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The complexes $[Ru(ClPC)(py)_2]\cdot 4py$ and $[Ru(ClPC)(PPh_3)_2]$ show good thermal stability in the absence of air. The compounds can be dried in vacuo or air at 110 °C without weight loss. In the range 200–400 °C, however, the solids decompose in air to yield, among other things, metal-free phthalocyanine and RuO_2. On the other hand, thermal gravimetric measurements show that in an N_2 stream neither complex shows weight loss up to 250 °C. The complex $[Ru(ClPC)(py)_2]\cdot 4py$ starts to lose weight at 360 °C, and this continues to 420 °C where the TGA trace levels off. The weight loss (22% observed, 21% calculated) corresponds to reaction 1.

$$[Ru(ClPC)(py)_2]\cdot 4py \xrightarrow{360\text{–}420\ ^\circ C} [Ru(ClPC)(py)_2]\cdot py + 3py \quad (1)$$

For $[Ru(ClPC)(PPh_3)_2]$, the solids start to lose weight at 280 °C and this continues to 340 °C. The next weight loss starts at 370 °C and finishes at 440 °C. The weight losses (22% observed, 23% calculated and 21% observed, 23% calculated) correspond to reactions 2 and 3.

$$[Ru(ClPC)(PPh_3)_2] \xrightarrow{280\text{–}340\ ^\circ C} [Ru(ClPC)PPh_3] + PPh_3 \quad (2)$$

$$[Ru(ClPC)(PPh_3)] \xrightarrow{370\text{–}440\ ^\circ C} [Ru(ClPC)] + PPh_3 \quad (3)$$

It is interesting to note that syntheses of Ru(II) phthalocyanines have been detailed that involve the high-temperature, 280–300 °C, reaction of excess phthalonitrile and $RuCl_3\cdot 3H_2O$. As shown here, the procedure yields [Ru(ClPC)] as the major product. The chlorination activity of the reaction mixture may arise from the formation of chlorine in the thermal reduction of $RuCl_3$ to yield a lower oxidation state species which then undergoes a redox condensation reaction with phthalonitrile to form [Ru(PC)]. Subsequent chlorination to give [Ru(ClPC)] is most likely since chlorination of phthalonitrile prior to condensation should lead to several polychlorinated macrocycles instead of the high yield of monochlorinated phthalocyanine. In the presence of naphthalene the reaction of $RuCl_3\cdot 3H_2O$ and excess *o*-cyanobenzamide gives [Ru(PC)] although in low yield.[2] In this case the chlorination of naphthalene may occur in preference to that of the phthalocyanine. Further, when the high-temperature synthesis is carried out with a reducing atmosphere of CO, the product is exclusively [Ru(PC)CO].[4] In this case the CO reduces the Ru(III) to a Ru(0) carbonyl which is then involved in the redox condensation reaction with phthalonitrile. No chlorination occurs since $RuCl_3$ does not undergo thermal reduction.

Finally, this work has not been able to establish unequivocally the existence of a Ru(III) phthalocyanine complex. We have shown that, with use of the procedure of Keen and Malerbi,[5] the major product isolated after suitable workup is a Ru(II) complex of the chlorinated PC macrocycle $[Ru(ClPC)(py)_2]\cdot 4py$. This corresponds to the Keen and Malerbi product $[Ru(PC)Cl]\cdot n py$ (n = 4 to 5).[5] We have not studied the first product of their procedure, $[Ru(PC)Cl]\cdot C_6H_4(CN)_2$, which is later converted to the pyridine complex. Thus, we cannot say whether it is a Ru(III) complex or not. It should be pointed out, however, that the elemental analysis of this compound is in poor agreement with the proposed formulation; e.g., percent C found is low by 4.7% (absolute). Further, the magnetic moment of the material is low for a Ru(III) compound. All in all, it is reasonable to suggest that the isolated product is a mixture of several materials and not a pure compound. In fact, the method of purification which only utilizes acetone extraction of the reaction mixture to remove soluble impurities would not be expected to yield a pure material.

