halide still appears to be the primary reason for the different axial splittings with different counterions and provides a reasonable explanation for the high-temperature behavior of *D*. A third lattice mechanism will be necessary to explain the increase observed for *D* at low temperatures.

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Registry No. $[Co(NH_3)_5Cl]Cl_2$, 13859-51-3; $[Co(NH_3)_5Cl]Br_2$, 13601-43-9; $[Co(NH_3)_5Cl]I_2$, 57255-93-3; $[Co(NH_3)_5Cl](NO_3)_2$, 13842-33-6; $[Co(NH_3)_5Br]Cl_2$, 13601-38-2; $[Co(NH_3)_5Br]Br_2$, 14283-12-6; $[Co(NH_3)_5Br]I_2$, 14591-70-9; $[Co(NH_3)_5Br](NO_3)_2$, 21333-43-7; $[Cr(NH_3)_5Cl]$, 14482-76-9; $[Cr(NH_3)_5Br]$, 22289-65-2.

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Synthesis of Mo(IV) and Mo(V) Complexes Using Oxo Abstraction by Phosphines. Mechanistic Implications

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The reactions of the Mo(VI) compounds MoO_2L_2 (L = S_2CNR_2, S_2PR_2, cysteinato methyl ester, acetylacetonato, 8-hydroxyquinolinato) with tertiary phosphines provides a convenient route to the Mo(V) species $Mo_2O_3L_4$ and in some cases (L = S_2CNR_2, S_2PR_2) to the Mo(IV) complexes $OMoL_2$. The extent of the reduction, i.e., to Mo(V) or Mo(IV), is rationalized in terms of the magnitude of the equilibrium constant for reaction of $OMoL_2$ (formed by oxo abstraction) with unreacted MoO_2L_2 to form $Mo_2O_3L_4$ which must dissociate to be reducible. Infrared and visible spectral properties are given for the new dithiophosphinato complexes prepared by this method.

It has been reported[1] that triphenylphosphine abstracts an oxo group from dioxobis(*N*,*N*-dialkyldithiocarbamato)molybdenum(VI) $[MoO_2(S_2(S_2CNR_2)_2]$ yielding $OMo(S_2CNR_2)_2$ and triphenylphosphine oxide. This reaction, together with the recently discovered[1,2] equilibrium (eq 1), was

$$Mo_2O_3(S_2CNR_2)_4 \rightleftarrows MoO_2(S_2CNR_2)_2 + OMo(S_2CNR_2)_2 \qquad (1)$$

used in the design[1] of a system for the catalytic aerial oxidation of phosphines. Because of our continuing interest in the chemistry of oxomolybdenum species as possible models for molybdoenzymes,[2-5] we have utilized and extended this type of oxo abstraction reaction to provide a convenient method of synthesis for a variety of oxomolybdenum(V) and -(IV) complexes. This report describes the synthetic methods and gives data which provide insight into the mechanism of the reactions.

Experimental Section

All reactions were carried out under an argon atmosphere using standard techniques. All solvents were dried over molecular sieves and degasses prior to use. The compounds $MoO_2(S_2CNR_2)_2$ (R = Me, Et, *n*-Pr), $MoO_2(ox)_2$ (ox = 8-hydroxyquinolinato), and MoO_2(cyst-OMe)$_2$ (cyst-OMe = cysteinato methyl ester) were synthesized by literature methods.[6-8]

Infrared spectra were recorded on a Beckman IR20A spectrophotometer and uv–visible spectra on a Cary 118C instrument. Elemental analyses for CHN were determined in this laboratory using either a Hewlett-Packard 185 or a Perkin-Elmer 240 instrument.

Synthesis of Compounds. $MoO_2(acac)_2$. The complex was prepared by a modification of the literature methods.[9,10] $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (30.0 g) was dissolved in H_2O (100 ml) and acetylacetone (acacH; 40 ml) was added. The pH of the solution was adjusted to 3.5 using 10% HNO_3 and a solid began to precipitate. After 1.5 h, yellow $MoO_2(acac)_2$ (28 g, 51% yield) (identified by ir spectrum) was isolated by filtration, washed with H_2O, ethanol, and ether, and dried in vacuo.

