

## Dioxomolybdenum(VI) Complexes of the Hydrotris(3,5-dimethyl-1-pyrazolyl)borate Ligand. Synthesis and Oxygen Atom Transfer Reactions

Sue A. Roberts, Charles G. Young,<sup>1a</sup> Cary A. Kipke, W. E. Cleland, Jr.,<sup>1b</sup> Katsumoto Yamanouchi, Michael D. Carducci, and John H. Enemark\*

Received May 22, 1989

The complexes  $\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{MoO}_2\text{X}$  ( $\text{HB}(\text{Me}_2\text{pz})_3^-$  = hydrotris(3,5-dimethyl-1-pyrazolyl)borate;  $\text{X} = \text{F}^-, \text{Cl}^-, \text{Br}^-, \text{NCS}^-, \text{OPh}^-, \text{OMe}^-, \text{SPh}^-$ ) have been prepared and characterized, and the crystal structure of the  $\text{X} = \text{NCS}^-$  complex has been determined.  $\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{MoO}_2(\text{NCS})$  crystallizes in the space group  $P\bar{1}$ , with  $a = 8.049$  (1) Å,  $b = 8.669$  (1) Å,  $c = 17.397$  (2) Å,  $\alpha = 79.98$  (1)°,  $\beta = 81.30$  (1)°,  $\gamma = 78.39$  (1)°, and  $Z = 2$ ; refinement resulted in  $R_w = 0.056$  (3136 reflections with  $F_o^2 > 3\sigma(F_o^2)$ , 273 variable parameters). Three representative complexes ( $\text{X} = \text{Cl}^-, \text{SPh}^-, \text{OPh}^-$ ) react with  $\text{Ph}_3\text{P}$  at room temperature to yield  $\text{Ph}_3\text{PO}$  and a molybdenum-containing product having a composition dependent upon the solvent used. In DMF, pyridine, or acetonitrile, the Mo(IV) complexes  $\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{MoOX}(\text{solvent})$  are formed as a result of the oxygen atom transfer reaction and subsequent solvent coordination. In dichloromethane, the ultimate products are the Mo(V) complexes  $\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{MoOClX}$ . In toluene, binuclear Mo(V) complexes  $\{\text{HB}(\text{Me}_2\text{pz})_3\}_2\text{Mo}_2\text{O}_3\text{X}_2$  form from reaction of the transient  $\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{MoOX}$  and the starting complex. The identities of two reaction products have been confirmed by crystal structure determinations.  $\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{MoO}(\text{Cl})(\text{NCS})$  crystallizes in space group  $P\bar{1}$ , with  $a = 8.093$  (1) Å,  $b = 8.840$  (1) Å,  $c = 17.432$  (3) Å,  $\alpha = 79.30$  (1)°,  $\beta = 80.66$  (1)°,  $\gamma = 78.40$  (1)°, and  $Z = 2$ ; refinement resulted in  $R_w = 0.053$  (2864 reflections with  $F_o^2 > 3\sigma(F_o^2)$ , 277 variable parameters). The structure is isomorphous with that of  $\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{MoO}_2(\text{NCS})$ .  $\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{MoO}(\text{Cl})(\text{NC}_5\text{H}_9)$  crystallizes in  $P\bar{1}$ , with  $a = 9.636$  (1) Å,  $b = 14.319$  (2) Å,  $c = 20.802$  (3) Å,  $\alpha = 79.90$  (1)°,  $\beta = 84.47$  (1)°,  $\gamma = 77.82$  (1)°, and  $Z = 4$ ; refinement resulted in  $R_w = 0.071$  (6777 reflections with  $F_o^2 > 3\sigma(F_o^2)$ , 589 variable parameters). The oxidation of  $\text{Ph}_3\text{P}$  to  $\text{Ph}_3\text{PO}$  by  $\text{Me}_2\text{SO}$  is catalyzed by  $\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{MoO}_2\text{X}$  complexes with  $\text{X} = \text{Cl}^-, \text{SPh}^-,$  and  $\text{OPh}^-$ .

### Introduction

The ligand hydrotris(3,5-dimethyl-1-pyrazolyl)borate ( $\text{HB}(\text{Me}_2\text{pz})_3^-$ ) has been used to stabilize mononuclear Mo(V) complexes and allow a systematic investigation of their electronic and spectroscopic properties.<sup>2</sup> We now report the synthesis and characterization of related cis dioxo-Mo(VI) complexes,  $\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{MoO}_2\text{X}$ , and describe the oxygen atom transfer reactions of these complexes with  $\text{Ph}_3\text{P}$ .

Oxygen atom transfer reactions of dioxomolybdenum(VI) complexes containing sulfur-donor ligands are well-known,<sup>3</sup> the prototypical reaction being that of  $\text{MoO}_2(\text{S}_2\text{CNEt}_2)_2$  with  $\text{Ph}_3\text{P}$  to yield  $\text{Ph}_3\text{PO}$  and  $\text{MoO}(\text{S}_2\text{CNEt}_2)_2$ .<sup>4</sup> Such reactions are usually accompanied by the formation of oxo-bridged dimers unless ligands of sufficient steric bulk are used to hinder dimer formation. When dimer formation is inhibited, the resulting Mo(IV) complex can react with an oxygen atom donor such as  $\text{Me}_2\text{SO}$  and regenerate the original Mo(VI) complex. The first and most complete description of such a catalytic cycle involved the five-coordinate dioxomolybdenum(VI) complex of 2,6-bis(2,2-diphenyl-2-mercaptoethyl)pyridine.<sup>5</sup>  $\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{MoO}_2(\text{S}_2\text{P}(\text{OEt})_2)$  catalyzes the same reaction cycle.<sup>6</sup>

In contrast, when the ligand set of the starting Mo(VI) complex contains only O and N atoms, oxygen atom transfer reactions are uncommon and usually produce binuclear complexes as products.  $\text{MoO}_2(\text{acac})_2$  and  $\text{MoO}_2(\text{ox})_2$  react with  $\text{Ph}_3\text{P}$  in refluxing dichloroethane to produce the binuclear  $\text{Mo}_2\text{O}_3\text{L}_4$  complexes.<sup>7</sup>

$\text{MoO}_2(\text{sap})$  reacts with  $\text{PPh}_2\text{Et}$  in refluxing DMF.<sup>8</sup> Recently, the products of this reaction have been shown to be  $\text{Mo}_2\text{O}_3\text{L}_2$  complexes.<sup>9</sup> In general, sulfur-donor atoms facilitate oxygen atom transfer reactions, resulting in mononuclear Mo(IV) complexes as products.<sup>10</sup>

In most known oxygen atom transfer reactions, the final molybdenum(IV)-containing product is a five-coordinate square-pyramidal  $[\text{MoO}]^{2+}$  complex having a vacant coordination site trans to the oxo ligand. The sole exception is a six-coordinate Mo(IV) complex,  $\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{MoO}(\text{S}_2\text{P}(\text{OEt})_2)$ , formed by oxygen atom transfer from  $\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{MoO}_2(\text{S}_2\text{P}(\text{OEt})_2)$ , in which the initially monodentate dithiophosphate ligand becomes bidentate after reaction.

When oxygen atom transfer occurs from the  $\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{MoO}_2\text{X}$  complexes described in this paper, the resulting Mo(IV) species is left with the vacant coordination site cis to the remaining Mo=O bond. This geometry leads to some interesting and unusual reactivities, as described herein. A preliminary report of some of these results appeared previously.<sup>11</sup>

### Experimental Section

**Materials and Methods.** Unless specified, all reactions were carried out under a nitrogen atmosphere. The solvents employed were dried and distilled before use. Dimethylformamide (DMF) was distilled from BaO and stored over Linde 4-Å molecular sieves. The compounds  $\text{MoO}_2\text{X}_2$  ( $\text{OPPh}_3$ ),<sup>12</sup>  $\text{MoO}_2\text{Br}_2(\text{Me}_2\text{SO})_2$ ,<sup>13</sup>  $(\text{Et}_4\text{N})_2[\text{MoO}_2(\text{NCS})_4]$ ,<sup>14</sup> and  $\text{K}[\text{HB}(\text{Me}_2\text{pz})_3]$ <sup>15</sup> were prepared by published methods.  $\text{MoO}_2\text{X}_2$  ( $\text{X} =$

- (1) Present address: (a) Department of Chemistry, La Trobe University, Bundoora, Victoria, Australia 3083. (b) Department of Chemistry, University of Mississippi, University, MI 38677.
- (2) Cleland, W. E., Jr.; Barnhart, K. M.; Yamanouchi, K.; Collison, D.; Mabbs, F. E.; Ortega, R. B.; Enemark, J. H. *Inorg. Chem.* **1987**, *26*, 1017-1025.
- (3) Holm, R. H. *Chem. Rev.* **1987**, *87*, 1401-1449.
- (4) (a) Barral, R.; Bocard, C.; Roch, I. S.; Sajus, L. *Tetrahedron Lett.* **1972**, 1693-1696. (b) Mitchell, P. C. H.; Scarle, R. D. *J. Chem. Soc., Dalton Trans.* **1975**, 2552-2555. (c) Durant, R.; Garner, C. D.; Hyde, M. R.; Mabbs, F. E. *J. Chem. Soc., Dalton Trans.* **1977**, 955-956. (d) Reynolds, M. S.; Berg, J. M.; Holm, R. H. *Inorg. Chem.* **1984**, *23*, 3057-3062.
- (5) (a) Berg, J. M.; Holm, R. H. *J. Am. Chem. Soc.* **1985**, *107*, 925-932. (b) Harlan, E. W.; Berg, J. M.; Holm, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 6992-7000. (c) Holm, R. H.; Berg, J. M. *Acc. Chem. Res.* **1986**, *19*, 363-370.
- (6) Roberts, S. A.; Young, C. G.; Cleland, W. E., Jr.; Ortega, R. B.; Enemark, J. H. *Inorg. Chem.* **1988**, *27*, 3044-3051.

