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Articles

Isovalent and Mixed-Valent Dinuclear μ-Oxo and μ-Oxo μ-Disulfido Complexes of Molybdenum(V) and Molybdenum(VI)

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Reactions of $\{HB(Me_2pz)_3\}Mo^{VI}O_2Br$ with aqueous ammonia solution or $Bu^n{}_4NSH$ in dry dichloromethane produce the isovalent dinuclear complexes $[\{HB(Me_2pz)_3\}Mo^{VI}O_2]_2(\mu\text{-}O)$ (**1**) and $[\{HB(Me_2pz)_3\}Mo^{V}O]_2(\mu\text{-}O)(\mu\text{-}S_2)$ (**2**), respectively. Reaction of $\{HB(Me_2pz)_3\}Mo^{VI}O_2(SPh)$ and PPh_3 in dry toluene results in the formation of isovalent $[\{HB(Me_2pz)_3\}Mo^{V}O(SPh)]_2(\mu\text{-}O)$ (**3**) via a comproportionation reaction involving Mo(VI) and Mo(IV) centers. Mixed-valent $\{HB(Me_2pz)_3\}Mo^{VI}O_2(\mu\text{-}O)Mo^{V}OX\{HB(Me_2pz)_3\}$ (X = Br (**4**), SPh (**5**)) form upon reaction of $\{HB(Me_2pz)_3\}Mo^{VI}O_2Br$ and PhSH/Et_3N in dry dichloromethane. Reliable syntheses and infrared, ^1H NMR (EPR), and UV–visible spectroscopic and mass spectrometric data for compounds **1**–**5** are reported.

Introduction

The propensity of high-valent oxomolybdenum complexes to form di-, tri-, and polynuclear species is well documented.[1–4] Consequently, the synthesis of models of the *mononuclear* active sites of pterin-containing molybdenum enzymes requires the prevention of polynucleation, especially at the Mo(V) level. This has been achieved through the use of sterically bulky ligands which prevent close approach of molybdenum centers.[5,6] In models exploiting the hydrotris(3,5-dimethylpyrazol-1-yl)borate ligand, $HB(Me_2pz)_3{}^-$, the protection of the metal center by the 3-methyl groups is generally sufficient to ensure mononuclearity.[6] However, a number of di- and polynuclear complexes containing this ligand have been reported: these include $[\{HB(Me_2pz)_3\}Mo^{VI}O_2]_2(\mu\text{-}O)$ (**1**),[7] $[\{HB(Me_2pz)_3\}MoO]_2(\mu\text{-}O)(\mu\text{-}S_2)$ (**2**),[8] and mixed-valent $\{HB(Me_2pz)_3\}Mo^{VI}O_2(\mu\text{-}O)Mo^{V}OCl\{HB(Me_2pz)_3\}$.[9] We report here the synthesis and characterization of the new complexes $[\{HB(Me_2pz)_3\}Mo^{V}O(SPh)]_2(\mu\text{-}O)$ (**3**) and $\{HB(Me_2pz)_3\}Mo^{VI}O_2(\mu\text{-}O)Mo^{V}OX\{HB(Me_2pz)_3\}$ (X = Br (**4**), SPh (**5**)), as well as improved syntheses and characterization data for **1** and **2**. Combined with our studies of mononuclear molybdenum complexes,[6] this work provides valuable insights into the factors and conditions promoting the formation of dinuclear tris(pyrazolyl)borate compounds of molybdenum. In turn, these insights enhance our ability to better control the nuclearity of reaction products. Moreover, the reported physical and spectroscopic data should assist the rapid, conclusive detection and identification of these and similar compounds in related systems.

Experimental Section

Samples of $\{HB(Me_2pz)_3\}MoO_2X$ (X = Br, SPh) were prepared according to literature procedures[10] or modifications thereof.[11] Infrared spectra were obtained on a Perkin-Elmer 1430 ratio-recording spectrophotometer using pressed KBr disks with polystyrene as reference. NMR spectra were recorded on a Bruker FT AM 300 spectrometer using $CHCl_3$ as an internal standard ($\delta = 7.24$). EPR spectra were run on a Bruker ES-106 spectrometer using DPPH as reference. Electron impact (70 eV) mass spectra were recorded on a VG TRIO-1 spectrometer. The purity of the compounds was established by thin layer chromatography and NMR spectroscopy.

