Figure 9. Probable structure of [Mo(Ntol)S(S$_2$P(OEt)$_2$)]$_4$. The ethoxy groups are not shown.

having stoichiometries of MoX$_2$Y$_2$L$_2$ (L = bidentate ligand; X = Y = O or S and X = O, Y = S). Moreover the dinuclear natures of [(η^5-C$_5$H$_5$)Mo(NR)S]$_2$ (R = *t*-Bu) and [(η^5-C$_5$H$_5$)MoOS]$_2$ have been established.[23,39] A retrospective rationale has been found, however. Replacing the cyclopentadienyl rings, each being a five-electron donor, with bidentate ligands which are three-electron donors forces the dinuclear complex to attempt to compensate for the loss of four electrons. While it may be argued that the electron-rich bridging ligands allow compensation through multiple bonding, the chemistry of the Mo$_2$O$_4$ group points to some degree of unsaturation.[40] Alternatively, compensation can occur by way of the formation of a tetranuclear complex. It is possible that [Mo(Ntol)S(S$_2$P(OEt)$_2$)]$_4$ adopts the cubic [Mo(Ntol)]$_4$S$_4$ cluster since this structure would provide an easy means for joining two Mo$_2$(Ntol)$_2$S$_2$(S$_2$P(OEt)$_2$)$_2$ systems providing these systems include cis-imido ligands rather than the centrosymmetric structure found in [(η^5-C$_5$H$_5$)Mo(NR)S]$_2$.[23] Although

other structures may explain the ^{1}H and ^{31}P NMR spectra of this compound equally well, these spectra are in accord with the cubic structure (see Figure 9). We are not aware of any authenticated cubic structures containing molybdenum only, but reduced complexes containing a Mo$_4$S$_4$ cluster, [MoOS(S$_2$CNEt$_2$)]$_4^{n-}$ (n = 1 and 2), have been postulated previously.[41] Cubic Fe$_3$MoS$_4$ clusters are now known.[42]

Although the retrospective argument provides a means to rationalize the formation of this compound, it is clear from the large number of crystallographically authenticated dinuclear compounds that a very delicate balance of stereochemical forces must be operative. These forces may originate from either the imido ligand or the dithiophosphate ligand. If the former is responsible, then these forces, along with differences in trans effects, constitute two remarkable manifestations of differences in the chemistries of the imido and oxo ligands which otherwise appear to be very similar.[6]

Registry No. Mo(NPh)(S$_2$P(OEt)$_2$)$_3$, 72967-92-1; Mo(Ntol)(S$_2$P(OEt)$_2$)$_3$, 72967-91-0; Mo(NPh)Cl(S$_2$P(OEt)$_2$)$_2$, 72967-90-9; Mo(Ntol)Cl(S$_2$P(OEt)$_2$)$_2$, 72967-89-6; [Mo(Ntol)S(S$_2$P(OEt)$_2$)]$_4$, 73037-71-5; PhN$_3$, 622-37-7; tolN$_3$, 2101-86-2; Mo(CO)$_4$Cl$_2$, 15712-13-7; Mo(^{15}NPh)Cl(S$_2$P(OEt)$_2$)$_2$, 72967-88-5; Mo(^{15}NPh)(S$_2$P(OEt)$_2$)$_3$, 72967-87-4.

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Formation of Mo(S$_2$P(OEt)$_2$)$_3$, a Molybdenum(III) Complex with Ligation Only by Sulfur, and Its Reactions with Azobenzene

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The synthesis of Mo(S$_2$P(OEt)$_2$)$_3$ from Mo(CO)$_4$Cl$_2$, HS$_2$P(OEt)$_2$, and aryl azides is described. The reaction of this compound with azobenzene in ether containing HCl yields MoCl(S$_2$P(OEt)$_2$)$_3$ and benzidine rearrangemment products. The reaction of the Mo(III) complex with azobenzene in methanol gives Mo(OMe)$_2$(S$_2$P(OEt)$_2$)$_2$ and hydrazobenzene. Possible mechanisms are discussed.