- (7) Chen, G. J.-J.; McDonald, J. W.; Newton, W. E. *Inorg. Chem.* **1976**, *15*, 2612-2615.
- (8) Boyd, I. W.; Spence, J. T. *Inorg. Chem.* **1982**, *21*, 1602-1606.
- (9) Craig, J. A.; Harlan, E. W.; Snyder, B. S.; Whitener, M. A.; Holm, R. H. *Inorg. Chem.* **1989**, *28*, 2082-2091.
- (10) (a) Nakamura, A.; Nakayama, M.; Sugihashi, K.; Otsuka, S. *Inorg. Chem.* **1979**, *18*, 394-400. (b) Topich, J.; Lyon, J. T. *Inorg. Chem.* **1984**, *23*, 3202-3206.
- (11) Presented in part at the 197th National Meeting of the American Chemical Society, Dallas, TX, April 1989; Abstract INOR 269.
- (12) Butcher, R. J.; Penfold, B. R.; Sinn, E. *J. Chem. Soc., Dalton Trans.* **1979**, 668-675.
- (13) Butcher, R. J.; Gunz, H. P.; MacLagan, G. A. R.; Powell, H. K. J.; Wilkins, C. J.; Hian, Y. S. *J. Chem. Soc., Dalton Trans.* **1975**, 1223-1227.
- (14) Brisdon, B. J.; Edwards, D. A. *Inorg. Nucl. Chem. Lett.* **1974**, *10*, 301-303.
- (15) Trofimenko, S. *J. Am. Chem. Soc.* **1967**, *89*, 6288-6294.

$\text{Cl}^-$ ,  $\text{Br}^-$ ) were purchased from Morton Thiokol (Alfa Inorganics). Infrared spectra were recorded with either a Perkin-Elmer 983 (KBr) or a Perkin-Elmer 1800 (solution) spectrophotometer. Cyclic voltammetry was performed by using an IBM EC225 potentiostat and a glassy-carbon working electrode; potentials were measured relative to saturated calomel (SCE).  $^{31}\text{P}$  and  $^{95}\text{Mo}$  NMR spectra were recorded on a Bruker AM-500 spectrometer.  $^{95}\text{Mo}$  chemical shifts were referenced to an external standard of 2 M  $\text{Na}_2\text{MoO}_4$  in  $\text{D}_2\text{O}$ , effective pH 11 (positive chemical shifts are deshielded relative to the reference). Microanalyses were performed by Atlantic Microlabs. Electronic spectra were taken on either an IBM 9420 or a modified Cary 14 spectrophotometer equipped with an OLIS interface and software.

**[HB(Me<sub>2</sub>pz)<sub>3</sub>]MoO<sub>2</sub>Cl (1).** Method 1.  $\text{MoO}_2\text{Cl}_2$  (2.00 g, 10 mmol) was dissolved into DMF (30 mL) at room temperature.  $\text{K}[\text{HB}(\text{Me}_2\text{pz})_3]$  (3.30 g, 10.1 mmol) was added to the solution and the mixture stirred for 1.5 h. The yellow precipitate was collected by filtration, washed with acetone, dried, and recrystallized from dichloromethane. Yield: 3.0 g (75%). Anal. Calcd for  $\text{C}_{15}\text{H}_{22}\text{BClMoN}_6\text{O}_2$ : C, 39.12; H, 4.81; N, 18.25; Cl, 7.71. Found: C, 39.10; H, 4.80; N, 18.27; Cl, 7.66. IR (KBr):  $\nu(\text{B}-\text{H})$  2546 w,  $\nu(\text{Mo}=\text{O})$  930 s, 898 s,  $\nu(\text{Mo}-\text{Cl})$  348 s  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) (all resonances singlets unless otherwise specified):  $\delta$  2.36 (3 H), 2.38 (6 H), 2.63 (3 H), 2.68 (6 H), 5.84 (1 H), 5.86 (2 H).  $^{95}\text{Mo}$  NMR (DMF):  $\delta$  85 ( $W_{1/2} = 400$  Hz).

**Method 2.** *cis*- $\text{MoO}_2\text{Cl}_2(\text{OPPh}_3)_2$  (5.8 g, 7.68 mmol) and  $\text{K}[\text{HB}(\text{Me}_2\text{pz})_3]$  (2.58 g, 7.68 mmol) were stirred in  $\text{CH}_2\text{Cl}_2$  (50 mL). After being stirred for 1 day, the solution was filtered, and the resulting yellow precipitate was washed with ethanol and ether and air-dried. The solid was Soxhlet-extracted with  $\text{CH}_2\text{Cl}_2$ . The solution was partially evaporated, and the yellow product was precipitated by addition of ether. Yield: 2.2 g (63%).

**[HB(Me<sub>2</sub>pz)<sub>3</sub>]MoO<sub>2</sub>Br (2).** Method 1 above was followed by using  $\text{MoO}_2\text{Br}_2$  as the starting material. Anal. Calcd for  $\text{C}_{15}\text{H}_{22}\text{BrMoN}_6\text{O}_2$ : C, 35.67; H, 4.39; N, 16.64; Br, 15.84. Found: C, 35.59; H, 4.39; N, 16.61; Br, 15.88. IR (KBr):  $\nu(\text{B}-\text{H})$  2546 w,  $\nu(\text{Mo}=\text{O})$  929 s, 897 s  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  2.35 (3 H), 2.38 (6 H), 2.60 (3 H), 2.72 (6 H), 5.85 (1 H), 5.87 (2 H).  $^{95}\text{Mo}$  NMR ( $\text{CH}_2\text{Cl}_2$ ):  $\delta$  129 ( $W_{1/2} = 270$  Hz).

**Method 2.**  $\text{MoO}_2\text{Br}_2(\text{Me}_2\text{SO})_2$  was used as the starting material. Method 2 above was followed. Yield: 2.0 g (59%).

**[HB(Me<sub>2</sub>pz)<sub>3</sub>]MoO<sub>2</sub>F (3).** A suspension of  $\text{MoO}_2\text{F}_2(\text{OPPh}_3)_2$  (4.0 g, 5.5 mmol) and  $\text{K}[\text{HB}(\text{Me}_2\text{pz})_3]$  (2 g, 6.0 mmol) in dry dichloromethane (70 mL) was stirred for 2 days. A light blue solid was filtered out, washed with methanol until the filtrate was colorless, and dried in vacuo. Soxhlet extraction for 3 days using dry dichloromethane left a pale yellow solid that was filtered out and washed with a small amount of  $\text{CH}_2\text{Cl}_2$ . Yield: 1.46 g (60%). Anal. Calcd for  $\text{C}_{15}\text{H}_{22}\text{BFMoN}_6\text{O}_2$ : C, 40.57; H, 4.99; N, 18.92. Found: C, 40.65; H, 5.02; N, 18.90. IR (KBr):  $\nu(\text{B}-\text{H})$  2540,  $\nu(\text{Mo}=\text{O})$  940, 910,  $\nu(\text{Mo}-\text{F})$  596  $\text{cm}^{-1}$ .

**[HB(Me<sub>2</sub>pz)<sub>3</sub>]MoO<sub>2</sub>(NCS) (4).** A solution of  $(\text{Et}_4\text{N})_2[\text{MoO}_2(\text{NCS})_4]$  (6.2 g, 10 mmol) and  $\text{K}[\text{HB}(\text{Me}_2\text{pz})_3]$  (3.4 g, 10.1 mmol) in dried DMF (20 mL) was stirred for 20 h and filtered, and the yellow solid was washed with acetone until the filtrate was colorless. The vacuum-dried product was recrystallized from dichloromethane/methanol to yield yellow crystals. Crystals suitable for structure determination were grown by slow diffusion of ether into a dichloromethane solution of the complex. Yield: 3.0 g (62%). Anal. Calcd for  $\text{C}_{16}\text{H}_{22}\text{BMoN}_7\text{O}_2\text{S}$ : C, 39.77; H, 4.59; N, 20.29; S, 6.64. Found: C, 39.96; H, 4.64; N, 20.10; S, 6.50. IR (KBr):  $\nu(\text{B}-\text{H})$  2546 w,  $\nu(\text{NCS})$  2025 s,  $\nu(\text{Mo}=\text{O})$  926 s, 895 s  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  2.37 (3 H), 2.39 (6 H), 2.59 (3 H), 2.62 (6 H), 5.87 (2 H), 5.88 (1 H).  $^{95}\text{Mo}$  NMR (DMF):  $\delta$  -5 ( $W_{1/2} = 250$  Hz).

