pr)(NCMe) exhibited singlets at δ 28.87 and 28.96, assigned to the diastereotopic methyl carbons, and a singlet peak at δ 39.04, assigned to the secondary carbon.

Synthesis and Characterization of Tp$^{i\mathrm{Pr}}$MoO(SR)(CO). Unstable red-purple Tp*MoO(SPh)(CO) [ν(CO) 2020 cm^{-1} and ν(Mo=O) 933 cm^{-1}], isolated from the reaction of Tp*MoO(SPh)(NCMe) with CO in toluene under scrupulously dry and anaerobic conditions, resisted purification and full characterization. However, its synthesis encouraged efforts to prepare more stable carbonyloxo complexes containing the sterically demanding Tp$^{i\mathrm{Pr}}$ ligand.

Reactions of Tp$^{i\mathrm{Pr}}$MoO(SR)(NCMe) with CO in toluene resulted in the displacement of acetonitrile by CO to form stable brown, diamagnetic Tp$^{i\mathrm{Pr}}$MoO(SR)(CO). The reactions were carried out anaerobically at room temperature, and workups required dry solvents and low temperatures; otherwise, reduced yields were obtained. The complexes are soluble in chlorinated and aromatic solvents and slightly soluble in hexane and alcohols. They are stable in chlorinated solutions for a short time but stable for hours in benzene or toluene. The carbonyl ligand is labile and is readily lost into solution. The solids are stable for long periods at low temperature (ca. −30 °C) under dinitrogen but decompose in air over a period of weeks to form Tp$^{i\mathrm{Pr}}$MoO$_2$(SR). We have been unable to develop low-valent syntheses such as those used to prepare Tp*WOX(CO) complexes.[20,21]

Microanalytical results were consistent with the proposed formulations. Decarbonylation and fragmentation attended mass spectrometric interrogation. The IR spectra of Tp$^{i\mathrm{Pr}}$MoO(SR)(CO) exhibited strong ν(CO) and ν(Mo=O) bands at 2036−2017 cm^{-1} and 940−923 cm^{-1}, respectively, as well as bands attributable to the Tp$^{i\mathrm{Pr}}$ and thiolate ligands. The ν(CO) bands are close in energy to those of MoCl$_2$(CO)L$_2$ (L = PMe$_3$, ν(CO) 2020 cm^{-1}; L = PMePh$_2$, ν(CO) 2041 cm^{-1}) but much higher in energy than ν(CO) bands in related carbonyloxotungsten complexes (2006−1945 cm^{-1}). The ν(Mo=O) bands are 13−26 cm^{-1} lower in energy than the corresponding band of the acetonitrile precursors but still within the range established for oxomolybdenum(IV) complexes (960−900 cm^{-1}).[30]

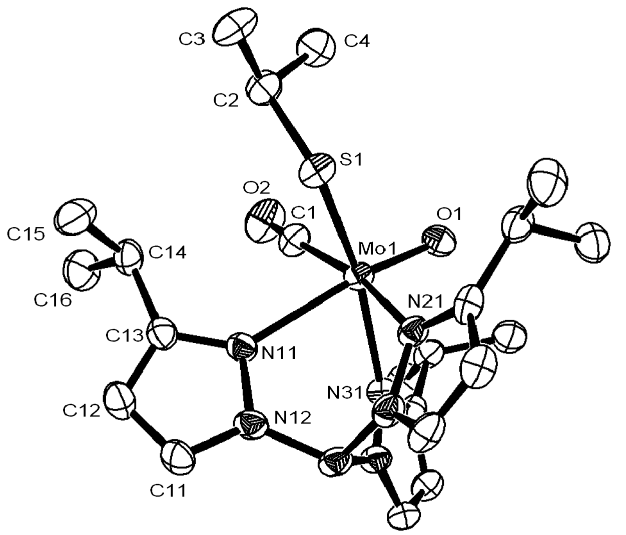

Figure 4. Structure of Tp$^{i\mathrm{Pr}}$MoO(S^{i}Pr)(CO). See Figure 1 for comments.

The ^{1}H NMR spectra of the complexes were indicative of molecular C_1 symmetry. For Tp$^{i\mathrm{Pr}}$, sets of three ring 5-H, ring 4-H, and ^{i}Pr methine resonances were observed in the regions δ 7.2−7.9, 5.8−6.4, and 3.1−4.2, respectively (each integrating for one proton). Six doublet resonances between δ 0.9 and 1.5, each integrating for three protons, were assigned to the methyl protons of the inequivalent isopropyl methyl groups. Expected coligand resonances were also observed, with the diastereotopic nature of groups in the ethyl (CH_AH_B), isopropyl (CMe_AMe_B), and benzyl (CH_AH_B) derivatives being evident in resonance patterns.