$MoO_2(S_2PPh_2)_2$. A solution of HS_2PPh_2 (4.0 g) in ethanol (50 ml) was added to a solution of $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (1.5 g) in H_2O (70 ml). After stirring for 20 min, yellow $MoO_2(S_2PPh_2)_2$ (2.54 g, 48% yield) was isolated by filtration, washed with H_2O, ethanol, and ether, and dried in vacuo. Anal. Calcd for $C_{24}H_{20}MoO_2P_2S_4$: C, 46.0; H, 3.22. Found: C, 46.3; H, 3.09.

$MoO_2[S_2P(i\text{-}Pr)_2]_2$. This compound was prepared in an identical manner to $MoO_2(S_2PPh_2)_2$. The yield was 5.10 g, 53%. Anal. Calcd for $C_{12}H_{28}MoO_2P_2S_4$: C, 29.38; H, 5.75. Found: C, 29.53; H, 5.87.

$Mo_2O_3(acac)_4$. PPh_2Et (0.90 ml) was added to a solution of $MoO_2(acac)_2$(1.0 g) in dichloroethane (50 ml) and the solution was refluxed for 45 min. The reaction mixture was cooled and the dark precipitate of $Mo_2O_3(acac)_4{\cdot}C_2H_4Cl_2$ (0.70 g, 72% yield) was isolated by filtration, washed with ethanol and ether, and dried in vacuo. Anal. Calcd for $C_{22}H_{32}Cl_2Mo_2O_{11}$: C, 35.9; H, 4.35. Found: C, 35.4; H, 4.12.

$Mo_2O_3(ox)_4$. PPh_2Et (1.5 ml) was added to a suspension of $MoO_2(ox)_2$ (1.0 g) in dichloroethane (60 ml) and the reaction mixture was refluxed for 3.5 h. The dark precipitate of $Mo_2O_3(ox)_4$ (0.90 g, 92% yield) (identified by its ir and visible spectra) was isolated by filtration, washed with ethanol and ether, and dried in vacuo. Anal. Calcd for $C_{36}H_{24}N_4Mo_2O_7$: C, 52.9; H, 2.94; N, 6.86. Found: C, 52.3; H, 2.94; N, 6.55.

Mo_2O_3(cyst-OMe)$_4$. PPh_3 (0.86 g) was added to a suspension of MoO_2(cyst-OMe)$_2$ (1.0 g) in CH_2Cl_2 (50 ml). The reaction mixture was refluxed for 18 h, cooled to room temperature, and filtered, and the filtrate was evaporated to dryness under vacuum to yield a purple oil. Trituration with ethanol yielded the purple product (0.65 g, 67% yield), which was isolated by filtration, washed with ethanol and ether, and dried in vacuo. Anal. Calcd for $C_{16}H_{32}Mo_2N_4O_{11}S_4$: C, 24.7; H, 4.10; N, 7.22. Found: C, 25.0; H, 4.20; N, 7.00.

$Mo_2O_3[S_2PPh_2]_4$. PPh_2Et (0.084 g) was added to a solution of $MoO_2(S_2PPh_2)_2$ (0.475 g) in CH_2Cl_2 (30 ml). The reaction mixture immediately became purple and after 1 h the purple precipitate (0.38 g, 81% yield) was filtered off, washed with ethanol and ether, and dried in vacuo. Anal. Calcd for $C_{48}H_{40}Mo_2O_3P_4S_8$: C, 46.6; H, 3.26. Found: C, 46.3; H, 3.56.

$Mo_2O_3[S_2P(OEt)_2]_4$. The known[6] compound was synthesized by utilizing the reducing ability of the ligand. $HS_2P(OEt)_2$ (6.6 ml) was added to a solution of $MoO_2(acac)_2$ (4.0 g) in methanol (80 ml). After stirring for 45 min, the dark purple product (3.9 g, 65% yield) (identified by its ir spectrum) was isolated by filtration, washed with methanol and ether, and dried in vacuo. Anal. Calcd for $C_{16}H_{40}Mo_2O_{11}P_4S_8$: C, 19.6; H, 4.08. Found: C, 20.0; H, 4.00.