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Oxygen-17 Nuclear Magnetic Resonance Spectroscopy of Certain Molybdenum(IV) and Dinuclear Molybdenum(V) Complexes

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The sensitivity of the ^{17}O chemical shift of ligated oxygen atoms to metal–oxygen bond multiplicity has been established for several classes of metal–oxo compounds.[1,2] In a recent study of mononuclear oxomolybdenum(VI) complexes, we have shown that bond distances, stretching force constants, and estimated π-bond orders for a series of MoO bonds are directly related to the ^{17}O chemical shifts of the oxo ligands.[3] Oxo ligands are also prevalent in the coordination chemistries of Mo(V) and, to a lesser degree, Mo(IV). We have examined the ^{17}O NMR spectra of several of these complexes to determine the extent of similar correlations for the lower oxidation states and the effect of the oxidation state upon the chemical shift of the ^{17}O resonances. The compounds which we have examined were chosen because they have been of recent chemical interest to us.

Experimental Section

The Mo(VI) complexes $MoO_2(acac)_2$ (acac = acetylacetonate), $MoO_2(Etcys)_2$ (Etcys = ethyl ester of cysteinate), and $MoO_2(Et_2dtc)_2$ (Et_2dtc = diethyldithiocarbamate) were isotopically enriched in ^{17}O as previously described[3] and used as starting materials for the preparation of lower oxidation state complexes. Reduction of $MoO_2(acac)_2$ with excess diethyldithiophosphoric acid (Et_2dtpH) provided samples of $Mo_2O_3(Et_2dtp)_4$.[4] Reduction of $MoO_2(Et_2dtc)_2$, $Mo_2O_3(Et_2dtp)_4$, and $MoO_2(Etcys)_2$ with triphenylphosphine led to $MoO(Et_2dtc)_2$, $MoO(Et_2dtp)_2$, and $Mo_2O_3(Etcys)_4$, respectively.[4,5] A solution of $Mo_2O_3(Et_2dtc)_4$ was generated by the rapid reaction of a 1:1 mixture of enriched samples of $MoO_2(Et_2dtc)_2$ and $MoO(Et_2dtc)_2$. Condensation of the Etcys ligands of $Mo_2O_3(Etcys)_4$ with acetone (previously equilibrated with enriched water) was used to prepare $Mo_2O_4(Etcys)_2$.[6] All syntheses were confirmed by infrared spectroscopy. Solutions of $Mo_2O_3(Et_2dtc)_4$, $MoO(Et_2dtc)_2$, and $MoO(Et_2dtp)_2$ were prepared anaerobically. Instrumentation and instrumental methods were identical with those described previously.[3] The chemical shifts and line widths of the ^{17}O NMR resonances as well as the enrichment levels and solvents are given in Table I.

Discussion of Results

As shown in Table II, the ^{17}O NMR chemical shifts of the Mo(V) complexes fall into two groups: one located between 850 and 978 ppm and the other between 530 and 612 ppm. The results of previous work[1,2] suggest that the former should be assigned to terminal oxo ligands while the latter are due to this ligand in bridging sites. This assignment finds further support in the spectra of those complexes containing the Mo_2O_3 moiety, since the resonances in the vicinity of 900 ppm are more intense than those near 500 ppm. The Mo(IV) complexes, containing only one terminally bound oxo ligand, have resonances at 820 and 842 ppm. The terminal and bridging stretching frequencies and the corresponding MoO bond

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Table I

complex	solvent	concn, M	% ^{17}O	chem shift,[a] ppm	$\Delta\nu_{1/2}$
$Mo_2O_3(Etcys)_4$	CH_2Cl_2	0.15	12	877 ± 15[b]	1500 ± 100
				544 ± 40	3000 ± 100
$Mo_2O_4(Etcys)_2$	DMF	0.10	~5	850 ± 5[b]	240 ± 20
				530 ± 5	425 ± 40
$Mo_2O_3(Et_2dtc)_4$	CH_2Cl_2	0.15	22	935 ± 10[b]	330 ± 20
				588 ± 20	550 ± 40
$MoO(Et_2dtc)_2$	CH_2Cl_2	0.15	27	820 ± 2	24 ± 1[c]
$Mo_2O_3(Et_2dtp)_4$	CH_2Cl_2	0.20	16	978 ± 5[b]	390 ± 40
				612 ± 10	660 ± 40
$MoO(Et_2dtp)_2$	CH_2Cl_2	0.05	16	842 ± 2	75 ± 5