Introduction

Our interest in the reaction of aryl azides with low-valent molybdenum complexes has led to a series of (arylimido)-molybdenum(VI) compounds[1,2] as well as the Mo(V) complexes Mo(NR)(S$_2$P(OEt)$_2$)$_3$ and Mo(NR)Cl(S$_2$P(OEt)$_2$)$_2$ (R = Ph and tol).[3,4] The latter were obtained from reaction of Mo(CO)$_4$Cl$_2$ with excess aryl azide in the presence of the

bidentate ligand. However, as we show herein, if this reaction is conducted with lesser quantities of the aryl azide, the Mo(III) complex Mo(S$_2$P(OEt)$_2$)$_3$ results. Our original intention was to establish another means to prepare (arylimido)molybdenum(V) complexes by the reaction of this compound with various azobenzenes. The only precedent for this reaction is the cleavage of hexafluoroazomethane by (Ph$_2$MeP)$_2$Ir(CO)Cl to give (Ph$_2$MeP)$_2$Ir(NCF$_3$)Cl.[5] While we have found that the desired reaction does not occur, the reaction with azobenzene does provide new Mo(IV) complexes and the reduction of azobenzene to hydrazobenzene.

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Experimental Section

Reagents and Procedures. Most of the reagents were either obtained or prepared by methods which were previously described.[4] An established method[6] was used to prepare $Mo(CO)_3(PPh_3)_2Cl_2$. The reaction of this compound (2.5 g) with a threefold excess of HS_2P-$(OEt)_2$ in 100 mL of methanol produced 2 g of precipitated Mo-$(CO)_2(PPh_3)(S_2P(OEt)_2)_2$[7] after 24 h. All of the subsequent reactions were routinely performed under an atmosphere of argon. Solvents were dried and distilled directly into reaction vessels whenever rigorously anhydrous and anaerobic conditions were required.

Preparation of Compounds. $Mo(S_2P(OEt)_2)_3$. The slow addition of $Mo(CO)_4Cl_2$ (11 mmol) to a solution of $HS_2P(OEt)_2$ (10 mL) and RN_3 (R = Ph or tol; 5.5 mmol) in ether (100 mL) was accompanied by the vigorous evolution of gas. After about 12 h, the solution was filtered and the solvent was removed under reduced pressure. Precipitation of the complex occurred after the addition of 20 mL of methanol. After filtration, the product was washed with methanol. Recrystallization from CH_2Cl_2/methanol gave bright red crystals (33%). Anal. Calcd for $Mo(S_2P(OEt)_2)_3$: C, 22.1; H, 4.6; S, 29.6; N, 0.0; mol wt 651. Found: C, 22.3; H, 4.8; S, 29.4; N, <0.1; mol wt (MS) 651. Magnetic moment (CH_2Cl_2, 33 °C): 3.8 μ_B. IR (Nujol): 1284 (m), 1160 (m), 1102 (m), 1010 (s), 965 (s), 807 (s), 633 (s), 522 (m), 384 (w), 354 (w), 287 (s) cm^{-1}.

$Mo(OMe)_2(S_2P(OEt)_2)_2$. A solution of $Mo(CO)_2(PPh_3)(S_2P$-$(OEt)_2)_2$ (0.9 mmol) and $tolN_3$ (1 mmol) in 25 mL of dry methanol was briefly refluxed. When the solvent was removed under reduced pressure, a light green product was obtained. Recrystallization from CH_2Cl_2/methanol afforded green acicular crystals (81%). Anal. Calcd for $Mo(OMe)_2(S_2P(OEt)_2)_2$: C, 22.8; H, 4.9; S, 24.3; N, 0.0; mol wt 528. Found: C, 22.9; H, 5.2; S, 24.2; N, <0.05; mol wt (MS) 528. ^1H NMR (CD_2Cl_2): δ 1.36 (6 H, t, CH_3), 3.43 (3 H, s, OCH_3), 4.07 (4 H, m, OCH_2). IR (nujol): 1140 (m), 1093 (s), 962 (s), 810 (m), 779 (m), 635 (m), 550 (m), 315 (w) cm^{-1}.

