

bond length for this reinforced macrocyclic complex is much longer at 2.09 Å than any of the unreinforced analogues, as seen in Figure 2. This supports the idea that the reinforcement of a large macrocyclic ring can lead to considerable bond stretching ability. What is striking, and rather unexpected, about the complex is the fact that the Cu(II) lies considerably out of the plane of the nitrogen donors, being some 0.36 Å out of the plane (Table IV). This is surprising in view of the fact that the Cu-N bond is being stretched, which can only be increased by the fact of the Cu(II) lying out of the plane. At this stage one must conjecture that this effect might be a result of the steric requirements of coordination to the homopiperazine part of the macrocycle.

One of the striking properties of the tetraazamacrocycles is the very high ligand field (LF) strength that is found in some of the complexes, seen for the Cu(II) complex of 2,3,2-NE in Figure 2. This was first interpreted by Busch et al.<sup>13</sup> as arising from compression of the metal ion in the too-small cavity of the macrocyclic ligand. This is a reasonable interpretation, except that the cases where the LF is highest correspond to the situation where the metal ion fits best into the cavity of the macrocycle, rather than where the metal ion is too large. This observation fits very nicely the set of complexes in Figure 2, where it is seen that the short Cu-N bonds in the 2,2,2-NE complex do not produce a higher LF strength. We have suggested on many occasions<sup>4,5,19-21</sup> that the higher LF strength is derived from the higher donor strength of the nitrogens as one moves along the series zeroth (ammonia) < primary < secondary < tertiary. The factors governing LF strength depend on the amount of overlap in the M-N bond, which is controlled by (1) the nature of the nitrogen donors in the series primary < secondary < tertiary, (2) the extent of stretching of the M-N bond away from the ideal value, and (3) N-M-N bond angle distortion, which appears to lower overlap strongly in the M-N bond and hence lessen LF strength. This last contribution will be discussed more fully in a future paper. At this stage, it appears that N-M-N bond angle deformation involving the in-plane N-M-N angles and also N-M-N bond angle deformation due to the metal ion rising out of the plane of the donor atoms contribute to a lowering of the LF strength. With respect to factor 2, no doubt bond compression should raise the LF strength, but metal ions appear to escape compression by N-M-N bond angle deformation to lie outside of the plane of the donor atoms, which leads to an overall lowering of LF strength due to factor 3, which is bond angle deformation.

One thus sees in Figure 2 that the LF strength of the complex [Cu(NE-3,3-HP)]<sup>2+</sup> is exceedingly low and is higher only than that of the 3,3,3-NE complex. One might say from the contribution from factor 1 above, the donor strength of the nitrogens, that the LF strength of the NE-3,3-HP complex should be exceedingly high, with its two tertiary nitrogens as compared to all secondary nitrogens in the unbridged analogues, but the very great extent of bond stretching and N-Cu-N bond angle deformation overwhelm this contribution. The effect of the tertiary nitrogens is apparent however, in that the LF strength in the NE-3,3-HP complex is actually higher than that in the 3,3,3-NE complex, in spite of the much lower extent of Cu-N bond stretching and N-Cu-N bond angle deformation in the 3,3,3-NE than in the NE-3,3-HP complex. That the tertiary nitrogens present in reinforced macrocycles can lead to high LF strengths is seen<sup>11</sup> in that the low-spin Ni(II) complex of AM-2,2-HP has the highest LF strength reported for any complex of this ion with a tetradentate saturated nitrogen donor ligand.

The structure of the [Cu(NE-3,3-HP)Cl]ClO<sub>4</sub> complex has demonstrated how much more strongly M-N bonds may be stretched in the cavities of reinforced macrocycles than in their unreinforced analogues. Previous work has shown<sup>8</sup> how strongly the reinforced macrocycles can compress metal ions. We are currently attempting the synthesis of the NE-3,3-DAC complex of Cu(II) to see how more strongly this might stretch the Cu-N bond.

**Acknowledgment.** We thank the Foundation for Research Development and the University of the Witwatersrand for generous support for this work.