[a] Chemical shifts were measured from external H_2O. The errors associated with the chemical shifts were estimated on the basis of the overall peak shape, the signal to noise ratio, and the broadness of the resonance. [b] The ratios of the integrations for the terminal and bridging oxo ligands were approximately 2:1 for all $Mo_2O_3L_4$ complexes. The ratio for $Mo_2O_4L_2$ was 1.7:1 (theoretical 1:1). See ref 21 for discussion of potential errors in ^{17}O integrations. [c] Spectrum obtained by using increased digital resolution and no exponential multiplication.

distances (where known) are also collected in Table II. The infrared assignments either are due to Newton and McDonald[7] or are analogous to their assignments. Similar data for two Mo(VI) complexes containing the *cis*-MoO_2 moiety are also included in Table II for comparison.

Several comparisons within Table II indicate that the degree of Mo–O π bonding present in Mo(V) and Mo(IV) oxo complexes is reflected in the magnitude of the ^{17}O chemical shift. Within the series of structurally related $Mo_2O_3L_4$ (L = Etcys, Et_2dtc, and Et_2dtp) and MoO_2L_2 (L = Et_2dtc and Et_2dtp) complexes, increases in the chemical shifts of the ^{17}O resonances of the terminal and bridging oxo ligands are accompanied by increases in the corresponding Mo–O stretching frequencies. These increases appear to reflect slight increases in the π-bond orders of the terminal and bridging MoO bonds. Where a comparison of structural data is possible, the errors associated with the bond distances make it difficult to judge if increases in the observed ^{17}O chemical shifts and the stretching frequencies are actually accompanied by decreases in the MoO bond distances. Since the extent of π bonding in a MoO bond will depend upon the number of oxo ligands within the complex competing for the available orbitals of the metal, the chemical shifts of the terminal and bridging oxo ligands of $Mo_2O_3(Etcys)_4$ are expected and are found to be somewhat larger than the analogous chemical shifts for $Mo_2O_4(Etcys)_2$. Although a comparison between the bridging MoO bond distances in $Mo_2O_4(Etcys)_2$ and $Mo_2O_3L_4$ complexes suggests that a considerable smaller π-bond order is associated with the bridging ligands in the dioxo bridged complex, the chemical shifts due to the bridging oxo ligands of $Mo_2O_3(Etcys)_4$ and $Mo_2O_4(Etcys)_2$ differ by only 14 ppm. However, a direct comparison of the bonding based on the bridging MoO bond distances in $Mo_2O_3L_4$ and $Mo_2O_4L_2$ complexes may not be appropriate because of differing steric restraints and particularly because of the metal-to-metal bond in the latter.[8,9]