$[\{HB(Me_2pz)_3\}MoO_2]_2(\mu\text{-}O)$ (1). A concentrated ammonia solution (2.0 mL) was added to a solution of $\{HB(Me_2pz)_3\}MoO_2Br$ (1.0 g, 2.0 mmol) in dichloromethane (30 mL) and acetonitrile (20 mL). The reaction mixture was stirred in air at 50 °C for 30 min. The solvent was evaporated and the residue dried under vacuum. The pale yellow residue was suspended in dichloromethane, the mixture was filtered to remove insoluble materials, and the filtrate was chromatographed on silica gel using dichloromethane as eluant. The pale yellow product was isolated by addition of methanol to the partially evaporated yellow fraction from the column. Yield = 0.38 g (44%). Infrared (KBr disk): ν(BH) 2539 m, 1542 s, 1448 s, 1417 s, 1383 s, 1369 s, 1211 s, 1188 m, 1069 s, 1045 m, $\nu(MoO_2)$ 931 s and 900 s, 861 m, 810 s, ν(MoOMo) 753 vs br, 648 m, 460 m, 380 m, 310 m, 267 m cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.07 (s, 6H, 2 CH_3), 2.26 (s, 6H, 2 CH_3), 2.33 (s, 6H, 2 CH_3), 2.34 (s, 6H, 2 CH_3), 2.73 (s, 6H, 2 CH_3), 3.09 (s, 6H, 2 CH_3), 5.39 (s, 2H, 2 CH), 5.74 (s, 2H, 2 CH), 5.84 (s, 2H, 2 CH). Electronic spectrum (CH_2Cl_2): 250 (22 400), 230 nm (28 200 $M^{-1}\,cm^{-1}$). Mass spectrum: $[\mathbf{1} - H]^+$ *m/z* 862 (60), 863 (81), 864 (77), 865 (100), 866 (88), 867 (82), 868 (65), 869 (53); 769 (100); 755 (100); 673 (100% within multiplet).

$[\{HB(Me_2pz)_3\}MoO]_2(\mu\text{-}O)(\mu\text{-}S_2)$ (2). A mixture of $\{HB(Me_2pz)_3\}MoO_2Br$ (0.5 g, 1.0 mmol) and $Bu^n{}_4NSH$ (0.38 g, 1.38 mmol) was treated

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with dry, deoxygenated dichloromethane (30 mL) under an atmosphere of dinitrogen. After being stirred at room temperature for 1 h, the brown solution was reduced in volume and chromatographed (in air) on a silica gel column using dichloromethane as eluant. The purple-brown band was collected and the product recrystallized from dichloromethane/pentane. Yield = 0.22 g (49%). Infrared (KBr disk): ν(BH) 2545 m, 1542 s, 1448 s, 1415 s, 1382 s, 1366 s, 1207 s, 1192 s, 1074 s, 1065 s, 1039 s, 985 m, ν(MoO) 933 s, 856 s, 814 s, 776 s, 734 m, 694 m, 652 s, 493 m, 459 m, 346 s, 311 s cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.89 (s, 6H, 2 CH_3), 2.30 (s, 6H, 2 CH_3), 2.40 (s, 6H, 2 CH_3), 2.40 (s, 6H, 2 CH_3), 2.76 (s, 6H, 2 CH_3), 2.87 (s, 6H, 2 CH_3), 5.65 (s, 2H, 2 CH), 5.78 (s, 2H, 2 CH), 5.94 (s, 2H, 2 CH). Electronic spectrum (CH_2Cl_2): 782 (380), 574 (2 550), 425 (12 300), 230 nm (32 500 M^{-1} cm^{-1}). Mass spectrum: $[\mathbf{2}-H]^+$ m/z 890 (10), 891 (24), 892 (37), 893 (50), 894 (60), 895 (75), 896 (84), 897 (100), 898 (99), 899 (93), 900 (80), 901 (68), 902 (41), 903 (33), 904 (14%); $[\mathbf{2} - 2S - H]^+$ m/z 835 (100% within multiplet).