**Supplementary Material Available:** Tables of fractional coordinates, anisotropic temperature factors, complete bond angles and lengths, and details of the crystallographic analysis for [Cu(NE-3,3-HP)Cl]ClO<sub>4</sub> and a stereoview of the complex (9 pages); a listing of observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

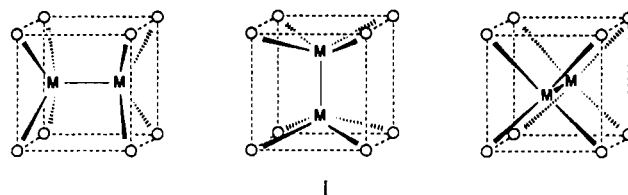
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### Are Internal Flips of M-M Multiple Bonds within Cubic or Octahedral Ligand Fields Symmetry Allowed?

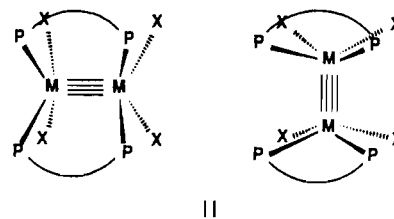
Roger H. Cayton and Malcolm H. Chisholm\*

Received August 6, 1990

Many dinuclear complexes of the general formula M<sub>2</sub>X<sub>8</sub> that contain a M-M quadruple bond exhibit a nearly cubic arrangement of the ligands X. Often complexes of this type display a crystallographic disorder of the M<sub>2</sub> vector among the three possible M-M orientations within the cube defined by the eight ligands; see I.<sup>1-5</sup> Upon lowering of the symmetry of the M<sub>2</sub>X<sub>8</sub> system



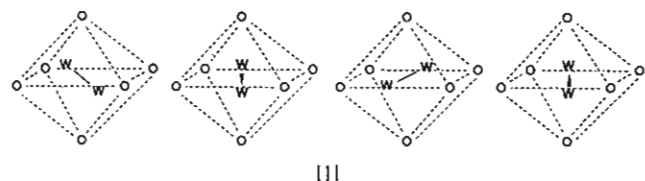
by ligand substitution, compounds such as M<sub>2</sub>X<sub>4</sub>(L<sup>+</sup>L<sup>-</sup>)<sub>2</sub> have been prepared and shown to adopt both α and β isomeric forms (II).<sup>6-10</sup>



Cotton and co-workers have studied the isomerization of α and β isomers of complexes of type II and provided evidence that this process, which occurs even in the solid state, proceeds via an "internal flip" of the M<sub>2</sub> vector.<sup>11-14</sup> More recently in the study of M<sub>2</sub>X<sub>6</sub> triple-bonded compounds, there have been examples of disordering of M<sub>2</sub> units within an octahedral ligand arrangement. For example, in the X-ray crystal structure of W<sub>2</sub>(OSi(*t*-Bu)Me<sub>2</sub>)<sub>6</sub>, the W-W axis was found to be disordered over three of the four

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possible orientations of an  $M_2$  unit inscribed within an octahedral array of oxygen atoms (III).<sup>15</sup> Similarly, Cotton and co-workers

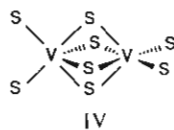


found a disorder of the  $Mo_2$  unit in  $Mo_2(OC(CF_3)_3)_4(NMe_2)_2$  and suggested that an internal flip might be responsible for the observed exchange of proximal and distal *N*-methyl groups.<sup>16</sup> The above prompted us to consider further the internal flip mechanism for rearrangements within the solid state and specifically to address the problem via orbital symmetry: Are internal flips of metal-metal multiple bonds symmetry allowed within a cubic or an octahedral ligand arrangement?

### $M_2X_8$ : Cubic Internal Flips

We have considered the motion of a  $d^4$ - $d^4$  dinuclear  $M_2$  unit within a cube of chloride ligands by performing Fenske-Hall<sup>17</sup> type molecular orbital calculations on  $Mo_2Cl_8^{4-}$ . The calculational details and geometric parameters are provided in the Appendix. The orbital energetics of the  $Mo_2$  internal flip were followed by the construction of a Walsh diagram as depicted in Figure 1. The MO technique is unable to provide a reliable energetic barrier for the motion described; however, it does allow us to examine the symmetry allowedness of the process and provide a general description of the changes in M-M bonding.