Alternatively, a solution of freshly recrystallized $Mo(S_2P(OEt)_2)_3$ (0.5 mmol) and azobenzene (2.5 mmol) in 10 mL of dry methanol was refluxed for 2 h. After the volume of the solvent was decreased under reduced pressure, $Mo(OMe)_2(S_2P(OEt)_2)_2$ was removed by filtration. Aniline (0.2 mmol) was found in the mother liquor by gas chromatography. The mother liquor was then treated with 20 mL of 3 M HCl and washed three times with ether. The aqueous phase was reduced to dryness, yielding a white powder. The latter was washed with absolute ethanol to remove anilinium chloride. The IR and ^1H NMR spectra of this material showed it to be primarily *p*-benzidine bis(hydrochloride).

$MoCl(S_2P(OEt)_2)_3$. A mixture of $Mo(S_2P(OEt)_2)_3$ (0.7 mmol) and azobenzene (1.1 mmol) was stirred in 25 mL of ether under gaseous HCl (4.0 mmol) for 24 h. The white precipitate which formed during the course of the reaction was removed by filtration, washed with ether, and identified as a mixture of *p*-benzidine bis(hydrochloride) and other products from the rearrangement of hydrazobenzene from the IR and ^1H NMR spectra. The green solution was taken to dryness to yield an oil. This material was solidified by covering it with pentane and recrystallized from ether/pentane. Dark green crystals were obtained (67%). Anal. Calcd for $MoCl(S_2P(OEt)_2)_3$: C, 21.0; H, 4.4; S, 28.0; N, 0.0; Cl, 5.2; mol wt 687. Found: C, 21.0; H, 4.5; S, 28.3; N, <0.5; Cl, 5.2; mol wt (osmometry) 689 ± 8. Magnetic moment (CH_2Cl_2, 33 °C): 2.7 μ_B. IR (Nujol): 1297 (w), 1166 (m), 1100 (w), 1038 (s), 1005 (s), 965 (s), 820 (m), 794 (s), 647 (m), 535 (w), 439 (w), 356 (w), 299 (m) cm^{-1}.

When this compound is dissolved in dry methanol, $Mo(OMe)_2$-$(S_2P(OEt)_2)_2$ can be recovered. If the alcohol contains water, the product is $MoO(S_2P(OEt)_2)_2$.

Attempted Reaction of $Mo(S_2P(OEt)_2)_3$ with Azobenzene in Aprotic Solvents. Attempts were made to induce a reaction between Mo-$(S_2P(OEt)_2)_3$ and azobenzene in CH_2Cl_2, benzene, or 1,2-dimethoxyethane under a wide range of thermal and photolytic conditions. In every case, no change in color was observed and starting materials were recovered at the completion of each attempt.

Reaction of $HS_2P(OEt)_2$ with Azobenzene. A solution of HSP-$(OEt)_2$ (0.1 mL) and azobenzene (1.1 mmol) in 10 mL of methanol was refluxed for 3 h. With the use of the technique described above,

p-benzidine bis(hydrochloride) was found to be present when the reaction was terminated.

Physical and Analytical Methods. Molecular weights were obtained either from the spectra obtained from a Varian Associates CH 7 mass spectrometer or by osmometry in 1,2-$C_2H_4Cl_2$ using a Mechrolab 301A instument operating at 37 °C. Elemental analyses were obtained as described previously.[4]

Discussion of Results

The oxidation of 2 equiv of $Mo(CO)_4Cl_2$ with 1 equiv of an aryl azide in the presence of $HS_2P(OEt)_2$ results in the formation of $Mo(S_2P(OEt)_2)_3$ without incorporation of the NR moiety. The red Mo(III) complex (3.8 μ_B) appears to be totally analogous to $Mo(S_2PF_2)_3$, a compound which had been reported previously.[8] For example, the ligand field bands in the spectrum of the latter occur at 20 000 and 24 300 cm^{-1} while those of $Mo(S_2P(OEt)_2)_3$ occur at 20 000 and 23 600 cm^{-1}. To our knowledge, these compounds are the only derivatives of Mo(III) in which sulfur is the only ligating atom. The structure of each compound is probably described by near-octahedral stereochemistry.