$[\{HB(Me_2pz)_3\}MoO(SPh)]_2(\mu\text{-}O)$ (3). To a mixture of $\{HB(Me_2pz)_3\}MoO_2(SPh)$ (0.16 g, 0.30 mmol) and PPh_3 (0.08 g, 0.30 mmol) in a nitrogen-filled Schlenk flask was added freshly dried (activated alumina) toluene (6 mL). After being stirred at room temperature for 1 h, the brown solution was reduced in volume and chromatographed (in air) on a silica gel column using dichloromethane/pentane (1:1) as eluant. The major dark purple-brown band was collected and the product recrystallized from dichloromethane/methanol. Yield = 21 mg (13%). Infrared (KBr disk): ν(BH) 2546 m, 1577 m, 1543 s, 1474 m, 1448 s, 1416 s, 1381 s, 1363 s, 1205 s, 1185 m, 1069 s, 1040 m, ν (MoO) 949 s, 857 m, 814 m, 785 m, 739 s, 694 s, 644 m, 484 m, 432 m cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.11 (s, 6H, 2 CH_3), 2.11 (s, 6H, 2 CH_3), 2.33 (s, 6H, 2 CH_3), 2.33 (s, 6H, 2 CH_3), 2.42 (s, 6H, 2 CH_3), 3.35 (s, 6H, 2 CH_3), 5.43 (s, 2H, 2 CH), 5.45 (s, 2H, 2 CH), 5.84 (s, 2H, 2 CH), 6.54 (d, 4H, J = 6.4 Hz, SPh^-), 6.72 (m, 6H, SPh^-). Electronic spectrum (CH_2Cl_2): 650 (2900, sh), 482 (20 300), 274 (27 700), 229 nm (43 300 M^{-1} cm^{-1}).

$\{HB(Me_2pz)_3\}Mo^{VI}O_2(\mu\text{-}O)Mo^VOX\{HB(Me_2pz)_3\}$ (X = Br (4), SPh (5)). To a yellow suspension of $\{HB(Me_2pz)_3\}MoO_2Br$ (1.5 g, 3.0 mmol) and PhSH (0.66 mL, 12.0 mmol) in dry, deoxygenated dichloromethane (50 mL) was added Et_3N (1.65 mL, 12.0 mmol). A transient green coloration was rapidly replaced by a brown coloration. The reaction mixture was stirred at room temperature for 3 h and evaporated to a small volume. Column chromatography (silica gel, dichloromethane) resulted in the collection of three bands. The first deep-brown band contained the major product, $\{HB(Me_2pz)_3\}MoO_2(SPh)$[12] (0.90 g, 57%); the second orange-brown and third green bands contained **4** (0.20 g, 15%) and **5** (90 mg, 6%), respectively. These three complexes were recrystallized from CH_2Cl_2/MeOH.

4. Anal. Calcd for $C_{30}H_{44}B_2BrN_{12}Mo_2O_4$: C, 38.74; H, 4.77; N, 18.07; Br, 8.59. Found: C, 39.00; H, 4.91; N, 18.10; Br, 8.42. Infrared (KBr disk): ν(BH) 2543 m, 1543 s, 1446 s, 1415 s, 1382 s, 1363 s, 1205 s, 1188 s, 1067 s, 1044 m, ν(MoO) 955 s, $\nu(MoO_2)$ 926 m and 896 s, 860 m, 809 s, ν(MoOMo) 755 vs br, 646 m, 460 m, 380 m cm^{-1}. Electronic spectrum (CH_2Cl_2): 475 (520, sh), 335 (7900, sh), 285 (12 400, sh), 230 nm (25 300 M^{-1} cm^{-1}). EPR spectrum (CH_2Cl_2): g = 1.943, $a(^{95,97}Mo) = 45.5 \times 10^{-4}$ cm^{-1}, $a(^{79,81}Br)$ = *ca.* 7.1×10^{-4} cm^{-1}. Mass spectrum: $[\mathbf{4} - Br]^+$ m/z 841 (13), 842 (14), 843 (30), 844 (43), 845 (55), 846 (77), 847 (93), 848 (86), 849 (100), 850 (100), 851 (94), 852 (76), 853 (57), 854 (56), 855 (27); 769 (100); 754 (100); 673 (100% within multiplet).

5. Infrared (KBr disk): ν(BH) 2544 m, 1540 s, 1445 s, 1413 s, 1380 s, 1362 s, 1204 s, 1186 s sh, 1065 s, 1042 m, ν(MoO) 945 s, $\nu(MoO_2)$ 927 m and 896 s, 860 m, 810 s, ν(MoOMo) 756 vs br, 690 m, 645 m, 460 m, 379 m cm^{-1}. EPR spectrum (CH_2Cl_2): g = 1.944, $a(^{95,97}Mo)$ = 42.3×10^{-4} cm^{-1}.