**[HB(Me<sub>2</sub>pz)<sub>3</sub>]MoO<sub>2</sub>(OMe) (5).** **2** (0.4 g, 0.8 mmol) and methanol (1.0 mL) were dissolved in degassed toluene.  $\text{Et}_3\text{N}$  (0.5 mL, excess) was added and the reaction mixture heated to 60 °C for 4 h. The reaction mixture was filtered and the solid washed with toluene and ethanol. Yield: 0.21 g (48%). Anal. Calcd for  $\text{C}_{16}\text{H}_{22}\text{BMoN}_6\text{O}_3$ : C, 42.13; H, 5.52; N, 18.42. Found: C, 41.99; H, 5.54; N, 17.90. IR (KBr):  $\nu(\text{B}-\text{H})$  2548 s,  $\nu(\text{Mo}=\text{O})$  921 s, 897 s,  $\nu(\text{Mo}-\text{O})$  536 m  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  2.34 (3 H), 2.35 (6 H), 2.57 (6 H), 2.76 (3 H), 4.26 (3 H,  $\text{MeO}^-$  ligand), 5.81 (2 H), 5.83 (1 H).  $^{95}\text{Mo}$  NMR ( $\text{CH}_2\text{Cl}_2$ ):  $\delta$  -34 ( $W_{1/2} = 170$  Hz).

**[HB(Me<sub>2</sub>pz)<sub>3</sub>]MoO<sub>2</sub>(Sph) (6).** To an evacuated Schlenk flask containing **1** (1.5 g, 3.2 mmol) and  $\text{NaSC}_6\text{H}_5$  (0.40 g, 3.2 mmol) was added dry, degassed toluene (5 mL), and the reaction mixture was stirred at 70 °C for 2 h. The solution was filtered while hot and allowed to cool. The reaction mixture was chromatographed on silica gel with toluene as the eluant. The product eluted as a brown band. Yield: 0.24 g (14%). Anal. Calcd for  $\text{C}_{21}\text{H}_{27}\text{BMoN}_6\text{O}_2\text{S}$ : C, 47.42; H, 5.12; N, 15.81; S, 6.03. Found: C, 47.17; H, 5.12; N, 15.64; S, 5.92. IR (KBr):  $\nu(\text{B}-\text{H})$  2538 s,  $\nu(\text{Mo}=\text{O})$  921 s, 894 s  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ ):  $\delta$  2.38 (3 H),

Table I. Crystallographic Data

	4	8	9
formula	$\text{C}_{16}\text{H}_{22}\text{MoBN}_7\text{O}_2\text{S} \cdot \frac{1}{2}\text{C}_4\text{H}_{10}\text{O}$	$\text{C}_{16}\text{H}_{22}\text{MoBClN}_7 \cdot \text{OS} \cdot \frac{1}{2}\text{C}_4\text{H}_{10}\text{O}$	$\text{C}_{20}\text{H}_{27}\text{MoBClN}_7\text{O} \cdot \frac{1}{2}\text{CH}_2\text{Cl}_2$
fw	520.3	571.8	566.2
a, Å	8.049 (1)	8.093 (1)	9.636 (1)
b, Å	8.669 (1)	8.840 (1)	14.319 (2)
c, Å	17.397 (2)	17.432 (3)	20.802 (3)
$\alpha$ , deg	79.98 (1)	79.30 (1)	79.90 (1)
$\beta$ , deg	81.30 (1)	80.66 (1)	84.47 (1)
$\gamma$ , deg	78.39 (1)	78.40 (1)	77.82 (1)
V, Å <sup>3</sup>	1162 (1)	1190	2757 (1)
Z	2	2	4
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
$\rho$ , g cm <sup>-3</sup>	1.49	1.40	1.36
$\mu$ , cm <sup>-1</sup>	6.6	7.5	6.8
R	0.045	0.048	0.051
R <sub>w</sub>	0.056	0.053	0.071

2.40 (6 H), 2.53 (3 H), 2.69 (6 H), 5.97 (2 H), 6.00 (1 H), 7.18 (t, 1 H,  $J = 10$  Hz), 7.35 (t, 2 H,  $J = 10$  Hz), 7.63 (d, 2 H,  $J = 10$  Hz).  $^{95}\text{Mo}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  266 ( $W_{1/2} = 275$  Hz).

**[HB(Me<sub>2</sub>pz)<sub>3</sub>]MoO<sub>2</sub>(OPh) (7).** Toluene (20 mL) and triethylamine (0.3 mL) were added to a mixture of **1** (0.25 g, 0.54 mmol) and phenol (0.25 g, excess), and the reaction mixture was stirred at 70 °C overnight. The solution was filtered, evaporated to dryness, and separated by chromatography on a silica gel column using toluene as the eluant. The first orange band was collected and evaporated to dryness. Yield: 0.2 g (71%). Anal. Calcd for  $\text{C}_{21}\text{H}_{27}\text{BMoN}_6\text{O}_3$ : C, 48.67; H, 5.25; N, 16.22. Found: C, 49.08; H, 5.64; N, 15.50. IR (KBr):  $\nu(\text{B}-\text{H})$  2544,  $\nu(\text{Mo}=\text{O})$  922, 896  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  2.32 (6 H), 2.38 (2, 3 H), 2.39 (6 H), 2.81 (3 H), 5.81 (2 H), 5.89 (1 H), 6.94–7.31 (m, 5 H).  $^{95}\text{Mo}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -68 ( $W_{1/2} = 210$  Hz).

**[HB(Me<sub>2</sub>pz)<sub>3</sub>]MoO(Cl)(NCS) (8).** A suspension of **4** (0.17 g, 0.35 mmol) was added to  $\text{Ph}_3\text{P}$  (0.11 g, 0.42 mmol) in 10 mL of  $\text{CH}_2\text{Cl}_2$ . The solution immediately turned red. After being stirred at room temperature for 1.5 h, the reaction mixture was evaporated to a small volume and the product separated by chromatography on silica gel using  $\text{CH}_2\text{Cl}_2$  as the eluant. Large crystals formed after diffusion of ether into a  $\text{CH}_2\text{Cl}_2$  solution. The identity of the product was confirmed by comparison of the IR and EPR spectra with those previously reported.<sup>2</sup>

**[HB(Me<sub>2</sub>pz)<sub>3</sub>]MoO(Cl)(NC<sub>3</sub>H<sub>5</sub>) (9).** **1** (0.25 g, 0.53 mmol) was reacted at room temperature with  $\text{Ph}_3\text{P}$  (0.14 g, 0.53 mmol) in pyridine (10 mL). The reaction mixture turned gold, then orange, and then brown. After the reaction mixture was left standing in a stoppered flask for 2 weeks, green, block-shaped crystals of **9** appeared. The identity of the product was established by X-ray structure determination.

**Crystal Structure Determinations.** Crystals of **4**, **8**, and **9** were grown as described above. Crystallographic data are given in Table I. Intensity data were collected by using a Syntex P2<sub>1</sub> diffractometer; calculations were performed on a Microvax II computer using SDP/VAX.<sup>16</sup> Scattering factors<sup>17</sup> and anomalous dispersion corrections<sup>18</sup> were taken from standard tabulations. Details of the structure determination are given in the supplementary material, as are complete tables of positional and thermal parameters, calculated hydrogen atom positions, bond distances and angles, and calculated and observed structure factors.

## Results and Discussion

**Synthesis.** Several synthetic routes have been employed in the preparation of **1**–**7**. The direct metathesis reaction of  $\text{MoO}_2\text{X}_2$  and  $\text{K}[\text{HB}(\text{Me}_2\text{pz})_3]$  (eq 1) is the best route to the halogen  $\text{MoO}_2\text{X}_2 + \text{K}[\text{HB}(\text{Me}_2\text{pz})_3] \rightarrow [\text{HB}(\text{Me}_2\text{pz})_3]\text{MoO}_2\text{X} + \text{KX}$  ( $\text{X} = \text{Cl}, \text{Br}$ ) (1)

complexes **1** and **2**. If  $\text{MoO}_2\text{X}_2$  is not readily available, the alternative syntheses using  $\text{MoO}_2\text{Cl}_2(\text{OPPh}_3)_2$  and  $\text{MoO}_2\text{Br}_2(\text{Me}_2\text{SO})_2$  provide good yields of **1** and **2**. This alternate route also allows preparation of the fluoride complex.

The reaction of  $(\text{Et}_4\text{N})_2[\text{MoO}_2(\text{NCS})_4]$  and  $\text{K}[\text{HB}(\text{Me}_2\text{pz})_3]$  yields at least three isolable products, depending upon the con-

(16) Frenz, B. A. In *Computing in Crystallography*; Schenk, H., Olthoff-Hazelkamp, R., van Koningsveld, H., Bassi, G. C., Eds.; Delft University Press: Delft, The Netherlands, 1978; pp 64–71.

(17) Cromer, D. T.; Waber, J. T. In *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.2B.

(18) Cromer, D. T. In *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.3.1.