We have searched for thermal or photolytic reactions between $Mo(S_2P(OEt)_2)_3$ and azobenzene (principally trans) in various aprotic solvents without success. Moreover, the absorption spectra of solutions containing these reagents are simply the superimposed spectra of the reagents within experimental error. However, we find that a rapid reaction will occur in ether when anhydrous HCl is also present. The products are the new Mo(IV) compound $MoCl(S_2P(OEt)_2)_3$ (2.7 μ_B) and near-quantitative amounts of the acid-induced benzidine rearrangement products. The latter clearly result from the initial presence of hydrazobenzene. Consequently, the reaction involves the two-electron reduction of azobenzene in the presence of a proton donor according to eq 1. The

$$2Mo(S_2P(OEt)_2)_3 + PhN{=}NPh + 2HCl \rightarrow$$
$$2MoCl(S_2P(OEt)_2)_3 + PhNHNHPh \quad (1)$$
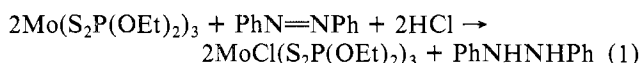
reductions of azobenzene by Ti(III) in alcohol[9] containing HCl and by $(\eta^5\text{-}C_5H_5)_2MoH_2$ in aprotic solvents[10] have been reported. The mechanism of these reactions remains in considerable doubt. We have found that there is no immediate reaction between $Mo(S_2P(OEt)_2)_3$ and HCl in ether although a slow decomposition of undetermined nature does occur. Furthermore, there is no evidence for the binding of azobenzene by the complex in the absence of HCl. On the other hand, azobenzene is a weak base[11] and moderate quantities of $PhNH{=}NPh^+$ are available under the conditions of the reaction. Consequently, it seems likely that this acid and the Mo(III) complex are the actual reactants. Indeed, electrochemical studies[12] have shown that the acid is reduced at a potential which is considerably more positive than that of the conjugate base. While it is possible that the protonation of azobenzene increases its ability to bind to the metal so that the reaction proceeds by an inner-sphere mechanism, the congested nature of the resulting seven-coordinate intermediate should cause this pathway to be somewhat unlikely. Furthermore, insofar as a ligand's ability to bind to a metal is reflected by its ability to bind a proton, $PhNH{=}NPh^+$ should be a very poor Lewis base since additional protonation does not occur.[11] We currently favor an outer-sphere mechanism on the basis of the collective evidence.

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We have measured the molecular weight of $MoCl(S_2P(OEt)_2)_3$ by osmometry in $1,2\text{-}C_2H_4Cl_2$ and obtained a result which is consistent with the expected molecular weight. However, this result is of no pertinence in distinguishing between a molecular complex and a six-coordinate ionic complex since we have also found that $(n\text{-}Bu_4N)I$ behaves as if it were a molecular compound in this solvent due to extensive ion pairing. However, the molar conductivity of $MoCl(S_2P(OEt)_2)_3$ in CH_3CN (1 mM) was found[13] to be 1 Ω^{-1} cm^2 mol^{-1}, a result which is only consistent with a molecular complex.[14] Unlike $Mo(NR)(S_2P(OEt)_2)_3$, another species which may be seven-coordinate,[4] the infrared spectrum of the Mo(IV) complex contains only one band near 640 cm^{-1} due to the P$\cdots$S antisymmetric vibration,[15] but the structural implications of this result are unclear for reasons which were noted earlier.[4] We note that $MoCl(S_2CNEt_2)_3$ has been reported previously,[16] but structural details are also lacking with that compound.