Results and Discussion

Synthesis and Properties of 1. A variety of complexes $\{HB(Me_2pz)_3\}MoO_2(OR)$ or $\{HB(Me_2pz)_3\}MoO_2(SR)$ (R = alkyl or aryl) may be prepared conveniently by the reaction of $\{HB(Me_2pz)_3\}MoO_2Br$ and ROH or RSH under basic conditions.[11,12] In an attempt to prepare $\{HB(Me_2pz)_3\}MoO_2(OH)$, the bromo complex was reacted with aqueous ammonia or $[Et_4N]OH$ solutions. The major product isolated from these reactions was the dinuclear Mo(VI) complex **1**; a net equation for its formation is given in (1). The mechanism of the reaction may involve the

$$2\{HB(Me_2pz)_3\}MoO_2Br + 2OH^- \rightarrow \mathbf{1} + 2Br^- + H_2O \quad (1)$$

formation and condensation of the intermediate hydroxo complex $\{HB(Me_2pz)_3\}MoO_2(OH)$. This reaction demonstrates that the $HB(Me_2pz)_3^-$ ligand alone is not bulky enough to prevent condensation of dioxo–Mo(VI) complexes and that the *size* and *nature* of the coligand X can have dramatic effects on a complex's ability to undergo condensation or dinucleation. Complex **1** is a major byproduct in the preparations of $\{HB(Me_2pz)_3\}MoO_2Br$ and $\{HB(Me_2pz)_3\}MoO_2(NCS)$ but can be conveniently removed by column chromatography.[11] The complex has been structurally characterized by Barnhardt and Enemark,[7] but a reliable synthesis and spectroscopic data are reported here for the first time. Interestingly, the conjugate base of $\{HB(Me_2pz)_3\}MoO_2(OH)$, $[\{HB(Me_2pz)_3\}MoO_3]^-$, has been isolated as its NEt_4^+ salt from the reaction of $NEt_4[\{HB(Me_2pz)_3\}Mo(CO)_3]$ with dimethyldioxirane in *anhydrous* acetone.[13] The sterically unencumbered hydrotris(pyrazolyl)borate ligand ($HB(pz)_3^-$) forms the analogous $[(HB(pz)_3)MoO_3]^-$ complex under similar conditions.[13]

Cream-colored, diamagnetic, air-stable **1** was characterized by mass spectrometry and by infrared, ^1H NMR, and electronic spectroscopy. The mass spectrum of **1** exhibited a cluster of peaks at m/z 865, assigned to the parent ion, as well as a number of fragment ions. The infrared spectrum showed bands characteristic of the tris(pyrazolyl)borate ligand along with two strong bands at 931 and 900 cm^{-1}, assigned to the $\nu_s(MoO_2)$ and $\nu_{as}(MoO_2)$ modes of the *cis*-$[Mo^{VI}O_2]^{2+}$ fragment. The presence of a μ-oxo ligand was clearly indicated by a strong and broad band at 753 cm^{-1} assigned to ν_{as}(MoOMo). The ^1H NMR spectrum of **1** exhibited six methyl resonances and three methine resonances, consistent with C_2 or C_i molecular symmetry in solution. It is likely, considering the C_2 structure of **1** in the solid state,[7] that the complex exhibits this structure in solution. The unit cell data for a crystal of **1**, grown by slow evaporation of a dichloromethane solution, were identical to those reported previously.[7]

Synthesis and Properties of 2. In an attempt to prepare $\{HB(Me_2pz)_3\}Mo^{VI}O_2(SH)$, $\{HB(Me_2pz)_3\}MoO_2Br$ was reacted with Bu^n_4NSH in dichloromethane. However, unlike OH^-, SH^- is a strong reducing agent and the major product isolated is neither $\{HB(Me_2pz)_3\}Mo^{VI}O_2(SH)$ nor $[\{HB(Me_2pz)_3\}Mo^{VI}O_2]_2(\mu\text{-}S)$ but the isovalent dinuclear Mo(V) complex **2**; a net equation for its formation is given in (2). The reaction mechanism is likely