**Table II.** Electrochemistry of  $\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{MoO}_2\text{X}$  Complexes<sup>a</sup>

complex	$E_0$ , V	$I_{pa}/I_{pc}$	$\Delta E_{pp}$ , mV
1, X = Cl <sup>-</sup>	-0.64	0.60	210
2, X = Br <sup>-</sup>	-0.50	<i>b</i>	<i>b</i>
4, X = NCS <sup>-</sup>	-0.32	0.97	140
5, X = OMe <sup>-</sup>	-1.02	0.91	175
6, X = SPh <sup>-</sup>	-0.70	0.97	150
7, X = OPh <sup>-</sup>	-0.82	0.93	160
$\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{MoOCl}_2$	-0.27	0.98	130

<sup>a</sup> Conditions: solvent = dichloromethane; glassy-carbon electrode; scan rate = 100 mV/s; 0.1 M Bu<sub>4</sub>NBF<sub>4</sub>; vs SCE. (Ferrocene = +0.568 V). <sup>b</sup> The observed wave is completely irreversible.

ditions employed. In order to isolate **4**, it is necessary to use carefully dried dimethylformamide, a relatively short reaction time, and a minimum volume of solvent. **4** may be recrystallized from dichloromethane/methanol, but if this procedure is prolonged, decomposition occurs. Prolonged reaction of (Et<sub>4</sub>N)<sub>2</sub>[MoO<sub>2</sub>(NCS)<sub>4</sub>] and K[HB(Me<sub>2</sub>pz)<sub>3</sub>] in dilute solution produces an orange, crystalline, sparingly soluble, polynuclear complex.<sup>19</sup>

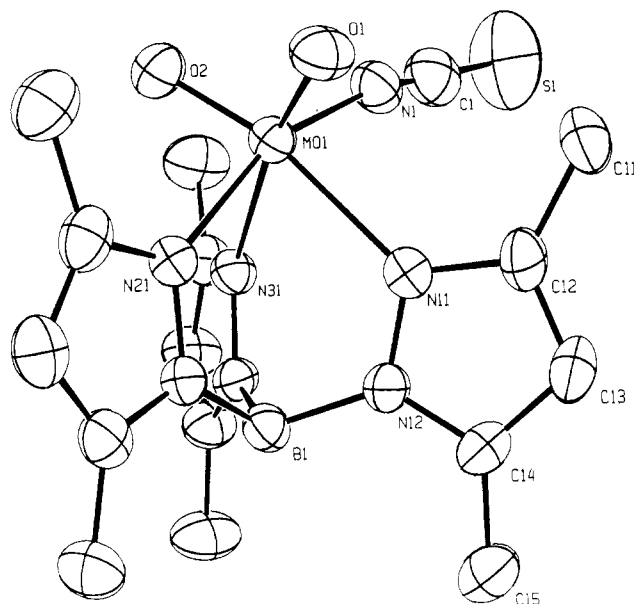
Complexes **5**–**7** may be prepared by a metathesis reaction of **1** with NaX. This method has also been used to prepare catecholate complexes.<sup>20</sup> The reaction is rapid above 60 °C, but no replacement of Cl<sup>-</sup> occurs below this temperature. For **5** and **7**, the desired complex is the major product of the reaction, but when thiophenol reacts with **1**, reduction occurs and the major product is  $\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{MoO}(\text{Cl})\text{SPh}$  rather than **6**. Reasonable yields occur only when minimal solvent is used and the starting molybdenum complex is in a slight excess.

**Spectroscopy.** The infrared spectra of the compounds exhibit two strong  $\nu(\text{Mo}=\text{O})$  bands at 920–940 and 890–900 cm<sup>-1</sup> characteristic of the *cis*-[MoO<sub>2</sub>]<sup>2+</sup> fragment.<sup>6</sup> Infrared bands characteristic of the HB(Me<sub>2</sub>pz)<sub>3</sub><sup>-</sup> ligand (e.g.  $\nu(\text{B}-\text{H})$  at ca. 2550 cm<sup>-1</sup>) are also present along with bands due to Mo—X.

The <sup>1</sup>H NMR spectra of the compounds are consistent with the formulations and the presence of molecular C<sub>s</sub> symmetry in solution. The mirror plane dictates the presence of six sets of inequivalent protons in the HB(Me<sub>2</sub>pz)<sub>3</sub><sup>-</sup> ligand. Singlet resonances having the intensity ratio 1:2:3:3:6:6 may be readily assigned to these proton sets. Resonances due to other protic ligands are also observed (see Experimental Section for assignments).

The compounds exhibit <sup>95</sup>Mo NMR resonances with chemical shifts close to the center of the chemical shift range of this nucleus. The observed chemical shifts exhibit an *inverse halogen dependence*,  $\delta(^{95}\text{Mo})$  increasing in the order Cl<sup>-</sup> < Br<sup>-</sup>. Inverse halogen dependences of the chemical shift have also been observed in other oxohalo-Mo(VI)<sup>21</sup> and -Mo(IV)<sup>22</sup> complexes. Some of the <sup>95</sup>Mo NMR results have been previously reported.<sup>23</sup>

**Electrochemistry.** Reversible one-electron reduction of [MoO<sub>2</sub>]<sup>2+</sup> complexes to analogous [MoO<sub>2</sub>]<sup>+</sup> complexes is rare and occurs only when aprotic ligands and solvents are used and when the ligand has sufficient steric bulk to prevent dimerization. Few such complexes capable of this reaction have been reported.<sup>24</sup> Usually electrochemical reduction of [MoO<sub>2</sub>]<sup>2+</sup> complexes results in formation of [MoO]<sup>2+</sup> species and, often, dimer formation.<sup>24</sup> When this occurs, several largely irreversible waves are observed in cyclic voltammetry. This type of behavior is seen for complexes **1** and **2**, with the reduction of **2** being irreversible. Complexes **4**–**7** all exhibit apparently reversible waves in their cyclic voltammograms at the potentials listed in Table II. No other waves



**Figure 1.** Molecular structure of  $\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{MoO}_2(\text{NCS})$ . Atoms are represented as 50% probability ellipsoids. Hydrogen atoms have been omitted for clarity. Pyrazole rings are labeled such that the first digit refers to the ring and the second digit is a sequence number assigned in the same manner for all rings.

**Table III.** Positional Parameters for  $\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{MoO}_2(\text{NCS})$  (**4**)

atom	x	y	z
Mo1	0.49848 (6)	0.38489 (5)	0.31188 (3)
S1	0.8328 (3)	0.5823 (4)	0.0808 (1)
O1	0.5834 (5)	0.4387 (4)	0.3844 (2)
O2	0.3090 (5)	0.5139 (4)	0.3074 (2)
N1	0.6366 (6)	0.4885 (5)	0.2192 (3)
N11	0.7192 (5)	0.1723 (5)	0.3079 (3)
N12	0.6982 (5)	0.0236 (5)	0.3010 (2)
N21	0.3840 (5)	0.2020 (5)	0.3902 (2)
N22	0.4058 (5)	0.0470 (5)	0.3770 (2)
N31	0.4210 (5)	0.2568 (5)	0.2218 (2)
N32	0.4387 (5)	0.0936 (5)	0.2304 (2)
C1	0.7190 (8)	0.5255 (7)	0.1600 (4)
C11	0.9643 (7)	0.3046 (7)	0.3139 (4)
C12	0.8891 (6)	0.1650 (7)	0.3071 (3)
C13	0.9731 (7)	0.0117 (7)	0.2994 (3)
C14	0.8512 (7)	-0.0754 (6)	0.2958 (3)
C15	0.8731 (8)	-0.2449 (7)	0.2843 (4)
C21	0.2277 (9)	0.3703 (7)	0.4898 (4)
C22	0.2818 (7)	0.2148 (7)	0.4583 (3)
C23	0.2386 (7)	0.0679 (7)	0.4893 (3)
C24	0.3170 (6)	-0.0354 (6)	0.4368 (3)
C25	0.3091 (8)	-0.2061 (7)	0.4422 (4)
C31	0.3103 (9)	0.4879 (7)	0.1256 (4)
C32	0.3491 (7)	0.3150 (7)	0.1556 (3)
C33	0.3206 (8)	0.1904 (7)	0.1220 (4)
C34	0.3777 (7)	0.0527 (6)	0.1703 (3)
C35	0.3801 (9)	-0.1171 (7)	0.1622 (4)
B1	0.5153 (7)	-0.0073 (7)	0.3020 (3)
O3	0.054 (2)	0.007 (2)	0.0183 (9)
C2	0.168 (3)	0.853 (2)	0.905 (1)
C3	0.095 (3)	0.892 (3)	0.979 (2)
C4	0.106 (4)	-0.034 (4)	0.927 (2)
C5	0.237 (4)	0.885 (3)	0.934 (2)

occur at potentials between +1.0 and -1.5 V (vs SCE). Values of  $I_{pa}/I_{pc}$  range from 0.91 to 0.97, indicating that significant decomposition does not occur on the CV time scale.

The reduction waves of **4**–**7** have been compared with that of  $\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{MoOCl}_2$ . Separate coulometric experiments have shown that the reduction wave exhibited by  $\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{MoOCl}_2$  at -0.251 V is due to a one-electron reduction.<sup>2</sup> Comparison of the peak currents of equimolar solutions of **4**–**7** and  $\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{MoOCl}_2$  shows that the reductions observed for **4**–**7** are also one-electron processes. Plots of  $I_{pc}$  vs (scan rate)<sup>1/2</sup> are linear

(19) Young, C. G. Unpublished results.

(20) Küsthardt, U.; LaBarre, M.; Enemark, J. H. *Inorg. Chem.*, in press.

(21) Minelli, M.; Young, C. G.; Enemark, J. H. *Inorg. Chem.* **1985**, *24*, 1111–1113.

(22) Young, C. G.; Enemark, J. H. *Inorg. Chem.* **1985**, *24*, 4416–4419.

(23) Minelli, M.; Yamanouchi, K.; Enemark, J. H.; Subramanian, P.; Kaul, B. B.; Spence, J. T. *Inorg. Chem.* **1984**, *23*, 2554–2556.