$Mo_2O_3(S_2CNEt_2)_4$. PPh_2Et (0.30 g) was added to a solution of $MoO_2(S_2CNEt_2)_2$ (1.19 g) in CH_2Cl_2 (40 ml). After stirring for 3 h at room temperature, the deep purple reaction mixture was evaporated to dryness under vacuum and the residue was triturated with ethanol. The resulting purple solid, $Mo_2O_3(S_2CNEt_2)_4 \cdot {}^1/_2CH_2Cl_2$ (1.09 g, 89% yield) (identified by its ir spectrum), was isolated by filtration, washed with ethanol and ether, and dried in vacuo. Anal. Calcd for $C_{20.5}H_{41}N_4ClMo_2O_3S_8$: C, 28.1; H, 4.69; N, 6.40. Found: C, 28.0; H, 4.59; N, 6.30.

OMo[S_2P(*i*-Pr)$_2$] Solid $MoO_2[S_2P(i\text{-}Pr)_2]_2$ (0.48 g) was added to a solution of PPh_2Et (0.5 ml) in CH_2Cl_2 (40 ml). After stirring for 30 min, the red-purple solution was evaporated to dryness under vacuum and the oily residue was triturated with MeOH. The resulting lavender solid (0.39 g, 85% yield) was isolated by filtration, washed with MeOH, and dried in vacuo. Anal. Calcd for $C_{12}H_{28}MoOP_2S_4$: C, 30.4; H, 5.90. Found: C, 30.0; H, 5.90.

$OMo(S_2PPh_2)_2$. PPh_2Et (0.3 ml) was added to a solution of $MoO_2(S_2PPh_2)_2$ (0.60 g) in dichloroethane (40 ml). After refluxing for 30 min, the reaction mixture was filtered and the red filtrate was evaporated under vacuum to a volume of 5 ml. Addition of ethanol (60 ml) caused the crystallization of pink $OMo(S_2PPh_2)_2$ (0.48 g, 83% yield), which was isolated by filtration, washed with ethanol and ether, and dried in vacuo. Anal. Calcd for $C_{24}H_{20}MoOP_2S_4$: C, 47.2; H, 3.30. Found: C, 46.8; H, 3.01.

$OMo(S_2CNEt_2)_2$. PPh_2Et (3.0 ml) was added to a solution of $MoO_2(S_2CNEt_2)_2$ (3.0 g) in dichloroethane (75 ml). After refluxing for 20 min, the red reaction mixture was filtered and the filtrate was evaporated to dryness under vacuum. Trituration of the residue with ethanol yielded pink $OMo(S_2CNEt_2)_2$ (2.6 g, 90% yield) (identified by ir and visible spectra) which was isolated by filtration, washed with ethanol and ether, and dried in vacuo. Anal. Calcd for $C_{10}H_{20}N_2MoOS_4$: C, 29.4; H, 4.90; N, 6.86. Found: C, 29.5; H, 4.85; N, 6.94.

Similar reactions were carried out to yield the analogous dimethyl- and di-*n*-propyldithiocarbamato complexes.

$OMo[S_2P(OEt)_2]_2$. PPh_3 (0.24 g) was added to a solution of $Mo_2O_3[S_2P(OEt)_2]_4$ (0.60 g) in dichloroethane and the reaction mixture was heated at reflux for 10 min. The pink solution was filtered and the filtrate was evaporated to dryness yielding a pink oil which was extracted with hexane. Evaporation of the extract to dryness under vacuum gave a pink solid which was identified as a mixture of $OPPh_3$ and $OMo[S_2P(OEt)_2]_2$ by ir spectroscopy.

$OMo(S_2P(OMe)_2]_2$. The synthesis was attempted as for $OMo[S_2P(OEt)_2]_2$ but again a mixture of PPh_3, $OPPh_3$, and the desired compound was obtained.

Attempted Reactions of $OMo(S_2CNEt_2)_2$. With $OPPh_3$. $OMo(S_2CNEt_2)_2$ (0.127 g; 0.311 mmol) was added to a solution of $OPPh_3$ (0.26 g; 0.935 mmol) in $CHCl_3$ (10 ml) from which EtOH had been removed and which had previously been completely degassed on a vacuum line. The reaction mixture initially was pink, after ~6 h it was orange, after 16 hr it was yellow-brown, and then it showed no further discernible color change for 2 days. *No purple color was ever observed.* Evaporation of the reaction mixture to dryness under vacuum and trituration of the residue with diethyl ether gave a brown solid (0.084 g) which was shown to be a mixture of $Mo_2O_4(S_2CNEt_2)_2$, $OMoCl_2(S_2CNEt_2)_2$, and $OPPh_3$ by ir spectroscopy. The complete absence of $Mo_2O_3(S_2CNEt_2)_4$ or $MoO_2(S_2CNEt_2)_2$ was confirmed by the ir spectrum.