The transition state of the internal flip within a cube is shown on the right side of Figure 1 ( $\phi = 45^\circ$ ), wherein there are four terminal chloride groups that lie in a plane and four bridging chlorides. It should be noted that the latter are not equidistant: two Cl--Cl separations represent the edge distance and the other Cl--Cl separations represent the diagonal distance of a face of the cube. There are no known compounds that exhibit this transition-state geometry, though a number of dinuclear compounds do contain four  $\mu$ -X ligands, e.g.  $Cp_2M_2(\mu-X)_4$  ( $M = Ta, Mo$ ;  $X = Br, Cl$ ),<sup>18</sup>  $[(PMe_2Ph)_2Cl_2Nb]_2(\mu-Cl)_4$ ,<sup>19</sup> and perhaps, most significantly,  $V_2(edt)_4^{2-}$ , which has the  $S_2V(\mu-S)_4VS_2$  skeleton shown in IV.<sup>20</sup>



From Figure 1 it can be seen that the Mo-Mo  $\sigma$  and  $\pi$  orbitals are raised in energy as  $\phi$  changes from  $0^\circ$  (the ideal M-M quadruple-bond geometry) to  $45^\circ$ , but the  $\delta$  orbital remains relatively constant in energy. Upon distortion from  $\phi = 0^\circ$ , the symmetry of the system is reduced from  $D_{4h}$  to  $C_{2h}$  until  $\phi = 45^\circ$ , whereupon the symmetry becomes  $D_{2h}$ . The symmetry labels of the orbitals in Figure 1 are taken from  $C_{2h}$  symmetry. At the transition state, the Mo-Mo  $\pi$  orbitals ( $1b_u, 1a_u$ ) are split significantly in energy, the  $1a_u$  orbital being strongly destabilized by Mo-Cl  $\sigma^*$  interactions from the terminal chloride ligands. However, the destabilization of the Mo-Mo  $\pi$  orbitals is not great

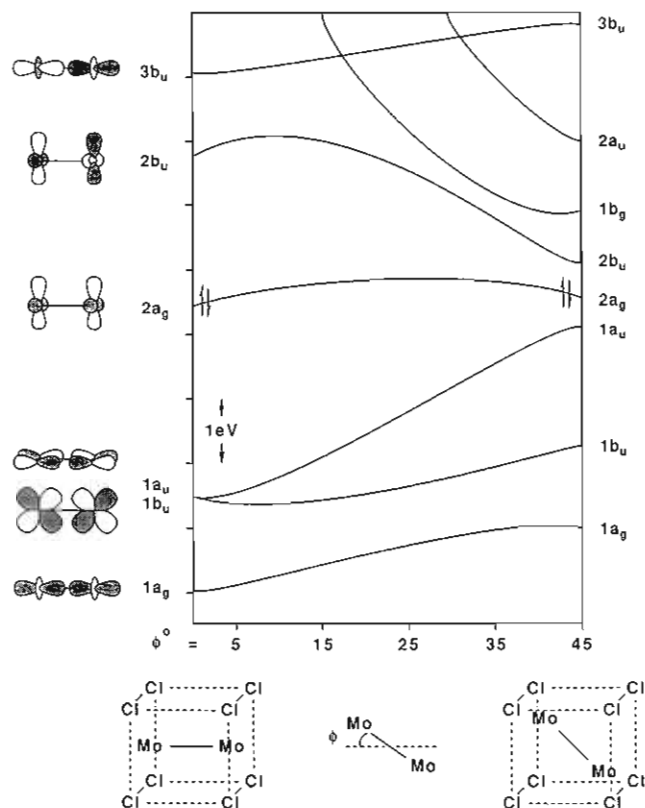
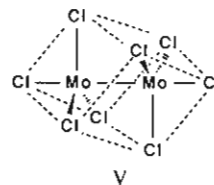