(24) (a) Dowerah, D.; Spence, J. T.; Singh, R.; Wedd, A. G.; Wilson, G. L.; Farchione, F.; Enemark, J. H.; Kristofzski, J.; Bruck, M. *J. Am. Chem. Soc.* **1987**, *109*, 5655–5665. (b) Farchione, F.; Hanson, G. R.; Rodrigues, C. G.; Bailey, T. D.; Bagchi, R. N.; Bond, A. M.; Pilbrow, J. R.; Wedd, A. G. *J. Am. Chem. Soc.* **1986**, *108*, 831–832. (c) Hinshaw, C. J.; Spence, J. T. *Inorg. Chim. Acta* **1986**, *125*, L17–L21.

**Table IV.** Selected Bond Distances (Å) and Angles (deg) in **4**, **8**, and **9**

$\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{MoO}_2(\text{NCS})$ ( <b>4</b> )			
Mo-O1	1.695 (3)	Mo-N11	2.291 (4)
Mo-O2	1.704 (4)	Mo-N21	2.162 (4)
Mo-N1	1.999 (5)	Mo-N31	2.293 (4)
O1-Mo-O2	103.4 (2)	Mo-N1-Cl	168.5 (5)
S1-Cl-N1	177.5 (6)		
$\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{MoO}(\text{Cl})(\text{NCS})$ ( <b>8</b> )			
Mo-OC11	2.012 (3)	Mo-N11	2.250 (4)
Mo-OC12	1.940 (3)	Mo-N21	2.239 (4)
Mo-N	2.014 (5)	Mo-N31	2.149 (4)
OC11-Mo-OC12	99.2 (1)	Mo-N-C	169.5 (5)
S-C-N	177.6 (6)		
$\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{MoO}(\text{Cl})(\text{NC}_5\text{H}_5)$ ( <b>9</b> ) <sup>a</sup>			
Mo-O	1.720 (4)	Mo-N11	2.163 (4)
Mo-Cl	2.428 (2)	Mo-N21	2.385 (4)
Mo-N	2.196 (5)	Mo-N31	2.156 (4)
O-Mo-Cl	100.6 (3)		

<sup>a</sup>Two molecules per asymmetric unit. The average values are tabulated.

**Table V.** Stoichiometry of  $\text{Ph}_3\text{P}$  and  $\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{MoOX}$  Reactions

complex	mol of $\text{Ph}_3\text{PO}$ produced/mol of Mo complex <sup>a</sup>		
	DMF solvent	$\text{C}_6\text{D}_6$ solvent	$\text{CDCl}_3$ solvent <sup>b</sup>
<b>1</b> , X = $\text{Cl}^-$	0.9	0.46	1.0
<b>6</b> , X = $\text{OPh}^-$	1.04	0.58	1.1
<b>7</b> , X = $\text{SPh}^-$	1.02		

<sup>a</sup>Measured by  $^{31}\text{P}$  NMR spectroscopy and integration of  $\text{Ph}_3\text{P}$  ( $\delta$  -4.6 ppm) and  $\text{Ph}_3\text{PO}$  ( $\delta$  26 ppm) signals. <sup>b</sup>Signals broadened due to presence of paramagnetic Mo(V) complex (see text).

for **6** and **7**. While the reaction appears to be largely reversible, a small amount of product decomposition may be occurring. Further work to characterize the electron transfer and reaction products is in progress in collaboration with Drs. A. G. Wedd and C. G. Young at La Trobe University. Results of these studies will be published later.

In general, substitution of sulfur-donor for oxygen-donor ligands leads to a decrease in the potential for reduction of the complexes. As Table II shows, **6** is 0.12 V easier to reduce than **7**. This is of the magnitude normally seen for substitution of one singly bonded sulfur-donor ligand for an oxygen-donor ligand.<sup>5b</sup>

**Crystal Structure of 4.** A view of the molecular structure of  $\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{MoO}_2(\text{NCS})$  along with the atomic labeling scheme is shown in Figure 1. Positional parameters are given in Table III. Selected bond distances and angles are listed in Table IV. The structure shows no unusual features. The ligands are arranged in a distorted-octahedral geometry, with three nitrogen atoms of the  $\text{HB}(\text{Me}_2\text{pz})_3^-$  ligand occupying one face of the octahedron and the two oxo and one thiocyanate ligands occupying the opposite face. The Mo=O bond distances are normal, 1.695 (3) and 1.704 (4) Å. The lengthening of the Mo-N bonds trans to the Mo=O bonds to 2.293 (4) and 2.291 (4) Å relative to the Mo-N bond trans to the NCS ligand (2.162 (4) Å) is the same as that observed in other  $\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{MoO}_2\text{X}$  structures.<sup>6,25</sup>

**Reactions of  $\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{MoO}_2\text{X}$  Complexes with  $\text{R}_3\text{P}$ : Solvent Effects.**  $\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{MoO}_2\text{X}$  (X =  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{NCS}^-$ ,  $\text{OPh}^-$ ,  $\text{SPh}^-$ ) react with  $\text{Ph}_3\text{P}$  to product  $\text{Ph}_3\text{PO}$ . The identity of the molybdenum-containing product and the reaction stoichiometry vary with solvent composition. The  $\text{OMe}^-$  complex does not undergo this reaction, and the  $\text{F}^-$  complex is insoluble in all solvents examined. All experiments were carried out at room temperature.  $^{31}\text{P}$  NMR spectroscopy was used to determine reaction stoichiometry by monitoring  $\text{Ph}_3\text{PO}$  formation during the reaction. Results of the NMR experiments are given in Table V, and visible

**Table VI.** Electronic Spectra after Oxygen Transfer to  $\text{Ph}_3\text{P}$ 

solvent	X	$\lambda$ , nm		solvent	X	$\lambda$ , nm	
		( $\epsilon$ , $\text{M}^{-1}\text{cm}^{-1}$ )				( $\epsilon$ , $\text{M}^{-1}\text{cm}^{-1}$ )	
toluene	Cl	484 (6000)		DMF	Cl	448 (3600), 800 (70)	
	OPh	480 (8000)			OPh	466 (1400), 750 (20)	
	SPh	480 (10000)			SPh	400 (sh), 720 (100)	

spectral parameters of some reaction products are given in Table VI.

**Reactions in Toluene.**  $^{31}\text{P}$  NMR spectroscopy demonstrates that only 0.5 mol of  $\text{Ph}_3\text{PO}$  is produced/mol of **1**, **6**, or **7** reacted. The molybdenum-containing product is dark purplish brown and diamagnetic with a strong visible absorption at 480–500 nm ( $\epsilon = 6000\text{--}10000$  ( $\text{M cm}^{-1}$ )), characteristic of the binuclear Mo(V) complexes  $\{\text{HB}(\text{Me}_2\text{pz})_3\}_2\text{Mo}_2\text{O}_3\text{X}_2$ . The extinction coefficients are similar to those reported for  $\{\text{HB}(\text{pz})_3\}_2\text{Mo}_2\text{O}_3\text{Cl}_2$ ,<sup>26</sup> but the peak positions are shifted to longer wavelength. For  $\{\text{HB}(\text{pz})_3\}_2\text{Mo}_2\text{O}_3\text{Cl}_2$ , the absorption maximum occurs at 460 nm; in the methylated complexes this maximum occurs near 485 nm. As in the unmethylated complex, extinction coefficients are unusually low for oxo-bridged dimers,  $6000\text{--}10000$  ( $\text{M cm}^{-1}$ ). Most known  $\text{Mo}_2\text{O}_3$  complexes have extinction coefficients of  $20000\text{--}30000$  ( $\text{M cm}^{-1}$ ) for this band.<sup>9,27</sup> The absorbance is proportional to concentration in the range  $0.1 < A_{480} < 2.0$ ; there is no evidence that the dimer disproportionates in solution.

Since Mo(IV) complexes can have absorption bands in the 400–500-nm region with extinction coefficients in the range  $2000\text{--}10000$  ( $\text{M cm}^{-1}$ ), unequivocal identification of the products of the oxygen atom transfer reaction as dimers or mononuclear Mo(IV) complexes is more difficult than in systems where the dimers have larger extinction coefficients. The reaction products have been identified as  $\{\text{HB}(\text{Me}_2\text{pz})_3\}_2\text{Mo}_2\text{O}_3\text{X}_2$  complexes when the spectrum of the reaction mixture agrees with those described in Table VI and when  $^{31}\text{P}$  NMR spectroscopy shows the stoichiometry of the reaction to be 1 mol of  $\text{Ph}_3\text{PO}$  produced/2 mol of Mo(VI) complex available for reaction.

**Reactions in Dichloromethane.** One mole of  $\text{Ph}_3\text{PO}$  is produced/mol of  $\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{MoO}_2\text{X}$  reacted, but the final products are not Mo(IV) complexes. Rather, the major products of the reactions are the known Mo(V) complexes  $\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{MoOClX}$ .<sup>2</sup> After the reaction of **1** with  $\text{Ph}_3\text{P}$ , the green oxo-Mo(V) complex  $\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{MoOCl}_2$  can be isolated in 90+% yield. Similar results are obtained beginning with **4** or **6**. The reaction with **7** is not as clean. While the major product is  $\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{MoOCl}(\text{OPh})$ , the Mo(V) complexes  $\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{MoO}(\text{OPh})_2$  and  $\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{MoOCl}_2$  can be identified in the EPR spectrum of the reaction mixture.