A reaction mixture prepared using the commonly available $CHCl_3$ containing 0.75% EtOH underwent color changes virtually identical with those described above. Again, no purple color was observed.

With N_2O. $OMo(S_2CNEt_2)_2$ (0.117 g; 0.287 mmol) was dissolved in $CHCl_3$ (10 ml) which contained 0.75% EtOH and had previously been completely degassed on a vacuum line. The solution was frozen in liquid N_2 and N_2O (150 ml; 6.0 mmol) was condensed into the reaction vessel. After condensation was complete, the reaction vessel was evacuated to ensure removal of all noncondensable gases, the vessel was sealed, and the solution was allowed to warm to room temperature. The reaction mixture was agitated on a mechanical shaker for 3 days when it was frozen in liquid N_2 and the evolved noncondensable gas (0.005 mmol N_2; identified by mass spectrum) was collected using a Toepler pump. The yield was 1.7% based on $OMo(S_2CNEt_2)_2$.

In an identical experiment but with the vessel containing only $CHCl_3$ [i.e., no $OMo(S_2CNEt_2)_2$ present], the yield of N_2 was also 0.005 mmol, showing that the Mo(IV) complex plays no role in the formation of the small amount of N_2.

With $CHCl_3$. A solution of $OMo(S_2CNEt_2)_2$ (0.30 g) in $CHCl_3$ (30 ml) which contained 0.75% EtOH was kept at room temperature for 3 days during which time it changed from pink to yellow-brown. After evaporation to dryness and trituration with diethyl ether, the yellow-brown solid was isolated by filtration, washed with diethyl ether, and dried in vacuo. The product was shown to be a mixture of $Mo_2O_4(S_2CNEt_2)_2$ and $OMoCl_2(S_2CNEt_2)_2$ by ir spectroscopy. In a similar experiment but using ethanol-free $CHCl_3$, the same two products in a slightly different ratio were isolated.

Results and Discussion

During our attempts to extend studies[3] of the reactivity of $OMo^{IV}L_2$ species, we found it necessary to develop a reliable synthetic procedure for $OMo[S_2P(i\text{-}Pr)_2]_2$, a compound not previously reported. Although both reduction of Na_2MoO_4–$HS_2P(i\text{-}Pr)_2$ mixtures with $Na_2S_2O_4$ (analogous to the known[11] procedure for $OMo(S_2CNEt_2)_2$) and Zn dust reduction of the dark-red product (presumably containing $Mo_2O_3[S_2P(i\text{-}Pr)_2]_4$) from acidification of ice-cold mixtures of $MoCl_5$ and $(i\text{-}Pr)_2PS_2H$ gave some $OMo[S_2P(i\text{-}Pr)_2]_2$, in neither case was the yield and purity of the complex or the method of preparation entirely satisfactory. We then tried the reduction of the easily synthesized $MoO_2[S_2P(i\text{-}Pr)_2]_2$ with PPh_3 and found it to be both a rapid and high-yield method. We have since discovered that the more basic PPh_2Et is an even better reducing agent and is preferable to PPh_3 in most cases. In addition, we have carried out the phosphine reductions of MoO_2L_2 [L = acetylacetonato (acac), cysteinato methyl ester (cyst-OMe), and 8-hydroxyquinolinato (ox)]. With excess phosphine in refluxing 1,2-dichloroethane, these Mo(VI) complexes produce the dinuclear oxo-bridged Mo(V) species, $Mo_2O_3L_4$, in good yield. The method is preferable to those previously described for $Mo_2O_3(ox)_4$ (where Mo(VI) was slowly reduced with Hg[12]) and for $Mo_2O_3(cyst\text{-}OMe)_4$ (where $MoCl_5$ was added to cyst-OR·HCl and the pH adjusted[8]) and is at least of comparable ease to the sealed tube method previously[10] used for $Mo_2O_3(acac)_4$.