The ^{13}C NMR spectra of the complexes (see the Supporting Information) exhibited Tp$^{i\mathrm{Pr}}$ and thiolate ligand resonances similar to those observed for Tp$^{i\mathrm{Pr}}$MoO(SR)(NCMe) but carbonyl resonances were difficult to observe even with reduced pulse widths and long pulse delays. However, a carbonyl resonance in the region δ 250−256 was observed for each of the more stable aromatic derivatives.

Crystal Structure of Tp$^{i\mathrm{Pr}}$MoO(S^{i}Pr)(CO). The molecular structure of Tp$^{i\mathrm{Pr}}$MoO(S^{i}Pr)(CO) was determined by X-ray diffraction; a view of the complex and structural parameters may be found in Figure 4 and Table 4, respectively. The six-coordinate, distorted octahedral complex features *fac*-tridentate Tp$^{i\mathrm{Pr}}$, monodentate thiolate, and terminal oxo and carbonyl ligands. The largest angular deviations from ideal octahedral geometry are observed in the O1−Mo−S1 [103.74(11)°], S1−Mo−N31 [162.44(9)°], and

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(34) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*; Wiley-Interscience: New York, 1986.

O1−Mo−N21 [99.67(14)°] angles and average N−Mo−N (82.2°) angle. The molybdenum atom sits 0.233 Å out of the plane formed by the atoms N21, N31, C1, and S1 (mean planar deviation of 0.0356 Å) toward the terminal oxo ligand. The Mo−O1 distance of 1.683(3) Å is typical of terminal oxomolybdenum(IV) complexes.[30] The Mo−C1 distance of 2.043(5) Å is at the high end of the range typical of carbonyl complexes. The marginal lengthening of Mo−C1 relative to the median value for molybdenum carbonyls (1.978 Å) puts it in the upper quartile for M−CO observations and may reflect the high oxidation state of the metal and reduced back-bonding.[32] Lengthening of the Mo−C bond is in keeping with the high energy of the ν(CO) vibrational mode. The oxo and carbonyl ligands are cis to one another, with an O1−Mo−C1 angle of 90.87(16)°; this arrangement permits optimal orbital overlap between the metal and the π-acid and π-base ligands (vide supra). The carbonyl ligand is essentially linear [Mo−C1−O2 = 175.6(4)°] and projects away from the thiolato ligand. The oxo ligand exerts a strong trans influence on the Mo−N11 bond, lengthening it by more than 0.13 Å relative to the other Mo−N bonds.[30,31,33] When not concealed by disorder, as is the case in Tp*WOI(CO),[20] a strong trans influence can be readily discerned in related carbonyloxotungsten complexes. The crystal structure of $\mathrm{Tp}^{i\mathrm{Pr}}\mathrm{MoO}(\mathrm{S}^i\mathrm{Pr})(\mathrm{CO})$ represents the first reported for any carbonyloxo complex of Mo.

Summary

A series of distorted-octahedral dioxomolybdenum(VI) complexes, $\mathrm{Tp}^{i\mathrm{Pr}}\mathrm{MoO_2(SR)}$ (R = Et, ^{i}Pr, ^{t}Bu, Ph,[22] *p*-tol, Bz), has been synthesized and fully characterized. These complexes (except when R = ^{t}Bu) react with triphenylphosphine to afford oxomolybdenum(IV) acetonitrile complexes, $\mathrm{Tp}^{i\mathrm{Pr}}\mathrm{MoO(SR)(NCMe)}$, which, in turn, react with CO gas to produce new carbonyloxomolybdenum(IV) complexes $\mathrm{Tp}^{i\mathrm{Pr}}\mathrm{MoO(SR)(CO)}$ (R = Et, ^{i}Pr, Ph, *p*-tol, Bz). These carbonyloxo complexes are members of the first extended series of stable, well-characterized, and structurally defined carbonyloxomolybdenum complexes.

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Note Added in Proof: A full paper reporting carbonyloxo- and carbonylsulfidotungsten(IV) Tp* complexes has recently appeared: Thomas, S.; Tiekink, E. R. T.; Young, C. G. *Inorg. Chem.* **2006**, *45*, 352−361. Leading results were communicated in refs 20 and 21.

Supporting Information Available: Full listings of IR and ^{13}C NMR data and crystallographic data in CIF format. This information is available free of charge via the Internet at http://pubs.acs.org.

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