$$2\{HB(Me_2pz)_3\}MoO_2Br + 2SH^- \rightarrow \mathbf{2} + 2Br^- + H_2O \quad (2)$$

to involve rapid reduction of $\{HB(Me_2pz)_3\}MoO_2Br$ by SH^-, subsequent loss of bromide, and bridge formation. Alternatively, the redox-driven condensation of initially formed $\{HB(Me_2pz)_3\}MoO_2(SH)$ could lead to formation of **2**. A number of other reactions involving a thio ligand also produce **2** as a major product or a byproduct. These reactions include[11] (i) air oxidation of the green solutions of $[\{HB(Me_2pz)_3\}MoOS(SCH_2Ph)]^-$, generated *in situ* upon incubation of $\{HB(Me_2pz)_3\}MoO_2(SCH_2Ph)$ and Bu^n_4NSH, (ii) reduction of $\{HB(Me_2pz)_3\}MoO_2(S_2PPr^i_2)$ with cobaltocene in acetonitrile, which produced **2** in *ca.* 10% yield, and (iii) sulfur atom transfer to $\{HB(Me_2pz)_3\}MoO(py)(SPh)$ by reaction with propylene sulfide in toluene at 60 °C. Roberts *et al.*[8] also isolated **2** from a reaction of $\{HB(Me_2pz)_3\}MoOCl_2$ and $NH_4[S_2P(OEt)_2]$ in dimethylacetamide and determined its structure by X-ray diffraction. However, the extremely low yield of the complex from that particular reaction prevented further characterization. The above observations suggest that **2** is the thermodynamic product of a system containing $[\{HB(Me_2pz)_3\}Mo^VO]^{2+}$ and thio ligands.

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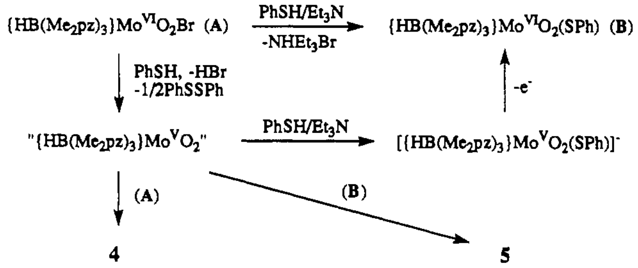
Scheme 1



Purple-brown, diamagnetic, air-stable **2** was characterized by mass spectrometry, infrared, ^{1}H NMR, and electronic spectroscopy, and X-ray crystallography. The mass spectrum exhibited a strong cluster of peaks at *m/z* 897 with an isotope pattern consistent with the $[M - H]^+$ ion. A strong cluster of peaks characteristic of the fragment ion $[M - 2S - H]^+$ was also observed. The infrared spectrum exhibited a strong band at 933 cm^{-1}, which was assigned to the ν(Mo═O) absorption. The infrared fingerprint of the $HB(Me_2pz)_3^-$ ligand was also present. The ^{1}H NMR spectrum was consistent with the formulation and the presence of C_2 molecular symmetry in solution; the spectrum consisted of six methyl resonances and three methine resonances. The electronic absorption spectrum was characterized by strong absorptions at 782, 574, 425, and 230 nm. Single crystals of **2**, grown by slow diffusion of *n*-pentane into a dichloromethane solution, were subject to an X-ray diffraction study which revealed a structure identical to that previously reported by Roberts *et al.*[8] Consistent with the ^{1}H NMR data above, the molecule possesses C_2 symmetry and contains two identical $[\{HB(Me_2pz)_3\}MoO]^{2+}$ fragments bridged by a μ-oxo and a μ-disulfido group.

Synthesis and Properties of 3. The purple-brown, diamagnetic, dinuclear complex **3** was prepared from the reaction of $\{HB(Me_2pz)_3\}MoO_2(SPh)$ and PPh_3 in *carefully dried* toluene. Its formation involves comproportionation between Mo(IV) and Mo(VI) complexes as shown in (3). However, this reaction is severely

$$\{HB(Me_2pz)_3\}Mo^{VI}O_2(SPh) + \text{“}\{HB(Me_2pz)_3\}Mo^{IV}O(SPh)\text{”} \rightarrow \mathbf{3} \quad (3)$$