The synthesis of the new complex $Mo_2O_3(S_2PPh_2)_4$ and the known $Mo_2O_3(S_2CNEt_2)_4$ by addition of exactly 0.5 mol of phosphine to solutions of the appropriate MoO_2L_2 was also very facile. Attempts to prepare $Mo_2O_3[S_2P(i\text{-}Pr)_2]_4$ by this method were unsuccessful, probably due to the disproportionation reaction which the Mo(VI) species was found[13] to undergo (eq 2). In fact, to our knowledge, $Mo_2O_3[S_2P(i\text{-}Pr)_2]_4$ has not been prepared in pure form by any method.

$$2MoO_2[S_2P(i\text{-}Pr)_2]_2 \rightarrow Mo_2O_4[S_2P(i\text{-}Pr)_2]_2 + (i\text{-}Pr)_2P(S)S\text{–}S(S)P(i\text{-}Pr)_2 \qquad (2)$$

Addition of excess phosphine to solutions of MoO_2L_2 [L = S_2CNEt_2, S_2PPh_2, $S_2P(i\text{-}Pr)_2$] in refluxing dichloroethane results in the rapid formation of the Mo(IV) species, $OMoL_2$. While the compound $OMo(S_2CNEt_2)_2$ can be prepared in one step by dithionite reduction of Na_2MoO_4–NaS_2CNEt_2 mixtures,[11] the two-step method described here (involving preparation of MoO_2L_2 and its subsequent reduction) is less time consuming overall and, in our hands, yields a more consistently pure product.

Reduction of the complexes $Mo_2O_3[S_2P(OR)_2]_4$ (R = Me, Et) with phosphine in boiling dichloroethane yielded impure preparations of the known[11] Mo(IV) compounds OMo-

Table I. Spectral Properties of Dithiophosphinate Complexes

Compd	Infrared[a]	Visible[b]
$MoO_2(S_2PPh_2)_2$	890, 925	375 sh (3870)
$MoO_2(S_2P(i\text{-}Pr)_2)_2$	890, 925	371 (3270)
$OMo(S_2PPh_2)_2$	970	540 (307), 475 sh (239), 395 sh (832), 352 (1540)
$OMo[S_2P(i\text{-}Pr)_2]_2$	975	555 (113), 475 sh (63), 331 (293)
$Mo_2O_3(S_2PPh_2)_4$	955	508 (3010)[c] 508 (5920)[d]

[a] Terminal Mo=O stretching frequencies in cm^{-1}. [b] Peak positions in nm with molar absorptivity in parentheses. [c] $[Mo_2O_3L_4] = 1.023 \times 10^{-4}$ M. [d] $[Mo_2O_3L_4] = 2.046 \times 10^{-4}$ M.

$[S_2P(OR)_2]_2$. Hence the phosphine method does not seem to offer any significant advantage over that previously[11] employed where the Mo(V) complexes were reduced with Zn in the presence of excess $HS_2P(OR)_2$.

Spectra of New Dithiophosphinate Complexes. The infrared spectra of the complexes $OMo(S_2PR_2)_2$ and $MoO_2(S_2PR_2)_2$ are summarized in Table I. The positions of the assigned bands are consistent with previous assignments involving Mo(IV) and Mo(VI) species.[2,11] The infrared spectrum of $Mo_2O_3(S_2PPh_2)_4$ contains a sharp band at 955 cm^{-1} assigned to the terminal Mo=O stretch of the Mo_2O_3 moiety. Unfortunately, the spectral regions expected[2] to contain the symmetric and antisymmetric bridge vibrations (~740 and ~480 cm^{-1}, respectively) are complicated by bands due to the ligand.

The electronic spectra of the Mo(IV) and Mo(VI) complexes are given in Table I. The band positions and molar absorptivities are fairly similar to those reported[2,11] for other $OMoL_2$ and MoO_2L_2 complexes. The visible spectrum of $Mo_2O_3(S_2PPh_2)_4$ contains a band at 508 nm which does not obey Beer's law (see Table I). This behavior is identical with that observed[1,2] for $Mo_2O_3(S_2CNR_2)_4$ and can be explained in terms of the equilibrium (eq 3) which is well established

$$Mo_2O_3(S_2PPh_2)_4 \rightleftarrows OMo(S_2PPh_2)_2 + MoO_2(S_2PPh_2)_2 \qquad (3)$$

for dithiocarbamate systems.