We have also found that the Mo(III) complex will react with azobenzene in refluxing methyl alcohol, yielding another Mo(IV) complex, diamagnetic $Mo(OMe)_2(S_2P(OEt)_2)_2$. The remaining product of interest is hydrazobenzene as evidenced by the recovery of *p*-benzidine bis(hydrochloride) after treating the reaction solution with HCl. Although small quantities of aniline were detected by VPC, this compound probably results from the thermal disproportionation of hydrazobenzene.[17] This reaction may be similar to the one in ether but with the alcohol acting as the proton donor. However, we have found that azobenzene is also reduced to hydrazobenzene by $HS_2P(OEt)_2$. Since the conjugate base of this acid is liberated during the conversion of $Mo(S_2P(OEt)_2)_3$ to $Mo(OMe)_2(S_2P(OEt)_2)_2$, we believe that the reaction probably occurs according to eq 2. Although the disulfide was not isolated
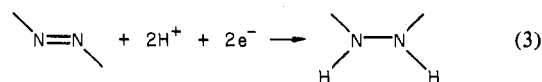
$$Mo(S_2P(OEt)_2)_3 + PhN{=}NPh + 2MeOH \rightarrow$$
$$Mo(OMe)_2(S_2P(OEt)_2)_2 + PhNHNHPh +$$
$$\tfrac{1}{2}(\text{-}SP(S)(OEt)_2)_2 \quad (2)$$

and identified, the formation of this substance has been noted in many reactions including the reduction of HN_3 by either $HS_2P(OEt)_2$ or $MoO(S_2P(OEt)_2)_2$.[18] We have also found that $Mo(OMe)_2(S_2P(OEt)_2)_2$ can be prepared by the oxidation of

$Mo(CO)_2(PPh)(S_2P(OEt)_2)_2$ with tolN$_3$ in methanol. Interestingly, the Mo(IV) compound is also obtained from $MoCl(S_2P(OEt)_2)_3$ by solvolysis while adventitious moisture converts the latter to $MoO(S_2P(OEt)_2)_2$.

The ^{1}H NMR spectrum of $Mo(OMe)_2(S_2P(OEt)_2)_2$ at 220 MHz and -40 °C contains only a singlet due to the alkoxo ligands and unbroadened and typical resonances due to a single type of dithiophosphate ligand. Although the alkoxo ligands would be equivalent in either cis or trans configurations, the ethyl groups of the bidentate ligand would only be equivalent in the trans geometry in the absence of accidental degeneracy in the cis isomer. Furthermore, equilibrium quantities of both isomers could be present providing the conversion of one isomer to the other is a process with a low activation barrier. We note that the preparation $MoX_2(S_2CNEt_2)_2$ (X = Cl and Br) of unknown stereochemistry has been previously reported.[19]

The reactions shown in eq 1 and 2 indicate the inferior reducing strength of these Mo(IV) complexes with respect to $Mo(S_2P(OEt)_2)_3$ since only the latter is capable of causing the reduction shown in eq 3. We have also shown previously[20]

$$\diagdown\!\!\text{N}{=}\text{N}\!\!\diagdown + 2\text{H}^+ + 2\text{e}^- \longrightarrow \underset{\text{H}}{\diagdown}\!\!\text{N}{-}\text{N}\!\!\underset{\text{H}}{\diagup} \quad (3)$$

that, although the Mo(IV) complex $MoO(S_2CNEt_2)_2$ will bind unactivated acetylenes, reduction according to eq 4 does not

$$\text{-C}{\equiv}\text{C-} + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{alkene} \quad (4)$$
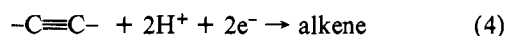
occur. In view of these results, it is not surprising that thermochemical studies[21] have shown that this complex is also unable to cause the fixation of dinitrogen. While these studies do not constitute an exhaustive survey of the chemistry of Mo(IV), it is clear that ligation by sulfur has not yet led to authenticated Mo(IV) complexes of superior reducing strengths. Consequently, any mechanism for biological fixation of dinitrogen or any mechanism involving fixation by model compounds should be viewed with caution if these mechanisms infer the presence of sulfur-ligated Mo(IV) as an active intermediate.

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