$\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{MoO}(\text{Cl})(\text{NCS})$  has been crystallized from the reaction of **4** with  $\text{Ph}_3\text{P}$  in  $\text{CH}_2\text{Cl}_2$ . The complex is isomorphous with **4**. Some bond distances and angles are included in Table IV. The oxo and chloro ligands are disordered; the best fit to the structural data is obtained by modeling the O and Cl atoms by an atom of intermediate scattering located at ca. 2.0 Å from the Mo. Refinements placing individual oxygen and chlorine atoms at chemically reasonable positions resulted in a significantly worse fit to the data (final  $R_w = 0.072$  for 286 variable parameters). No evidence of disorder was seen in any of the electron density maps during structure solution. The thermal parameters for the O and Cl atoms are not markedly anisotropic, although they are considerably larger than expected ( $7.5 \text{ \AA}^2$ ). Similar O and Cl disorder has been observed in other  $\text{HB}(\text{Me}_2\text{pz})_3^-$  and  $\text{HB}(\text{pz})_3^-$  complexes.<sup>26,28</sup>

**Reactions in Coordinating Solvents.** In DMF,  $^{31}\text{P}$  NMR spectroscopy confirms that 1 mol of  $\text{Ph}_3\text{PO}$  is produced/mol of Mo(VI) complex reacted with  $\text{Ph}_3\text{P}$ . A brown (**1**, **7**) or green (**6**) species is obtained. The reaction of **6** with  $\text{Ph}_3\text{P}$  has well-defined

(25) Roberts, S. A.; Darsey, G. P.; Cleland, W. E.; Enemark, J. H. *Inorg. Chim. Acta* **1988**, *154*, 95–97.

(26) Lincoln, S.; Koch, S. A. *Inorg. Chem.* **1986**, *25*, 1594–1602.  $\text{HB}(\text{pz})_3^-$  = hydrotris(pyrazolyl)borate anion.

(27) Stiefel, E. I. *Prog. Inorg. Chem.* **1977**, *22*, 1–223.

(28) Ferguson, G. A.; Kaitner, B.; Lalor, F.; Roberts, G. J. *Chem. Res.* **1982**, *1*, S6–7.

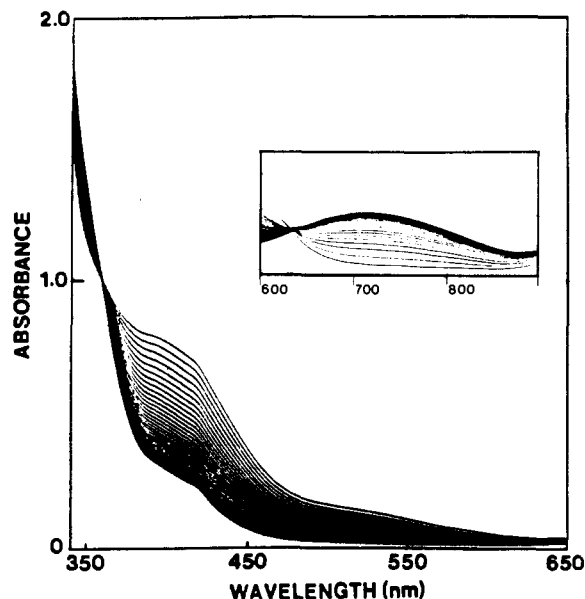


Figure 2. Spectra taken at 20-min intervals during the reaction of 6 with  $\text{Ph}_3\text{P}$ . Isosbestic points exist at 375 and 630 nm.

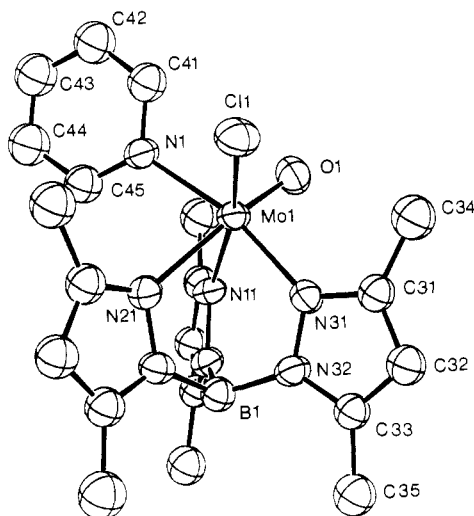


Figure 3. Molecular structure of  $[\text{HB}(\text{Me}_2\text{pz})_3]\text{MoO}(\text{Cl})(\text{NC}_5\text{H}_5)$ . Atoms are represented as 50% probability ellipsoids. Pyrazole rings are labeled as in Figure 1.

isosbestic points, indicating formation of only one product (Figure 2). The products have no EPR spectrum, and the visible spectrum is distinctly different from that obtained in toluene and ascribed to the  $\text{Mo}_2\text{O}_3$  complexes.  $^{31}\text{P}$  NMR spectroscopy detects only  $\text{Ph}_3\text{P}$  and  $\text{Ph}_3\text{PO}$  in solution; no evidence for  $\text{Ph}_3\text{P}$  or  $\text{Ph}_3\text{PO}$  coordination to the Mo(IV) product is seen. These results lead to the conclusion that the products of the reaction are Mo(IV) mononuclear complexes, most likely  $[\text{HB}(\text{Me}_2\text{pz})_3]\text{MoOX}(\text{DMF})$ .

The only ambiguity is in the reaction of 7, since the spectrum obtained could be due to partial formation of the  $[\text{HB}(\text{Me}_2\text{pz})_3]_2\text{Mo}_2\text{O}_3(\text{OPh})_2$  complex. In order to resolve this, the dinuclear complex was isolated from the reaction mixture in toluene and redissolved in DMF. In this solvent, the absorption band attributable to  $[\text{HB}(\text{Me}_2\text{pz})_3]_2\text{Mo}_2\text{O}_3(\text{OPh})_2$  shifts to longer wavelengths,  $\lambda_{\text{max}}$  is 498 nm with  $\epsilon = 5000 (\text{M cm}^{-1})$ , substantially different from the spectrum observed from the reaction mixture, reinforcing the conclusion that the major product of the reaction is the Mo(IV) complex, even for 7.

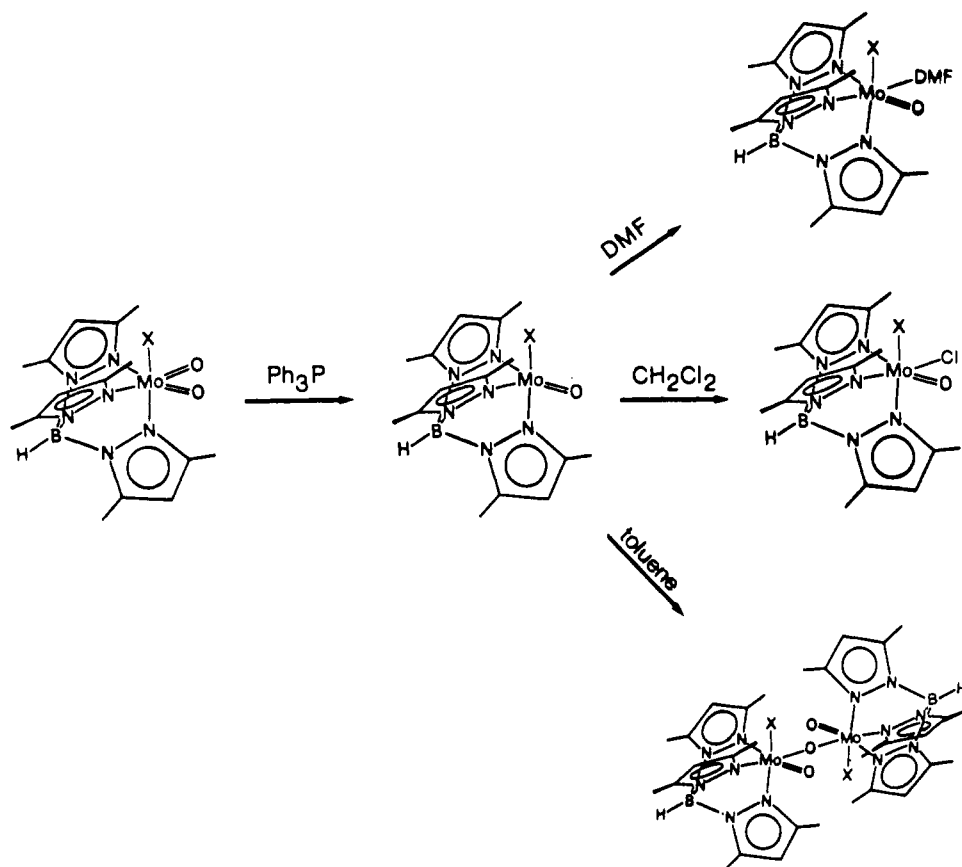
To further confirm that 7 reacts to form Mo(IV)-containing products and not the dinuclear  $[\text{HB}(\text{Me}_2\text{pz})_3]_2\text{Mo}_2\text{O}_3\text{X}_2$  complexes, FTIR spectra were taken of reactions of  $[\text{HB}(\text{Me}_2\text{pz})_3]\text{MoO}_2(\text{OPh})$  with  $\text{Ph}_3\text{P}$  in benzene and DMF. The Mo–O–Mo stretch is known to occur at  $784 \text{ cm}^{-1}$  in the corresponding  $[\text{HB}(\text{pz})_3]\text{Mo}_2\text{O}_3\text{Cl}_2$  complex.<sup>29</sup> After reaction in benzene, a strong band at  $785 \text{ cm}^{-1}$