inhibited by the *combined steric hindrance of the* $HB(Me_2pz)_3^-$ *and* SPh^- *ligands.* The reaction is not clean and at least six products form. Only in *carefully dried* solvent can **3** be isolated in low yield (*ca.* 13%). In wet solvent, water effectively prevents reaction 3 by reacting with "$\{HB(Me_2pz)_3\}Mo^{IV}O(SPh)$", permitting the regeneration of the starting material after workup in air.[12] In contrast, reactions 1 and 2 proceed readily because neither OH^- nor SH^- can provide steric protection for the Mo center. The formation of **3** upon reaction of $\{HB(Me_2pz)_3\}Mo^{VI}O_2(SPh)$ and PPh_3 in toluene was reported by Roberts *et al.* in 1990.[10] The characteristic electronic spectrum (*vide infra*) of **3** and the reaction stoichiometry established by ^{31}P NMR permitted its identification, but it was not isolated in pure form or fully characterized.

Complex **3** was characterized by infrared, ^{1}H NMR, and electronic spectroscopy. Its infrared spectrum exhibited characteristic bands for ν(BH) and ν(MoO) vibrations. The ^{1}H NMR spectrum was consistent with the formulation and the presence of C_2 or C_i molecular symmetry in solution. The electronic spectrum in dichloromethane shows an intense absorption at 482 nm, typical of species containing the $[Mo^V_2O_3]^{4+}$ center.[1,10,14,15] The extinction coefficient (ϵ 20 300 M^{-1} cm^{-1}) is comparable with those of many other complexes of this type (ϵ 20 000–30 000 M^{-1} cm^{-1}).[1,14] The related complex $[(HB(pz)_3)MoOCl]_2(\mu\text{-}O)$, which adopts both C_2 and C_i structures, was reported by Lincoln and Koch in 1986.[15]

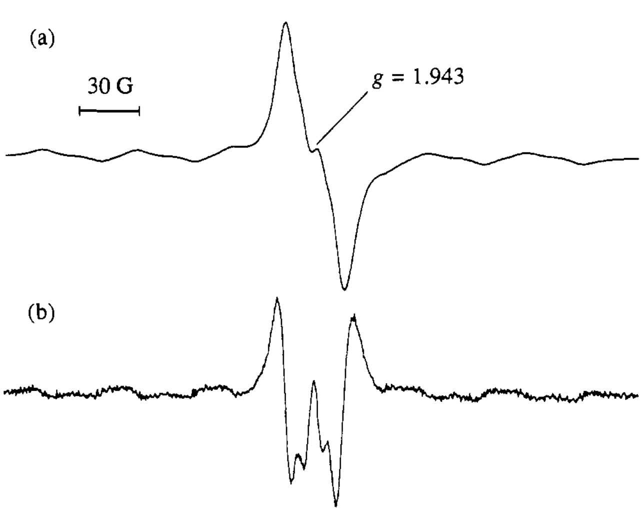


Figure 1. (a) First-derivative X-band EPR spectrum of **4** in 3 mM dichloromethane solution at room temperature. (b) Second-derivative EPR spectrum of **4** showing ^{79,81}Br superhyperfine coupling.

Synthesis and Properties of 4 and 5. Orange-brown, paramagnetic **4** was isolated as a byproduct from the preparation of $\{HB(Me_2pz)_3\}MoO_2(SPh)$ by reaction of $\{HB(Me_2pz)_3\}MoO_2Br$ with PhSH in the presence of Et_3N.[11,12] The yield appears to be dependent upon the mode of preparation. Addition of a mixture of PhSH and Et_3N in toluene to a solution of the bromo complex in dichloromethane produced a good yield of $\{HB(Me_2pz)_3\}MoO_2(SPh)$ (70–90%) but very little **4**. On the other hand, when $\{HB(Me_2pz)_3\}MoO_2Br$ and PhSH were mixed *first* and then Et_3N was added, the yield of $\{HB(Me_2pz)_3\}MoO_2(SPh)$ decreased (<60%) while **4** was isolated in more than 10% yield. In addition, a small amount of **5** was also isolated as a mixture with $\{HB(Me_2pz)_3\}Mo^{VI}O_2(\mu\text{-}O)Mo^VOCl\{HB(Me_2pz)_3\}$ (**6**). Attempts to purify **5** were not successful due to its conversion into **6** during chromatography. However, pure **6** may be isolated after incubation of **5** in chloroform or dichloromethane for *ca.* 1 month. Complex **6** was first prepared by Eagle *et al.*[9] from the reaction of $\{HB(Me_2pz)_3\}MoO_2Cl$ with the Grignard reagent MeMgCl. A proposed mechanism for the formation of **6** involves (a) initial formation of coordinatively unsaturated $\{HB(Me_2pz)_3\}Mo^VO_2$, (b) its reaction with $\{HB(Me_2pz)_3\}Mo^{VI}O_2Cl$ to give $\{HB(Me_2pz)_3\}Mo^VO_2(\mu\text{-}O)Mo^{VI}OCl\{HB(Me_2pz)_3\}$, and (c) intramolecular electron transfer to produce **6**.[9] Considering that thiophenol may reduce $\{HB(Me_2pz)_3\}MoO_2Br$ and thereby labilize the Mo–Br bond, the reactions occurring in the present system may be summarized as shown in Scheme 1.