Figure 1. Walsh diagram for  $Mo_2Cl_8^{4-}$  depicting the variations in frontier orbital energies as the Mo-Mo vector is rotated through  $45^\circ$  from a position directed at the opposite faces of the cube to edges of the cube. The orbitals are labeled according to  $C_{2h}$  symmetry, which is maintained throughout the  $D_{4h} \rightarrow D_{2h} \rightarrow D_{4h}$  transformation.

enough to push them above the Mo-Mo  $\delta$  orbital such that the HOMO and the LUMO remain the  $\delta$  orbital ( $2a_g$ ) and the  $\delta^*$  orbital ( $2b_u$ ), respectively, throughout the internal flip. The process is symmetry allowed.

There is another way in which an  $M_2$  unit can "flip" within a cube. The intermediate geometry has the M-M axis coincident with a diagonal of the cube, and the disposition of the ligands is as shown in V. The geometry has  $D_{3d}$  symmetry. The intro-



duction of M-Cl bonds along the M-M axis destabilizes the M-M  $\sigma$  orbital and causes extensive mixing with M-Cl bonding. The frontier orbital region is shown in Figure 2, and the M-M MO configuration can be described as  $\pi^4\sigma^2\delta^2$ . In  $D_{3d}$  symmetry, this would give rise to a triplet ground state, since the HOMO is a doubly degenerate set of  $\delta$  orbitals.

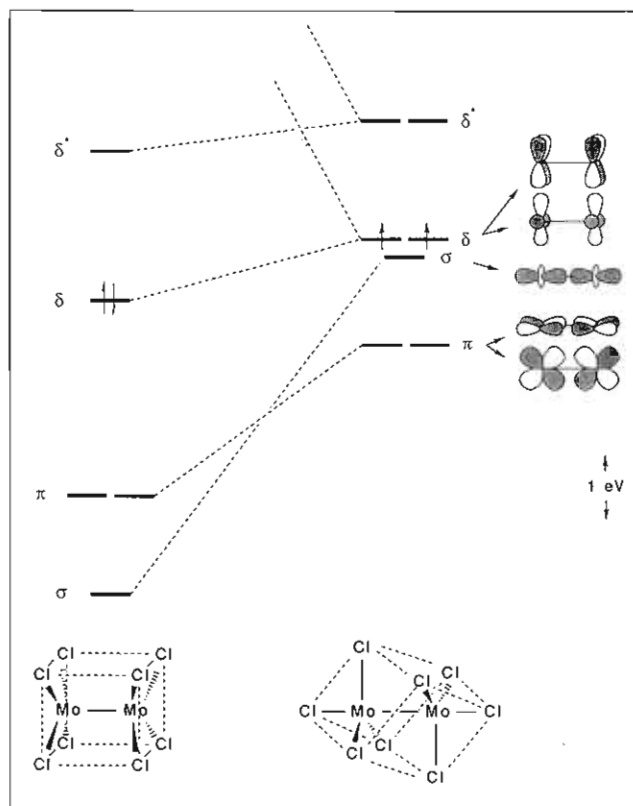
The reaction pathway leading from I to V is not easy to picture. It is equivalent to the sum of two  $C_8$  operations applied consecutively about two of the 4-fold axes of a cube (of course, the cube does not have an 8-fold axis). The highest symmetry maintained during this reaction pathway is  $C_i$ . The transition state V for the isomerization requires occupation of a formerly M-Cl  $\sigma^*$  orbital (M-M  $\delta$ ), and thus the isomerization would be thermally forbidden.

In summary, a comparison of the two "internal flips" within the cube shows that the quadruply bridged pathway would be favored.