Mechanistic Implications. In the oxo abstraction reactions from the complexes MoO_2L_2, the degree of reduction, i.e., to Mo(IV) or Mo(V), depends on the ligands involved. Thus, with L = cyst-OMe, ox, and acac, reduction only proceeds to the $Mo^V{}_2O_3L_4$ level even when a large excess of phosphine is utilized. In contrast, with L = S_2CNR_2 and S_2PR_2, reduction to $OMo^{IV}L_2$ is easily achieved under mild conditions. These two ligand groups are also differentiated by the fact that, in the former group (acac, ox, cyst-OMe), the $Mo_2O_3L_4$ complexes do not dissociate (i.e., their visible spectral band at ~510 nm obeys Beer's law) while the dinuclear species of the latter group (S_2CNR_2, S_2PR_2) dissociate via the equilibria shown in eq 1 and 3. These differences are related. The presence or absence of dissociation of the $Mo_2O_3L_4$ species can explain whether or not the $OMo^{IV}L_2$ species will be isolated for a particular ligand system.

The first step of reduction for the complexes of all ligands involves abstraction of an oxo group from MoO_2L_2 (eq 4).

$$MoO_2L_2 + PR_3 \rightarrow OMoL_2 + OPR_3 \qquad (4)$$

The next step of the reaction sequence, and the most important in determining the final product, is the reaction of the $OMoL_2$ just formed with unreacted MoO_2L_2 (eq 5).

$$MoO_2L_2 + OMoL_2 \rightleftarrows Mo_2O_3L_4 \qquad (5)$$

If eq 5 is not an equilibrium, but in fact lies completely toward $Mo_2O_3L_4$, then each mole of $OMoL_2$ formed will immediately react with a mole of MoO_2L_2 to form the dinuclear Mo(V) species. This situation must exist for the complexes with L = cyst-OR, acac, and ox because their visible spectra obey Beer's law. Thus, the final product for these complexes is predicted to be $Mo_2O_3L_4$ and not $OMoL_2$, *if* reaction 5 is fast and $Mo_2O_3L_4$ does not react with PR_3. This result is experimentally observed for these ligands.

If eq 5 is an equilibrium, then there will always be MoO_2L_2 present for reduction by PR_3 causing the equilibrium to shift to the left until only $OMoL_2$ remains. This equilibrium situation obviously exists for L = S_2CNR_2 and S_2PR_2 because the visible spectra of the $Mo_2O_3L_4$ species for these ligands do not obey Beer's law and $OMoL_2$ is the product of PR_3 reduction.

Thus, Mo(VI) may be reduced to Mo(IV) without the "intermediate" Mo(V) complex being at all reducible. Indeed, the above results (which show that the $Mo_2O_3L_4$ species which do not dissociate cannot be further reduced) support the idea that $Mo_2O_3L_4$ species which *do* dissociate are not directly reducible either. Only by dissociating to give Mo(VI) and Mo(IV) do these complexes undergo further reduction. Thus, the dinuclear Mo(V) species in both the S_2CNR_2 and S_2PR_2 systems are not intermediates in the reduction of Mo(VI) to Mo(IV) but are simply the products of a side reaction. This side reaction is so facile for the ox, acac, and cyst-OMe complexes that isolation of the Mo(IV) species is impossible by this method even though these complexes must be formed initially by oxo abstraction. This theory is in complete agreement with the ideas expressed in a review by Wentworth[14] (which appeared during the preparation of this article) to explain the observed products in the oxidation of aldehydes by Mo(VI).[15]

Our mechanism also predicts that the complexes $Mo_2O_3[S_2P(OR)_2]_4$ should undergo a similar dissociation to eq 3 because they are readily reduced to Mo(IV). In accordance with this suggestion, we find that the visible spectra of these species do not obey Beer's law. These data and other evidence for the dissociation of $Mo_2O_3[S_2P(OR)_2]_4$ will be given in a subsequent publication.