Complex **6** was identified by comparison of its spectroscopic data with those of an authentic sample.[9] Complex **4** was characterized by elemental analysis, mass spectrometry, and infrared, EPR, and electronic spectroscopy. The infrared spectrum of **4** was quite similar to that of **6** and exhibited three strong ν(Mo═O) bands in the 1000–850 cm^{-1} region. These three ν(Mo═O) bands are assigned to $[Mo^V{=}O]^{3+}$ (955 cm^{-1}) and *cis*-$[Mo^{VI}O_2]^{2+}$ (926 and 896 cm^{-1}) fragments. The presence of the μ-oxo ligand was indicated by a strong, broad band at *ca.* 755 cm^{-1} assigned as ν(MoOMo). Bands typical of the $HB(Me_2pz)_3^-$ ligand were also present. The complex exhibited an EPR spectrum typical of a Mo^V complex (Figure 1). The signal, characterized by g and $a(^{95,97}Mo)$ values of 1.943 and 45.5×10^{-4} cm^{-1}, respectively, consisted of a strong central line due to species containing Mo isotopes with $I = 0$ (74.82 atom %) flanked by six lines due to species containing Mo isotopes with $I = 5/2$ (25.18 atom %). Both the $I = 0$ and $^5/_2$ features of the spectrum were split due to superhyperfine coupling to ^{79,81}Br ($I = {^3/_2}$), but the expected quartet was not fully resolved (Figure

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1b). The *g* value for **4** was slightly higher than that for **6** (1.935), consistent with the behavior observed in other Mo(V) tris(pyrazolyl)borate complexes.[11] A parent ion was not observed in the mass spectrum of **4**, but a cluster of peaks at *m/z* 850 was assigned to the fragment ion $[\mathrm{M-Br}]^+$. Similar behaviour, *viz.* observation of $[\mathrm{M-Cl}]^+$ only, was observed for the analogous chloro complex **6**.[9] The electronic spectrum of **4** was characterized by absorptions at 230, 285, 335, and 475 nm. As was observed for **6**, a strong band at *ca.* 485 nm, indicative of the presence of a dinuclear Mo(V) complex (*vide supra*),[1,14] was not present in the electronic spectrum of **4**. Complex **5** was identified to be the same type of mixed-valent dinuclear complex by its infrared and EPR spectra. The $\langle g \rangle$ value of **5** was higher than that of **6**, consistent with the presence of a thiolate ligand at Mo(V).[16] The $\nu(\mathrm{Mo^V{=}O})$ stretching frequency of **5** (945 $\mathrm{cm^{-1}}$) was lower than those of both **4** and **6** (both 955 $\mathrm{cm^{-1}}$). This is also consistent with the presence of a thiolato ligand in **5**, since $\mathrm{SPh^-}$ is a stronger π donor ligand than $\mathrm{Cl^-}$ or $\mathrm{Br^-}$. Early-transition-metal mixed-valent complexes were exhaustively reviewed by Young in 1989.[17] No $\mathrm{Mo^VMo^{VI}}$ complex had been isolated or structurally characterized at that time. Since then, and despite rapid growth in mixed-valent chemistry in general, only two dinuclear $\mathrm{Mo^VMo^{VI}}$ compounds have been reported. The first, complex **6**,[9] has been discussed. The second, $[(\mathrm{Me_3tcn})\mathrm{MoO_2}(\mu\text{-O})\mathrm{MoOI}(\mathrm{Me_3tcn})]^{2+}$ ($\mathrm{Me_3tcn}$ = 1,4,7-trimethyl-1,4,7-triazacyclononane), was reported in 1993 by Wieghardt and co-workers.[18] This paramagnetic complex exhibits a nearly isotropic EPR signal with $g = 1.97$ and has been structurally characterized in a mixed crystal containing $[\{(\mathrm{Me_3tcn})\mathrm{MoO_2}\}_2(\mu\text{-O})]^{2+}$. The $\mathrm{Mo^VMo^{VI}}$–$\mathrm{Me_3tcn}$ complex, like the $\mathrm{HB(Me_2pz)_3^-}$ complexes described here and previously,[9] is a class I mixed-valent complex.