### $M_2X_6$ : Octahedral Internal Flips

For an internal flip of an M-M triple bond within an octahedron, the transition state contains four terminal ligands that

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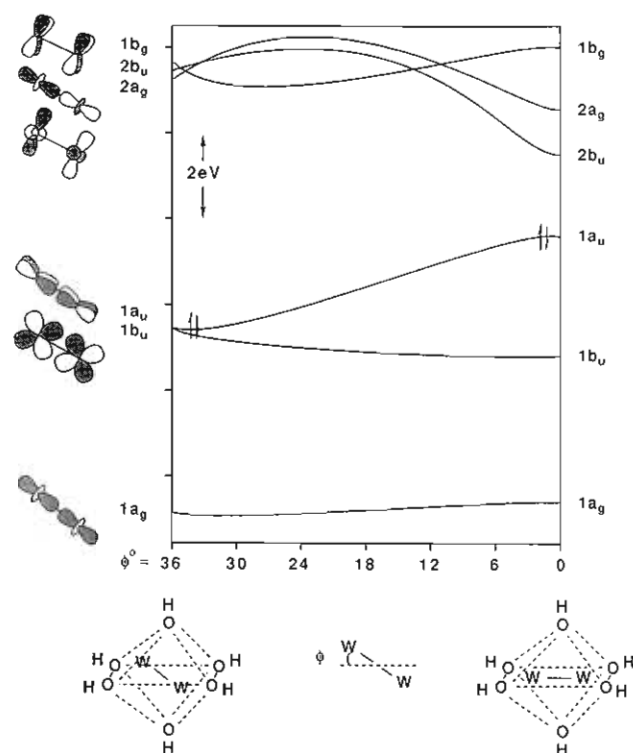


**Figure 2.** Frontier orbital region of the  $D_{3d}$  transition state geometry of  $\text{Mo}_2\text{Cl}_4^{4-}$  showing the correlation of these orbitals to those in the  $D_{4h}$  ground-state geometry. The arrows indicate the HOMO.

lie in a plane and two bridging ligands, a geometry adopted by numerous  $\text{M}_2\text{X}_6$  complexes. The transition state is, however, greatly distorted from tetrahedral about each metal. An orbital analysis was carried out on the model complex  $\text{W}_2(\text{OH})_6$ , the results of which are depicted in Figure 3. The distortion from ethane-like geometry,  $D_{3d}$  ( $\phi = 36^\circ$ ), leads to  $C_{2h}$  symmetry during the rotation and finally  $D_{2h}$  at the transition state ( $\phi = 0^\circ$ ). The M-M  $\pi$  orbitals ( $1a_u, 1b_u$ ) are again split in energy whereas the M-M  $\sigma$  orbital ( $1a_g$ ) remains essentially unperturbed throughout the flip. The  $1a_u$   $\pi$  orbital is destabilized significantly at the transition state, due to W-O  $\sigma^*$  interactions with the terminal OH ligands, yet remains the HOMO such that no filled-empty level crossing is observed and the process is again symmetry allowed.

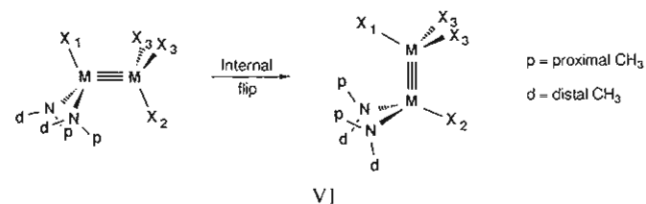
### Concluding Remarks

The orbital analysis presented here shows that the internal flip of a dinuclear metal unit within a cube or octahedral group of ligands represented by M-M quadruple ( $\sigma^2\pi^4\delta^2$ ) or triple bonds ( $\sigma^2\pi^4$ ), respectively, is not forbidden by symmetry, at least not within the limitation of the Fenske-Hall method. The calculational method employed does not allow us to estimate energy barriers, though it is clear from the Walsh diagrams that metal-metal bonding is weakened in the transition state. Cotton,<sup>16</sup> in reporting the disordered structure of  $\text{Mo}_2(\text{NMe}_2)_2(\text{OC}(\text{CF}_3)_3)_4$ , suggested that an internal flip might also be responsible for the observed exchange of proximal and distal *N*-methyl groups that is typically seen in the variable-temperature NMR behavior of dimethylamide groups attached to the  $(\text{M}\equiv\text{M})^{6+}$  unit ( $\text{M} = \text{Mo}, \text{W}$ ). We note here that although this cannot be discounted in the parent compounds  $\text{M}_2(\text{NMe}_2)_6$ ,<sup>21</sup> the internal flip mechanism can be discounted as the threshold mechanism for proximal = distal methyl exchange in situations of lower symmetry. For example,