While this paper was in preparation, a publication[16] by Mitchell and Scarle appeared, concerning the oxidation of $OMo(S_2CNEt_2)_2$ by various organic oxo donors. Of particular interest to us was the report that it was possible to oxidize $OMo(S_2CNEt_2)_2$ to purple $Mo_2O_3(S_2CNEt_2)_4$ and finally to yellow $MoO_2(S_2CNEt_2)_2$ over a 3-day period using a threefold excess of $OPPh_3$. We felt this to be unlikely as we were able to completely *reduce* $MoO_2(S_2CNEt_2)_2$ to $OMo(S_2CNEt_2)_2$ using a stoichiometric amount of PPh_3. Accordingly, we repeated the experiment under the conditions[17] described by Mitchell and Scarle but using strictly anaerobic vacuum line techniques. We observed a change from pink to yellow over a 12-h period but observed *no purple color whatsoever.* On the basis of the mechanism described in this paper, the absence of purple color rules out any oxo transfer to form $MoO_2(S_2CNEt_2)_2$ because this species would immediately react with $OMo(S_2CNEt_2)_2$ to form $Mo_2O_3(S_2CNEt_2)_4$. Workup of a reaction mixture[17b] yielded a solid which was shown by a comparison of ir spectra to be a mixture of $Mo_2O_4(S_2CNEt_2)_2$ (ref 2), $OMoCl_2(S_2CNEt_2)_2$ (ref 4, 18), and $OPPh_3$ confirming the complete absence of $Mo_2O_3(S_2CNEt_2)_4$ and $MoO_2(S_2CNEt_2)_2$. Furthermore, we found that the change from pink to yellow occurred at the same rate *in the absence of any oxidizing agent*, again confirming that the final yellow color is not due to $MoO_2(S_2CNEt_2)_2$. We then showed that the solid isolated after stirring $OMo(S_2CNEt_2)_2$ in $CHCl_3$[17] for 3 days was again a mixture of $Mo_2O_4(S_2CNEt_2)_2$ and $OMoCl_2(S_2CNEt_2)_2$. This latter compound has its terminal Mo=O stretching frequency at 945 cm^{-1} in the ir[4,18] and is probably the "unidentified species" reported by Mitchell and Scarle to be present in some of their reaction mixtures.[19]

This result also prompted us to question the oxidation of $OMo(S_2CNEt_2)_2$ by N_2O which was described[16] as producing N_2 and purple $Mo_2O_3(S_2CNEt_2)_4$ (amounts unspecified) in a 2-day period. Repetition of this experiment under the conditions described (but again using vacuum line techniques and a Toepler pump to collect the gas) showed that no more N_2 was produced from a $CHCl_3$[17a] solution of $OMo(S_2CNEt_2)_2$ than was produced from $CHCl_3$ alone and that no purple color was ever present in the reaction mixture. The same change from pink to yellow that was observed in the absence of oxidizing agent was also seen in the presence of N_2O.

Thus, we find no evidence for oxo transfer between $OMo(S_2CNEt_2)_2$ and $OPPh_3$ or N_2O as was reported.[16] Some of the discrepancies between our work and that of Mitchell and Scarle may be due to inadvertent aerial oxidation of $OMo(S_2CNEt_2)_2$ by these latter authors.

Conclusions. The reduction of easily prepared *cis*-dioxomolybdenum(VI) complexes (MoO_2L_2) by oxo transfer to tertiary phosphine is a convenient method of synthesis for Mo(IV) ($OMoL_2$) and/or Mo(V) ($Mo_2O_3L_4$) species. The Mo(IV) complexes are produced *only* if the interaction of $OMoL_2$ with unreacted MoO_2L_2 (eq 5) is an equilibrium because the $Mo_2O_3L_4$ complexes do not appear to be directly reducible by tertiary phosphines. Oxidation of $OMoL_2$ by oxo transfer from tertiary phosphine oxide does not occur. Kinetic and thermochemical studies, which should provide further insight into the mechanism of these oxo abstraction reactions, are currently in progress.