Table VII. Positional Parameters for  $[\text{HB}(\text{Me}_2\text{pz})_3]\text{MoO}(\text{Cl})(\text{NC}_5\text{H}_5)$  (9)

atom	x	y	z
Mo1	0.26274 (5)	0.31484 (3)	0.36265 (3)
Mo2	0.12486 (5)	0.12974 (4)	0.83175 (3)
Cl1	0.4424 (2)	0.3796 (1)	0.28765 (9)
Cl2	0.2787 (2)	0.2035 (1)	0.7482 (1)
O1	0.3549 (5)	0.2713 (3)	0.4316 (2)
O2	0.1300 (5)	0.1959 (4)	0.8930 (2)
N1	0.3260 (5)	0.1837 (3)	0.3161 (3)
N2	-0.0613 (5)	0.2268 (3)	0.7886 (2)
N11	0.0723 (5)	0.2661 (3)	0.4076 (2)
N12	-0.0599 (5)	0.3270 (3)	0.4038 (2)
N21	0.1040 (5)	0.3728 (3)	0.2759 (2)
N22	-0.0299 (5)	0.4228 (3)	0.2932 (2)
N31	0.1670 (5)	0.4545 (3)	0.3880 (3)
N32	0.0213 (5)	0.4856 (3)	0.3914 (3)
N211	0.2980 (5)	0.0122 (4)	0.8618 (2)
N212	0.2827 (5)	-0.0830 (4)	0.8687 (3)
N221	-0.0119 (5)	0.0393 (3)	0.8878 (2)
N222	0.0185 (5)	-0.0594 (3)	0.8892 (2)
N231	0.1000 (5)	0.0319 (3)	0.7543 (2)
N232	0.1283 (5)	-0.0673 (3)	0.7757 (2)
C11	0.0529 (7)	0.1815 (4)	0.4459 (3)
C12	-0.0903 (7)	0.1890 (4)	0.4646 (3)
C13	-0.1583 (6)	0.2800 (4)	0.4378 (3)
C14	0.1717 (8)	0.0977 (5)	0.4615 (4)
C15	-0.3131 (7)	0.3255 (5)	0.4389 (4)
C21	0.1129 (7)	0.3806 (4)	0.2110 (3)
C22	-0.0129 (7)	0.4343 (5)	0.1865 (3)
C23	-0.1011 (6)	0.4595 (4)	0.2394 (3)
C24	0.2436 (8)	0.3363 (6)	0.1736 (3)
C25	-0.2506 (8)	0.5167 (6)	0.2414 (4)
C31	0.2197 (7)	0.5214 (4)	0.4112 (3)
C32	0.1109 (7)	0.5929 (4)	0.4283 (3)
C33	-0.0132 (7)	0.5693 (4)	0.4159 (3)
C34	0.3764 (7)	0.5094 (5)	0.4183 (4)
C35	-0.1634 (8)	0.6222 (5)	0.4254 (4)
C41	0.4627 (7)	0.1392 (5)	0.3125 (4)
C42	0.5061 (8)	0.0545 (5)	0.2876 (4)
C43	0.4082 (8)	0.0137 (5)	0.2648 (4)
C44	0.2700 (8)	0.0571 (5)	0.2680 (4)
C45	0.2306 (7)	0.1430 (5)	0.2941 (3)
C51	-0.0670 (7)	0.3228 (4)	0.7780 (4)
C52	-0.1880 (9)	0.3884 (5)	0.7602 (4)
C53	-0.3078 (8)	0.3560 (6)	0.7506 (4)
C54	-0.3040 (8)	0.2588 (5)	0.7596 (4)
C55	-0.1792 (7)	0.1969 (4)	0.7785 (3)
C211	0.4237 (6)	0.0100 (5)	0.8849 (3)
C212	0.4893 (7)	-0.0848 (6)	0.9057 (4)
C213	0.4000 (7)	-0.1405 (5)	0.8941 (3)
C214	0.4739 (8)	0.1002 (6)	0.8886 (4)
C215	0.4182 (8)	-0.2475 (6)	0.9054 (4)
C221	-0.1234 (6)	0.0581 (5)	0.9306 (3)
C222	-0.1646 (6)	-0.0289 (5)	0.9592 (3)
C223	-0.0758 (6)	-0.0991 (5)	0.9317 (3)
C224	-0.1858 (7)	0.1580 (5)	0.9444 (3)
C225	-0.0737 (8)	-0.2055 (5)	0.9424 (4)
C231	0.0881 (7)	0.0439 (5)	0.6894 (3)
C232	0.1114 (7)	-0.0459 (5)	0.6695 (3)
C233	0.1362 (6)	-0.1139 (4)	0.7243 (3)
C234	0.0544 (9)	0.1413 (5)	0.6486 (4)
C235	0.1696 (8)	-0.2228 (5)	0.7313 (4)
B1	-0.0744 (7)	0.4290 (5)	0.3645 (4)
B2	0.1460 (8)	-0.1064 (5)	0.8483 (4)
Cl3	0.5172 (6)	0.0781 (3)	0.5475 (2)
Cl4	0.6204 (6)	0.2047 (4)	0.6106 (2)
C(s)	0.470 (1)	0.178 (1)	0.5841 (7)

exists in the spectrum of the reaction mixture. This band is almost completely missing when the reaction occurs in DMF. No other bands occur in the region that could be ascribed to this vibration. Both this experiment and the electronic spectra are consistent with the major product of the reaction being the Mo(IV) complex  $[\text{HB}(\text{Me}_2\text{pz})_3]\text{MoO}(\text{OPh})(\text{DMF})$ . There is, however, a possibility that about 10% of the product is the dinuclear complex.

(29) Lincoln, S. E.; Loehr, T. M. *Inorg. Chem.* **1990**, *29*, 1907–1915.



**Figure 4.** Solvent dependence of the reactions of  $\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{MoO}_2\text{X}$  complexes with  $\text{Ph}_3\text{P}$ .

The reaction products are not stable in DMF solution; however in pyridine the complex  $\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{MoO}(\text{Cl})(\text{NC}_5\text{H}_5)$  (**9**) can be crystallized from the reaction of  $\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{MoO}_2\text{Cl}$  and  $\text{Ph}_3\text{P}$ . The molecular structure is shown in Figure 3. Positional parameters are given in Table VII; selected bond distances and angles, in Table IV. The oxo, chloro, and pyridine ligands occupy one face of the distorted octahedron, with the other occupied by the  $\text{HB}(\text{Me}_2\text{pz})_3^-$  ligand. The  $\text{Mo}=\text{O}$  distance of 1.72 Å is 0.05 Å longer than the expected 1.67 Å, but still within the normal range for  $\text{Mo}(\text{IV})=\text{O}$  bonds. (All cited distances and angles are the average for the two independent molecules in the asymmetric unit.) The trans influence, as identified by the  $\text{Mo}-\text{N}$  bond lengths, is of the expected magnitude for  $[\text{HB}(\text{Me}_2\text{pz})_3\text{MoO}]^+$  complexes, with  $\text{Mo}-\text{N}$  trans to  $\text{Mo}=\text{O}$  equal to 2.39 Å, and the other  $\text{Mo}-\text{N}$  distances 2.19 and 2.18 Å.

**Kinetics.** Compounds **1**, **6**, and **7** undergo the same oxygen atom transfer reactions, but the rates of these reactions vary markedly. In all solvents, the reaction of  $\text{Ph}_3\text{P}$  with **1** is complete within minutes, reaction with **6** is complete within a few hours, and reaction with **7** becomes complete only after 36 h.

The reaction of **6** with  $\text{Ph}_3\text{P}$  in DMF was investigated under pseudo-first-order conditions ( $\text{Ph}_3\text{P}$  in excess) at 24 °C by following the loss in intensity at 430 nm. The reaction is first-order in molybdenum complex; plots of  $\ln [(A - A_\infty)/(A_0 - A_\infty)]$  are linear nearly to completion of the reaction. Plots of  $k_{\text{obs}}$  vs  $[\text{Ph}_3\text{P}]_0$  are straight lines and give a second-order rate constant  $k = 5.9 (2) \times 10^{-4} (\text{M s})^{-1}$ . This is 1 order of magnitude less than rate constants observed for the reaction of  $\text{Ph}_3\text{P}$  with other  $\text{Mo}(\text{VI})$  complexes.<sup>5,6</sup> As for other oxygen atom transfer reactions from  $\text{Mo}(\text{VI})$  complexes to  $\text{Ph}_3\text{P}$ , the reaction follows a simple second-order rate law,  $-\text{d}[\mathbf{6}]/\text{d}t = k[\mathbf{6}][\text{Ph}_3\text{P}]$ .