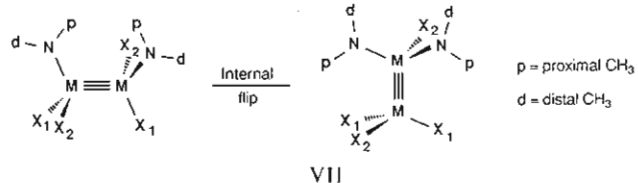


**Figure 3.** Walsh diagram for  $\text{W}_2(\text{OH})_6$  depicting the variations in frontier orbital energies as the W-W vector is rotated through  $36^\circ$  from a position directed at opposite faces of the octahedron to edges of the octahedron. The orbitals are labeled according to  $C_{2h}$  symmetry.

in a 1,1- $\text{M}_2(\text{NMe}_2)_2\text{X}_4$  compound such as was described for  $\text{M} = \text{Mo}$  and  $\text{X} = \text{CH}_2\text{SiMe}_3$ ,<sup>22</sup> the internal flip that would lead to proximal and distal exchange would also lead to an equivalence of the attendant ligands  $\text{X}_1$  and  $\text{X}_2$ ; see VI. The latter is not observed, yet proximal and distal methyl exchange is observed in both 1,1- and 1,2- $\text{M}_2(\text{NMe}_2)_2\text{X}_4$  isomers.



Similarly, in  $\text{M}_2\text{X}_4(\text{NMe}_2)_2$  compounds of the type shown in VII, proximal and distal *N*-methyl group exchange by an internal flip would scramble 1,1- and 1,2-isomers; see VII. Consequently,



we can say that if the internal flip mechanism is operative for a  $(\text{M}\equiv\text{M})^{6+}$  unit within a quasi-octahedral grouping of ligands, it is not a sufficiently low energy process to be detected by dynamic NMR techniques, and it is not operative in some instances such as for  $\text{Mo}_2(\text{NMe}_2)_2(\text{CH}_2\text{SiMe}_3)_4$ , which persists indefinitely in either of 1,1- or 1,2-isomers at room temperature.

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## Appendix

The geometry of  $\text{Mo}_2\text{Cl}_6^{4-}$  was constructed by placing a Mo-Mo vector of 2.14 Å in a cube of Cl atoms with a Cl--Cl edge distance of 3.38 Å. This provides a Mo-Cl bond length of 2.47 Å and a Mo-Mo-Cl angle of 104.6°. The Walsh diagram was constructed by rotating the Mo-Mo vector through 45° about an axis perpendicular to the Mo-Mo vector. The transition state pictured in V was generated by aligning the Mo-Mo vector along a diagonal defined by two opposite corners of the cube. This results in Mo-Cl distances of 1.85 Å (apical) and 2.76 Å (equatorial). The atomic parameters of  $\text{W}_2(\text{OH})_6$  were obtained by locating a W-W vector of 2.24 Å inside an octahedron of OH ligands with an O--O edge distance of 3.25 Å and an O-H distance of 0.96 Å. With the W-W vector oriented toward the centroid of two opposite faces ( $D_{3d}$  symmetry), a W-O distance of 1.89 Å and a W-W-O angle of 98° result. The Walsh diagram was constructed by rotating the W-W vector 36° toward an edge of the octahedron about an axis perpendicular to the W-W vector.

All atomic wave functions were generated by using the method of Bursten, Jensen, and Fenske.<sup>23</sup> Contracted double- $\zeta$  representations were used for the Mo 4d, W 5d, Cl 3p, and O 2p AOs. In the basis functions for Mo and W, the following exponents were fixed: Mo 5s and 5p, 2.20; W 6s and 6p, 2.40. All calculations were converged with a self-consistent-field iterative technique using a convergence criteria of 0.0010 as the largest deviation of atomic orbital populations between successive cycles.