The dominance of oxo ligation in three oxidation states of molybdenum provides a rare opportunity to investigate the effect of the formal oxidation state of the metal on the ^{17}O chemical shift. The π-bond order of a terminal MoO bond in MoO_2L_2 and $MoOL_2$ complexes should be 1.5 and 2, respectively, if π bonding to non-oxo ligands is ignored. The π-bond order of the terminal MoO bond in $Mo_2O_3L_4$ complexes will be larger than 1.5, but smaller than 2 since the bridging oxygen can compete with the terminal oxygen for one of the available Mo d orbitals, although not necessarily as effectively. The terminal Mo–O stretching frequencies within the dithiocarbamate series are in accord with this trend in π-bond order, as shown in Table II.[10] The MoO bond distance in $MoO(Et_2dtc)_2$ is approximately 0.03 Å smaller than the corresponding distances in $MoO_2(Et_2dtc)_2$ and thus is also consistent with a larger MoO π-bond order in the $MoOL_2$ complex relative to the MoO_2L_2 complex. Unfortunately, the errors associated with the MoO bond distances in the $Mo_2O_3(Et_2dtc)_4$ complex are too large to make any further comparisons in this series. Empirical evidence would suggest that the larger MoO π bonding in the lower oxidation states will be reflected in larger ^{17}O chemical shifts.[1-3] However, the ^{17}O chemical shifts show a relatively smooth decrease as the oxidation state decreases. Apparently, the influence of the oxidation state on paramagnetic shielding of the oxo ligand (i.e., the chemical shift) is opposite to and larger than the influence of the π-bond order of the MoO bond. The origin of the paramagnetic shielding is the field-induced mixing of the ground state and excited states associated with the MoO bond.[11] The extent of mixing is inversely proportional to the difference in the energies of these states. A transition from the ground state to an excited state will inevitably shift electron density from bonding orbitals, which tend to be localized on the oxo ligand, to antibonding orbitals which tend to be localized on the metal atom. Repulsion between electrons localized near the metal atom would then increase as the number of d electrons increases. Consequently, the energy difference between the ground state and an excited state in the lower oxidation state complexes should suffer an increase which will result in smaller chemical shifts.

Certain spectroscopic[12] and chemical properties[13] of $Mo_2O_3(Et_2dtc)_4$ and $Mo_2O_3(Et_2dtp)_4$ have been interpreted in terms of the disproportionation shown in eq 1. We have

$$Mo_2O_3L_4 \rightleftarrows MoOL_2 + MoO_2L_2 \qquad (1)$$

obtained additional evidence of disproportionation from the ^{17}O NMR spectra of these complexes. In the spectrum of $Mo_2O_3(Et_2dtc)_4$, we observed both the broad resonance due to $MoO_2(Et_2dtc)_2$ and the sharp resonance due to $MoO(Et_2dtc)_2$, in addition to the resonances due to $Mo_2O_3(Et_2dtc)_4$. In contrast, the only additional peak which could be assigned in the spectrum of $Mo_2O_3(Et_2dtp)_4$ was the sharp resonance due to $MoO(Et_2dtp)_2$. The incremental dilution of a solution of $Mo_2O_3(Et_2dtp)_4$ from 0.2 to 0.05 M resulted in a corresponding decrease in the ratio of the terminal oxo signal of $Mo_2O_3(Et_2dtp)_4$ relative to $MoO(Et_2dtp)_4$ from 9:1 to 2:1. Although this behavior is expected for the disproportionation described in eq 1, no signal could be assigned to $MoO_2(Et_2dtp)_2$ which should also be observable in the presence of the dinuclear complex. Interestingly, $MoO_2(Et_2dtp)_2$, unlike $MoO_2(Et_2dtc)_2$, has never been synthesized, and its existence in solution has only been postulated on the basis of the electronic spectrum of $Mo_2O_3(Et_2dtp)_4$[12] and the ability of $Mo_2O_3(Et_2dtp)_4$ to act

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Table II

complex	chem shift, ppm		$Mo-^{16}O$ stretch freq, cm^{-1}		Mo–O bond dist, Å	
	MoO	MoOMo	MoO	MoOMo	MoO	MoOMo
$MoO_2(Etcys)_2$[a]	921		905, 874			
$Mo_2O_3(Etcys)_4$	877	544	925	. . ., 425[b]		
$Mo_2O_4(Etcys)_2$	850	530	980, 945	735, 470[b]	1.663 (18)[d]	1.932 (16)[d]
$MoO_2(Et_2dtc)_2$[a]	975		908, 877		1.696 (5)[e]	
$Mo_2O_3(Et_2dtc)_4$	935	588	932	743, 437[c]	1.666 (12), 1.676 (12)[e]	1.856 (13), 1.870 (13)[e]
$MoO(Et_2dtc)_2$	820		962		1.664 (8)[e]	
$Mo_2O_3(Et_2dtp)_4$	978	612	961	764, 427[c]	1.647 (14)[f]	1.863 (12)[f]
$MoO(Et_2dtp)_2$	842		972[c]			

[a] From ref 3. [b] From ref 22. [c] From ref 7. [d] From ref 8. [e] Values determined for dtc = *N,N*-dipropyldithiocarbamate.[23] [f] From ref 24.