The reaction of **7** with  $\text{Ph}_3\text{P}$  was too slow to be studied at the reagent concentrations needed to keep the absorbance in the region  $0 < A < 2.0$ . Instead, the formation of  $\text{Ph}_3\text{PO}$  was monitored by  $^{31}\text{P}$  NMR spectroscopy at 25 °C. The reaction could not be run under pseudo-first-order conditions and was analyzed as a second-order reaction, first-order in each reactant. As expected, the plot of  $\ln \{([\mathbf{7}]_0([\text{Ph}_3\text{P}]_0 - [\text{Ph}_3\text{PO}])/([\text{Ph}_3\text{P}]_0([\mathbf{7}]_0 - [\text{Ph}_3\text{PO}]))\}$

is linear,<sup>30</sup> giving  $k = 2 (1) \times 10^{-6} (\text{M s})^{-1}$  for this reaction.

Unfortunately, **1** is soluble only in  $\text{CH}_2\text{Cl}_2$ , a solvent in which the final product of the electron transfer is not the  $\text{Mo}(\text{IV})$  complex  $\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{MoOX}$  but the green  $\text{Mo}(\text{V})$  complex  $\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{MoOCl}_2$ . In this solvent, the initially yellow solution turns gold immediately upon addition of  $\text{Ph}_3\text{P}$ , and within 30 s formation of the ultimate product is complete. This probably indicates that oxygen transfer to **1** is complete upon mixing and further absorbance changes are due to chlorine abstraction from the solvent to form the final product. The reaction is too fast to be followed by conventional spectroscopic methods.

**Catalysis of the Oxidation of  $\text{Ph}_3\text{P}$  by  $\text{Me}_2\text{SO}$ .** Complexes **1**, **6** and **7** were allowed to react overnight at 40 °C with a 20-fold excess of  $\text{Ph}_3\text{P}$  in a solvent mixture of 50%  $\text{Me}_2\text{SO}/50\%$  DMF. Solutions were analyzed for  $\text{Ph}_3\text{PO}$  via  $^{31}\text{P}$  NMR spectroscopy and for  $\text{Me}_2\text{S}$  by GC/MS of the headspace gas. During the reaction time allowed, **1** and **6** effected complete conversion of  $\text{Ph}_3\text{P}$  to  $\text{Ph}_3\text{PO}$ . (An identical sample without added molybdenum complex produced no  $\text{Ph}_3\text{PO}$ .) Complex **7**, however, converted only 35% of the  $\text{Ph}_3\text{P}$  to  $\text{Ph}_3\text{PO}$ . Even so, this is 7 mol of  $\text{Ph}_3\text{PO}$  produced/mol of complex present. Analysis for  $\text{Me}_2\text{S}$  was positive when any of the three complexes were present, and no  $\text{Me}_2\text{S}$  was produced in their absence. The relative amount of  $\text{Me}_2\text{S}$  formed by reaction with **7** is 30–40% of that formed by reaction with **1** or **6**. Thus, **7** undergoes the same reaction cycle as the other complexes, albeit more slowly. This is the first example of oxygen atom transfer catalysis by a complex containing only oxygen- and nitrogen-donor ligands.

#### Discussion

The reactivity of  $\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{MoO}_2\text{X}$  complexes with  $\text{Ph}_3\text{P}$  is summarized in Figure 4. In all reactions, regardless of solvent, the first step appears to be oxygen atom transfer from the  $[\text{MoO}_2]^{2+}$  moiety to  $\text{Ph}_3\text{P}$ . In coordinating solvents, the resultant  $\text{Mo}(\text{IV})$  complex is stabilized, presumably as  $\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{MoOX}(\text{solvent})$ . In chlorinated solvents, the oxygen atom transfer

(30) Laidler, K. J. *Chemical Kinetics*; McGraw-Hill, New York, 1965; p 9.

**Table VIII.** Rate Constants for the Reaction of Mo(VI) Complexes with Ph<sub>3</sub>P

Mo(VI) complex	T, °C	k, (M s) <sup>-1</sup>	ref
MoO <sub>2</sub> (S <sub>2</sub> CNEt <sub>2</sub> ) <sub>2</sub>	25	7 × 10 <sup>-2</sup>	4d
MoO <sub>2</sub> (LNS <sub>2</sub> )	25	7 × 10 <sup>-3</sup>	5
{HB(Me <sub>2</sub> pz) <sub>3</sub> }MoO <sub>2</sub> (S <sub>2</sub> P(OEt) <sub>2</sub> )	25	3 × 10 <sup>-3</sup>	6
<b>6</b>	25	6 × 10 <sup>-4</sup>	this work
<b>7</b>	25	2 × 10 <sup>-6</sup>	this work
MoO <sub>2</sub> (L-Cys-OEt) <sub>2</sub>	35	3 × 10 <sup>-3</sup>	32

reaction is followed by abstraction of a chlorine atom from the solvent to yield {HB(Me<sub>2</sub>pz)<sub>3</sub>}MoOCIX as the final product. In toluene, despite the steric barrier provided by the 3-methyl groups of HB(Me<sub>2</sub>pz)<sub>3</sub><sup>-</sup>, comproportionation of the initial Mo(IV) product with the starting Mo(VI) complex occurs to yield a binuclear Mo(V) complex.

The interesting solvent dependence of the reactions depicted in Figure 4 follows from the use of the HB(Me<sub>2</sub>pz)<sub>3</sub><sup>-</sup> ligand. Oxygen atom abstraction from {HB(Me<sub>2</sub>pz)<sub>3</sub>}MoO<sub>2</sub>X by Ph<sub>3</sub>P produces a five-coordinate {HB(Me<sub>2</sub>pz)<sub>3</sub>}MoOX species which must, because of the facial coordination of the HB(Me<sub>2</sub>pz)<sub>3</sub><sup>-</sup> ligand, have the vacant coordination site cis to the remaining oxo group. All known five-coordinate oxomolybdenum(IV) complexes have square-pyramidal geometry with the vacant coordination site trans to the Mo=O bond. Indeed, a trans vacancy is stabilized by the presence of the strong Mo=O bond. However, the HB(Me<sub>2</sub>pz)<sub>3</sub><sup>-</sup> ligand prevents rearrangement to a square-pyramidal isomer with a vacancy trans to the oxo group. The resulting Mo(IV) complex can be stabilized by coordination of a solvent molecule at the vacant site cis to the oxo ligand. In the absence of a coordinating solvent, rapid reactions occur with other available species, either chlorine abstraction from a solvent molecule or comproportionation with a molecule of the starting complex.

It has been asserted that facile oxygen atom transfer reactions of Mo(VI) complexes occur only when sulfur donor ligands are present in the coordination sphere, and several authors have commented upon the lack of reactivity of complexes containing only oxygen and nitrogen ligating atoms.<sup>10</sup> The observation of oxygen transfer from **7** to Ph<sub>3</sub>P demonstrates that oxygen atom transfer reactions forming Mo(IV) complexes are feasible for complexes with only oxygen and nitrogen atoms in the coordination sphere. However, the reactions are far slower than those of complexes containing sulfur-donor or halide ligands. It is interesting that the aryloxide complex reacted completely, albeit

slowly, with Ph<sub>3</sub>P while the alkoxide complex showed no reaction at all. Table VIII lists rate constants determined to date for oxygen atom transfer from Mo(VI) complexes to Ph<sub>3</sub>P. The rates order nicely according to the number of coordinated sulfur atoms in the initial Mo(VI) complex.

It is unfortunate that the rate constant for the reaction of **1** with Ph<sub>3</sub>P could not be determined. From the observations we have been able to make, it is clear that this reaction is far faster than the reaction of either **6** or {HB(Me<sub>2</sub>pz)<sub>3</sub>}MoO<sub>2</sub>(S<sub>2</sub>P(OEt)<sub>2</sub>).<sup>6</sup> Halide ligands, except possibly fluoride, can be expected to influence reactivity in the same manner as sulfur-donor ligands. Previous reports of oxygen-transfer reactions to complexes with the O, N, Cl donor atom set are rare,<sup>31</sup> and this is the first indication that halide complexes may be more proficient than sulfur-ligand-containing complexes at performing oxygen atom transfer reactions.

### Conclusions

This study of oxygen atom transfer reactions of {HB(Me<sub>2</sub>pz)<sub>3</sub>}MoO<sub>2</sub>X complexes has demonstrated the diversity of products that can be obtained when the intermediate oxo-Mo(IV) complex cannot rearrange to square-pyramidal stereochemistry.

**Acknowledgment.** We thank Kimber Wilson for preparation and characterization of the halide complexes during a research project in Chemistry 105H at the University of Arizona. We thank Mark Malcomson for the GC/MS analyses and Roger Sperline for obtaining the FTIR spectra. The crystal structure determinations were done by using the facilities of the Molecular Structure Laboratory at the University of Arizona; we thank Ann Copenhaver and Dr. Michael Bruck for assistance with the structure determinations. We are grateful for support of this work by the National Institutes of Health through Grant GM-37773. C.G.Y. thanks the Australian Research Council for financial support and Aston A. Eagle for assistance.

**Supplementary Material Available:** Tables of experimental details, positional parameters, anisotropic thermal parameters, calculated hydrogen atom positions, bond distances, and bond angles for **4**, **8**, and **9** (18 pages); tables of observed and calculated structure factors for **4**, **8**, and **9** (51 pages). Ordering information is given on any current masthead page.

(31) El-Essawi, M. M.; Weller, F.; Stahl, K.; Kersting, M.; Dehnicke, K. Z. *Anorg. Allg. Chem.* **1986**, *542*, 175-181.

(32) Deli, J.; Speier, G. *Transition Met. Chem.* **1981**, *6*, 227-229.