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Registry No. $MoO_2(acac)_2$, 21884-95-7; $MoO_2(S_2PPh_2)_2$, 31398-25-1; $MoO_2[S_2P(i\text{-}Pr)_2]_2$, 60349-60-2; $Mo_2O_3(acac)_4$, 18285-19-3; $Mo_2O_3(ox)_4$, 17979-39-4; $Mo_2O_3(cyst\text{-}OMe)_4$, 23700-02-9; $Mo_2O_3[S_2PPh_2]_4$, 59796-78-0; $Mo_2O_3[S_2P(OEt)_2]_4$, 60384-05-6; $Mo_2O_3(S_2CNEt_2)_4$, 20023-86-3; $OMo[S_2P(i\text{-}Pr)_2]_2$, 60349-61-3; $OMo(S_2PPh_2)_2$, 59796-76-8; $OMo(S_2CNEt_2)_2$, 25395-92-0; $OMo[S_2P(OEt)_2]_2$, 25395-91-9; $OMo[S_2P(OMe)_2]_2$, 59796-75-7; $(NH_4)_6Mo_7O_{24}$, 12520-87-5; $MoO_2(ox)_2$, 21884-98-0; $MoO_2(cyst\text{-}OMe)_2$, 29683-37-2; $MoO_2(S_2CNEt_2)_2$, 18078-69-8; $OPPh_3$, 791-28-6; N_2O, 10024-97-2; $CHCl_3$, 67-66-3.

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(19) The complex $OMo(S_2CNEt_2)_2$ is very stable under anaerobic conditions in CH_2Cl_2. We have observed *no* color change from pink over a 12-day period for a reaction mixture containing $OMo(S_2CNEt_2)_2$ and $OPPh_3$ in a 1:3 ratio.

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Substituted 1,8-Naphthyridine Complexes of Iron(II) and Iron(III)

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The compounds $[Fe(2\text{-methyl-}1,8\text{-naphthyridine})_4](ClO_4)_2\cdot 2H_2O$, $[Fe(2,7\text{-dimethyl-}1,8\text{-naphthyridine})_3](ClO_4)_2\cdot 2H_2O$, $[Fe(2\text{-methyl-}1,8\text{-naphthyridine})_4](ClO_4)_3\cdot H_2O$, $[Fe(2,7\text{-dimethyl-}1,8\text{-naphthyridine})_4](ClO_4)_3\cdot H_2O$, $[Fe(2\text{-methyl-}1,8\text{-naphthyridine})_2Cl_2]\cdot H_2O$, and $[Fe(2,7\text{-dimethyl-}1,8\text{-naphthyridine})_2Cl_2]\cdot 3H_2O$ have been prepared and characterized by their Mössbauer, magnetic, and spectral properties. Also, the Mössbauer parameters of the previously reported $[Fe(2,7\text{-dimethyl-}1,8\text{-naphthyridine})_3](ClO_4)_2$ have been obtained. A modified synthesis of the ligands has been perfected and is reported in detail.

Introduction

Complexes of transition metals with 1,8-naphthyridine (napy) and 2,7-dimethyl-1,8-naphthyridine (2,7-dmnapy) have been extensively studied by Hendricker and co-workers. The unique eight-coordinate complexes of the first-row transition metal ions and the napy ligand have been isolated and characterized.[2] The ligand binds through the two nitrogen sites creating a four-membered chelate ring.[3] The chelate "bite" of the 1,8-naphthyridine system is ~2.2 Å[4] and satisfies the steric requirements for the abnormally high coordination number. The crystallographic structure of the eight-coordinate Fe(II) complex prepared by Hendricker and Bodner[5] revealed that the planarity of the naphthyridine ligand was maintained although one Fe–N bond distance on each ligand was lengthened to accommodate bidentate bonding from all four ligands.[4] Thus, the complex has significant distortion from high symmetry since there are four "long" and four "short" Fe–N bond lengths. The presence of this distortion has been dramatically substantiated by the observation of a very large (4.49 mm/s) quadrupole splitting in the Mössbauer spectrum of the perchlorate salt $[Fe(napy)_4](ClO_4)_2$.[6,7]

1,8-Naphthyridine complexes have also been prepared with Pd(II),[2] Ag(I),[8] alkaline earths,[9] molybdenum and tungsten carbonyls,[10] rare earth nitrates,[11] and transition metal nitrates.[12] These studies have shown that the naphthyridine moiety behaves as a monodentate ligand in some cases. The ligand has also been found as a bridging ligand in a series of nickel complexes.[13,14] The ligand has a basicity nearly equivalent to that of pyridine and it usually competes effectively with water for metal coordination sites in aqueous media although mixed ligand–aquo complexes have been isolated.[15] One unique, seven-coordinate complex, $[Hg(napy)_3(ClO_4)](ClO_4)$, has been characterized by x-ray crystallography as having three coordinated bidentate napy