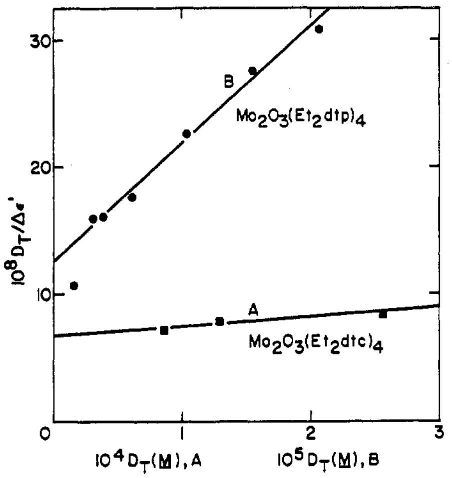

Figure 1. Application of eq 2 to the spectroscopic data which are available for $Mo_2O_3(Et_2dtc)_4$ and $Mo_2O_3(Et_2dtp)_4$.

as an oxo transfer agent.[13] However, several smaller signals in the terminal MoO region were observed at 1020, 945, and 895 ppm, which showed increases in intensity relative to the Mo(V) signals upon dilution. The addition of triphenylphosphine to the dilute sample resulted in the total conversion of these species, as well as the remaining dinuclear complex, to $MoO(Et_2dtp)_2$. Consequently, these species are not decomposition products which result in some way from the dilution of $Mo_2O_3(Et_2dtp)_4$. Rather, the observation of these species and their reactivity with triphenylphosphine indicates that, while disproportionation of $Mo_2O_3(Et_2dtp)_4$ occurs, it is not as simple a process as suggested in eq 1.

It is of interest to compare these results to those that can be obtained from a quantitative treatment of the existing[12] spectroscopic data. The variation in the apparent extinction coefficient (ϵ_{app}) at a given wavelength with the formal concentration (D_T) of the dinuclear compound (D) is given[14] in eq 2, where $\Delta\epsilon' = \epsilon_{app} - \epsilon(Mo^{IV})$ and $\Delta\epsilon = \epsilon(D) - \epsilon(Mo^{IV})$.

$$(D_T/\Delta\epsilon') = 2(D_T/\Delta\epsilon) + K/\Delta\epsilon \qquad (2)$$

The absorbance due to any Mo(VI) species should be negligible since the data were taken near 500 nm. The results for $Mo_2O_3(Et_2dtp)_4$, which are shown in Figure 1, lead to $K = 2.3 \times 10^{-3}$ M and $\epsilon(D) = 2.3 \times 10^4$ cm^{-1} M^{-1} where the solvent is 1,2-$C_2H_4Cl_2$. The results of more limited data for $Mo_2O_3(Et_2dtc)_4$ in benzene, which are also shown in Figure 1, lead to $K = 2.0 \times 10^{-3}$ M and $\epsilon(D) = 3.2 \times 10^4$ cm^{-1} M^{-1}. Others have found[15] from kinetic data an identical value for this equilibrium constant and $\epsilon(D) = 2.4 \times 10^4$ cm^{-1} M^{-1} at 25 °C in 1,2-$C_2H_4Cl_2$. Since the spectroscopic data for both compounds appear to adequately conform to eq 2 and since the equilibrium constants which we have obtained by using this equation are almost identical, it would normally be plausible to suggest that disproportionation of both compounds is governed by eq 1. However, our ^{17}O NMR results indicate that the apparent applicability of eq 2 to the spectroscopic data for $Mo_2O_3(Et_2dtp)_4$ must be considered fortuitous.