Conclusion

The formation of a variety of dinuclear complexes under certain conditions demonstrates that the tridentate $\mathrm{HB(Me_2pz)_3^-}$ ligand alone is not bulky enough to prevent dinucleation of high-valent oxo- and thio-molybdenum complexes. However, the steric bulk of the ligand appears sufficient to prevent the close approach of metal centers necessary to form $\mathrm{LMo}(\mu\text{-X})_2\mathrm{MoL}$ complexes. Additional steric encumbrance from the coligands appears to be another important factor in the maintenance of mononuclearity. The presence of small ligands with the capacity to form or be incorporated into bridging ligands and the presence of good leaving groups enhance dinucleation. The geometry, charge, and electronic properties of mononuclear species, as well as reaction conditions (especially the absence of water), may retard dinucleation by effectively blocking low-energy reaction pathways. The mutually *cis* arrangement of the coligands enforced by *facial* tris(pyrazolyl)borate ligands inhibits ligand exchange and dinucleation via dissociative mechanisms.[16] The negative charge of the novel dioxo–Mo(V) anions $[\mathrm{LMo^VO_2(SPh)}]^-$ (L = tris(pyrazolyl)borate or tris(triazolyl)borate ligand)[12,19] and the lack of a viable pathway for dinucleation account for the mononuclearity of such species. Their formation by one-electron reduction of $\mathrm{LMo^{VI}O_2(SPh)}$ avoids the Mo(IV) state and dinucleation via comproportionation (cf. formation of **3**). However, the steric bulk and kinetic inertness of the $\mathrm{SPh^-}$ ligand also appear to play crucial roles in stabilizing these complexes, as reduction of $\mathrm{LMoO_2X}$ (X = $\mathrm{Cl^-}$, $\mathrm{Br^-}$, $\mathrm{OR^-}$) complexes leads to decomposition (probably via dinucleation) rather than formation of dioxo–Mo(V) species.[11]

Tris(pyrazolyl)borate ligands with bulkier R groups can provide greater steric barriers to the dinucleation of complexes containing small coligands, allowing the mononuclear chemistry of such complexes to be explored. Thus, the formation of $[\{\mathrm{HB(Pr}^i\mathrm{pz)_3}\}\mathrm{MoO_2}]_2\mathrm{O}$ $[\mathrm{HB(Pr}^i\mathrm{pz)_3^-}$ = hydrotris(3-isopropylpyrazolyl)borate] does not accompany the synthesis of $\{\mathrm{HB(Pr}^i\mathrm{pz)_3}\}\mathrm{MoO_2Br}$ nor is the dinuclear complex formed upon reaction of $\{\mathrm{HB(Pr}^i\mathrm{pz)_3}\}\mathrm{MoO_2Br}$ with $\mathrm{NH_4OH}$.[11] Finally, dinucleation may be effectively circumvented by the intramolecular stabilization of potential bridging ligands, as demonstrated by the recent isolation of mononuclear oxo–thio–Mo(VI) complexes $\{\mathrm{HB(Me_2pz)_3}\}\mathrm{MoOS}\{\mathrm{SP(S)R_2}\}$, wherein the reactive thio ligand is stabilized by an intramolecular S···S interaction involving the monodentate dithiophosphinate ligand.[20]

Clearly, a number of factors must be controlled if the synthesis of mononuclear tris(pyrazolyl)borate complexes of molybdenum is to be achieved. Likewise, consideration of the factors enhancing dinucleation may assist the facile, high-yield synthesis of such species.

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