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### Synthesis and Characterization of the Mixed-Valence Complex $\text{LMo}^{\text{V}}\text{OCl}(\mu\text{-O})\text{Mo}^{\text{VI}}\text{O}_2\text{L}$ (L = Hydrotris(3,5-dimethyl-1-pyrazolyl)borate)

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Oxo-thio-Mo(VI) complexes are much sought after models of the active site of oxidized, active xanthine oxidase and xanthine dehydrogenase.<sup>1</sup> However, only a restricted number and variety of such complexes have been isolated to date;<sup>2-4</sup> these include the oxothiomolybdates,  $[\text{MoO}_4-x\text{S}_x]^{2-}$  ( $x = 1-3$ ),<sup>2</sup> and the  $\text{MoOS}(\text{ONR}_2)_2$  ( $\text{R} = \text{Et}$ ;  $\text{R}_2 = \text{C}_5\text{H}_{10}$ ) complexes reported by Wieghardt and co-workers.<sup>3</sup> These complexes were prepared by the reaction of a sulfiding agent such as  $\text{H}_2\text{S}$ ,  $\text{B}_2\text{S}_3$ , or  $(\text{Me}_3\text{Si})_2\text{S}$  with precursor oxo complexes. Fallner and Ma<sup>4</sup> recently reported the synthesis of stable  $\text{Cp}^*\text{MoOS}(\text{CH}_2\text{SiMe}_3)$  ( $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5^-$ ) and  $\text{Cp}^*\text{WOSR}$  ( $\text{R} = \text{Me}$ ,  $\text{CH}_2\text{SiMe}_3$ ) complexes by a similar methodology, viz., the reaction of  $\text{Cp}^*\text{MO}_2\text{R}$  complexes with  $\text{H}_2\text{S}$ . The organometallic dioxo-M(VI) precursors were prepared by reaction of  $\text{Cp}^*\text{MO}_2\text{X}$  with the appropriate Grignard reagent in tetrahydrofuran or diethyl ether.<sup>5</sup> Their synthesis parallels the

transmetalation reactions employed in the synthesis of other stable organometallic dioxo-Mo(VI) complexes such as  $\text{MoO}_2\text{Br}(\text{R})$ - $(\text{bpy})$  ( $\text{R} = \text{Me}$ ,  $\text{Et}$ ,  $\text{CH}_2\text{-}t\text{-Bu}$ ,  $n\text{-Pr}$ ,  $i\text{-Pr}$ ,  $t\text{-Bu}$ ;  $\text{bpy} = 2,2'$ -bipyridine)<sup>6</sup> and  $\text{MoO}_2(\text{R})_2(\text{bpy})$  ( $\text{R} = \text{Me}$ ,<sup>7</sup>  $\text{Et}$  through  $\text{C}_6\text{H}_{11}$ ,<sup>8</sup>  $\text{CH}_2\text{Ph}$ ,<sup>9</sup>  $\text{CH}_2\text{-}t\text{-Bu}$ <sup>10</sup>). Our interest in the synthesis of oxo-thio-Mo(VI) complexes of hydrotris(3,5-dimethylpyrazolyl)borate,  $\text{HB}(\text{Me}_2\text{pz})_3^-$ , as models of xanthine oxidase and the frequent similarity in the chemistries of  $\text{Cp}^*$ - and  $\text{HB}(\text{Me}_2\text{pz})_3^-$  complexes, led us to contemplate the reaction of  $[\text{HB}(\text{Me}_2\text{pz})_3]\text{MoO}_2\text{R}$  complexes with  $\text{H}_2\text{S}$  as a route to  $[\text{HB}(\text{Me}_2\text{pz})_3]\text{MoOSR}$  complexes. Our initial attempts to prepare the necessary  $[\text{HB}(\text{Me}_2\text{pz})_3]\text{MoO}_2\text{R}$  precursors focused on the reactions of  $[\text{HB}(\text{Me}_2\text{pz})_3]\text{MoO}_2\text{Cl}$ <sup>11</sup> with Grignard reagents, but in contrast to the chemistry observed in the  $\text{Cp}^*$ - system<sup>5</sup> these reactions resulted in the formation of the mixed-valence complex  $[\text{HB}(\text{Me}_2\text{pz})_3]\text{Mo}^{\text{V}}\text{OCl}(\mu\text{-O})\text{Mo}^{\text{VI}}\text{O}_2[\text{HB}(\text{Me}_2\text{pz})_3]$  (**1**). Mixed-valence compounds now attract considerable interest, and early-transition-metal compounds of this type have been exhaustively reviewed by Young.<sup>12</sup> Dinuclear  $\text{Mo}^{\text{V}}\text{Mo}^{\text{VI}}$  complexes are in fact rare, and none have been previously isolated or structurally characterized. The synthesis and characterization of complex **1** are reported herein.