In the absence of molecular exchange processes, the line width of an ^{17}O resonance is largely determined by the magnitude of the electrical field gradient associated with the oxygen nucleus. We have found that bridging oxo resonances have line widths approximately twice as large as the line widths of terminal oxo resonances within the same complex. Similar behavior has been observed for $Mo_2O_7^{2-}$[1] and for small organic molecules containing both terminal and bridging oxygen atoms[16] and is believed to be indicative of a larger electrical field gradient associated with bridging oxygen sites.[1] In contrast, the line widths observed for the oxo resonances of the Mo(IV) complexes, $MoO(Et_2dtc)_2$ and $MoO(Et_2dtp)_2$, are much smaller than the line widths typically observed for the terminal oxo resonances of mononuclear oxomolybdenum complexes.[17] The smaller line width observed for $MoO(Et_2dtc)_2$ (24 Hz) relative to $MoO_2(Et_2dtc)_2$ (362 Hz)[3] cannot be attributed to the effect of any significant difference in the molecular radii of these two complexes upon the rotational correlation time.[1,2] We have empirically found that when a terminal MoO bond lies along an axis of symmetry or in a plane of symmetry, smaller line widths are observed, if compared to those of other mononuclear complexes of comparable size.[3,18] This behavior presumably is the result of smaller electrical field gradients at the terminal oxo site, anisotropic molecular tumbling, or contributions from both.

Summary

In summary, we have found the chemical shift of the oxo ligands of Mo(V) and Mo(IV) complexes to be useful as a means of comparing the relative Mo–O π bonding in these oxomolybdenum complexes of lower oxidation states. However, the effect of the lower oxidation states of molybdenum upon the chemical shift of oxo ligands appears to be larger than and opposite to the effect due to increasing Mo–O bond multiplicity. Evidence concerning the disproportionation of $Mo_2O_3(Et_2dtc)_4$ and $Mo_2O_3(Et_2dtp)_4$ also suggests that ^{17}O NMR can be useful in observing equilibria associated with various oxomolybdenum species. These observations may impact on the eventual use of this spectroscopic technique to investigate the oxomolybdenum moiety in molybdenum oxidase

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(14) In the derivation of eq 2, the square of the concentration of the dinuclear complex [D] was assumed to be small and negligible at dilute concentrations.

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(17) Despite the narrow line widths for the Mo(IV) complexes, particularly $MoO(Et_2dtc)_2$, no coupling between ^{17}O and ^{95}Mo or ^{97}Mo was observed. Noncubic symmetry at the metal undoubtedly results in rapid quadrupolar relaxation of the molybdenum nuclei.

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enzymes[19,20] or the small molecular weight Mo cofactor which they have in common.[9]

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Registry No. $Mo_2O_3(Etcys)_4$, 24228-97-5; $Mo_2O_4(Etcys)_2$, 22775-76-4; $Mo_2O_3(Et_2dtc)_4$, 20023-86-3; $MoO(Et_2dtc)_2$, 25395-92-0; $Mo_2O_3(Et_2dtp)_4$, 60384-05-6; $MoO(Et_2dtp)_2$, 25395-91-9.

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Photoinduced Elimination of H_2 from $[MoH_4(diphos)_2]$ and $[MoH_4(PPh_2Me)_4]$

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Photolysis of a number of di- and trihydride complexes has been shown to lead to loss of H_2.[1-7] This appears to be a general reaction pathway for this class of compounds and in several cases has led to the formation of highly reactive complexes, many of which are not easily obtained thermally.[4-7] Photolysis of *poly*hydride complexes possessing four or more hydride ligands can, in principle, lead to *multiple* H_2 *loss* and hence to extremely reactive, coordinatively unsaturated species. To test this notion, we have examined the photochemical properties of a series of polyhydride complexes of Re[7] and the molybdenum tetrahydrides $[MoH_4(diphos)_2]$ (diphos = $Ph_2PCH_2CH_2PPh_2$) and $[MoH_4(PPh_2Me)_4]$. The results of this latter study are of relevance to recent reports[8-10] that describe the photoluminescent and photochemical properties of *trans*-$[W(L)_2(diphos)_2]$ (L = CO, N_2) complexes and are described herein.