### Results and Discussion

Reaction of *cis*- $[\text{HB}(\text{Me}_2\text{pz})_3]\text{MoO}_2\text{Cl}$  with the Grignard reagent  $\text{MeMgCl}$ ,  $\text{MeMgI}$ , or  $\text{PhCH}_2\text{MgBr}$  in tetrahydrofuran at  $-78$  or  $-42$  °C produced a deep brown reaction mixture after rapid disappearance of an initial transient green coloration. Examination of the reaction mixture by thin-layer chromatography (silica/ $\text{CH}_2\text{Cl}_2$ ) revealed the presence of up to six products depending on the reaction and the conditions used. Intense purple compounds, likely to possess di- or polynuclear structures, are observed along with orange-brown **1** ( $R_f$  ca. 0.46). Column chromatography allowed the separation and crystallization of all components, but the small quantities of the byproducts prevented their unambiguous characterization. The formation of **1** is clearly a multistep process, and a possible reaction sequence leading to its formation involves (1) initial reaction of  $[\text{HB}(\text{Me}_2\text{pz})_3]\text{Mo}^{\text{VI}}\text{O}_2\text{Cl}$  and  $\text{RMgX}$  to produce coordinatively unsaturated  $[\text{HB}(\text{Me}_2\text{pz})_3]\text{Mo}^{\text{V}}\text{O}_2$ ,  $\text{MgXCl}$ , and  $1/2 \text{R}_2$  (note, dibenzyl is isolated from reactions involving  $\text{PhCH}_2\text{MgBr}$ ), (2) reaction of  $[\text{HB}(\text{Me}_2\text{pz})_3]\text{Mo}^{\text{V}}\text{O}_2$  with  $[\text{HB}(\text{Me}_2\text{pz})_3]\text{Mo}^{\text{VI}}\text{O}_2\text{Cl}$  to form  $[\text{HB}(\text{Me}_2\text{pz})_3]\text{Mo}^{\text{V}}\text{O}_2(\mu\text{-O})\text{Mo}^{\text{VI}}\text{OCl}[\text{HB}(\text{Me}_2\text{pz})_3]$ , and (3) intramolecular electron transfer to produce the energetically favored class I<sup>13</sup> mixed-valence complex, **1**. The transient green coloration may arise from the presence of the initially formed  $[\text{HB}(\text{Me}_2\text{pz})_3]\text{Mo}^{\text{V}}\text{O}_2$  complex or the first mixed-valence species. Notably, we have not been able to detect or isolate any organometallic species  $[\text{HB}(\text{Me}_2\text{pz})_3]\text{MoO}_2\text{R}$  ( $\text{R} = \text{Me}$ ,  $\text{CH}_2\text{Ph}$ ) in the reactions above. This result contrasts with the isolation of the stable transmetalation products in reactions involving Grignard reagents and analogous dioxo-Mo(VI) species.<sup>5-10</sup>

Orange-brown, air-stable **1** was characterized by elemental analysis, infrared, electronic, and ESR spectroscopy, mass spectrometry, magnetic susceptibility measurements, and X-ray

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