Experimental Section

The $[MoH_4(diphos)_2]$ and $[MoH_4(PPh_2Me)_4]$ complexes were prepared by published procedures.[11] Solvents employed in these studies were dried by standard methods and were rigorously degassed prior to use. All manipulations of the compounds were carried out under prepurified Ar, N_2, or CO as appropriate.

Irradiations were conducted at 366 nm by using a 450-W Hanovia medium-pressure Hg lamp equipped with Corning Glass 0-52 and 7-37 filters, with a 100-W Blak-Ray B100A lamp equipped with a 366-nm narrow band-pass filter, or in a 350-nm Rayonet photoreactor. The complex to be studied was placed in an evacuable quartz UV cell or a Schlenk tube attached to the vacuum line, and after being degassed, the appropriate solvent was distilled onto the sample. Solutions were irradiated with the appropriate lamp, and IR, NMR, and electronic absorption spectra were periodically recorded.

Results and Discussion

We initially irradiated the $[MoH_4L_4]$ complexes under an N_2 atmosphere, expecting to form the known bis(dinitrogen) complexes if photoinduced loss of all four hydride ligands were to occur. This expectation was realized, and high yields of *trans*-$[Mo(N_2)_2(diphos)_2]$ and *trans*-$[Mo(N_2)_2(PPh_2Me)_4]$ were obtained. For example, photolysis of a benzene solution of $[MoH_4(diphos)_2]$ at 25 °C for 12 h with 366-nm light under a continuous N_2 purge gave a 93% yield of *trans*-$[Mo(N_2)_2(diphos)_2]$, eq 1. The nondescript spectral changes which

$$[MoH_4(diphos)_2] + 2N_2 \xrightarrow{h\nu} 2H_2 + trans\text{-}[Mo(N_2)_2(diphos)_2] \quad (1)$$

obtain upon photolysis and the necessity of the N_2 purge in order to drive the reactions have precluded accurate quantum yield measurements, although the time scale of the photolysis indicates that the quantum yields are low. The conversion shown in eq 1 has been observed to occur thermally[12] but at a rate much slower than that which obtains under photochemical conditions. We also found that photolysis of $[MoH_4(diphos)_2]$ under a CO atmosphere gives a mixture of *cis*- and *trans*-$[Mo(CO)_2(diphos)_2]$. Irradiation under C_2H_4, C_2H_2, and CO_2 atmospheres leads to complex arrays of products which have proven difficult to separate and characterize.

An important question is what happens in the absence of a suitable substrate that can trap the photogenerated intermediate(s): Are reactive species such as $[Mo(diphos)_2]$ and $[Mo(PPh_2Me)_4]$ photogenerated and do they persist in solution? Photolysis of rigorously degassed benzene solutions of $[MoH_4(diphos)_2]$ with 366-nm light gives a color change from yellow to bright orange over a period of several hours. This color change is accompanied by a steady decrease in intensity of the 1714-cm^{-1} ν_{Mo-H} vibration and the $\delta = -3.6$ ppm hydride resonance characteristic of $[MoH_4(diphos)_2]$. No new hydride resonances or metal hydride vibrations appear in either spectrum. The singlet at 83.5 ppm initially present in the ^{31}P NMR spectrum of $[MoH_4(diphos)_2]$ in benzene-d_6 solution also decreases in intensity as the photolysis proceeds, and a new singlet at 80.2 ppm appears and grows in.

Mass spectral, gas chromatographic, and Toepler pump analyses of the gases above irradiated benzene solutions show the formation of H_2 with an average of 1.9 mol of H_2 released per mole of $[MoH_4(diphos)_2]$ irradiated. Evaporation of solvent from these irradiated solutions gives an extremely air-sensitive orange solid which shows no metal hydride vibrations in its infrared spectrum and no hydride resonances in its ^1H NMR spectrum. The ^{31}P NMR spectrum of this compound is complex, showing 12 separate resonances, including an intense peak at 13.2 ppm attributable to free diphos. Repeated attempts at recrystallization and purification of this

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