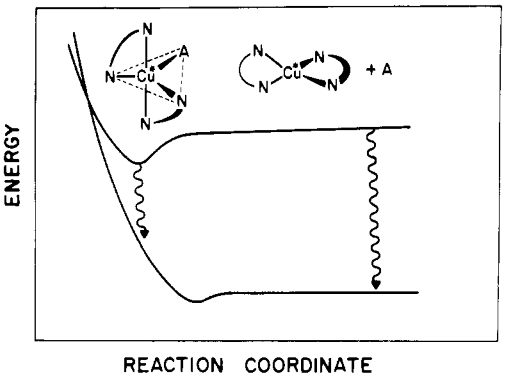

Figure 2. Schematic reaction coordinate for the approach of the anionic quencher A toward $Cu(dmp)_2^+$. (Charges are omitted for clarity.) The lower curve represents the ground state, where a shallow minimum occurs due to outer-sphere complex formation. The upper curve represents the CT excited state, in which the anion moves in close enough to form an inner-sphere complex. The wiggly arrows indicate the relative energies associated with the nonradiative decay process at two locations along the reaction coordinate.

explained because the bulky phenyl substituents interfere with formation of the five-coordinate adduct.[30]

The reaction coordinate diagram in Figure 2 indicates why association of a fifth donor can result in quenching of the excited state. From left to right, the reaction coordinate is constructed such that the center-to-center distance between the copper and the anion increases. Also implicit in the coordinate is the internal reorganization that occurs in the individual ions as they begin to interact with each other, as well as changes in solvation. The lower curve in Figure 2 depicts the energy of reaction between the anion and $Cu(dmp)_2^+$ in the ground state. The upper curve depicts the same reaction, except the copper complex is assumed to be in its CT excited state. Since the ground-state complex is an 18-electron system, only a weak outer-sphere interaction is expected at a relatively long copper-to-anion separation. On the other hand, the metal center is electron-deficient in the CT excited state, and any anion that can act as a Lewis base is liable to form an inner-sphere complex with copper. In accord with the ground-state structures of corresponding Cu(II) systems, the adduct is expected to have a trigonal-bipyramidal structure with the anion coordinated in an equatorial position. A deeper potential "well" is therefore associated with the excited-state system. This, plus the possibility that the corresponding interaction may be repulsive in the ground state, implies that the energy gap between the ground and excited states will be significantly narrowed as a consequence of binding the anion. In turn, the radiationless decay rate should be enhanced and excited states quenching should be observed.

Conclusions

The CT excited state of $Cu(dmp)_2^+$ is subject to static quenching by coordinating anions in fluid CH_2Cl_2. The anion-induced quenching can be explained in terms of excited state complex formation; however, the inner-sphere adducts are short-lived and have not been directly observed. Whether the associated species may be classified as bona fide intermediates along the quenching pathway or whether they are better classified as some type of transition-state species has yet to be established.

Acknowledgment. This work was supported by the National Science Foundation through Grant No. CHE-8414267. The authors thank Cynthia E. A. Palmer for her assistance.

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S-S Photohomolysis at Dimolybdenum(V) RSS^- and S_2^{2-} Bridges

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Received August 5, 1986

Dimolybdenum(V) complexes of the general form $[Mo_2(NC_6H_4CH_3)_2(S_2P(OC_2H_5)_2)_2S(O_2CCH_3)(SSR)]$ (R = alkyl or aryl), which contain the SMo_2SSR fragment with RSS^- bridging by its β-sulfur, and those of the form $[Mo_2(NAr)_2(S_2P(OC_2H_5)_2)_2S(O_2CR')]_2S_2$ (Ar = p-$C_6H_4CH_3$, C_6H_5; R' = CH_3, n-C_7H_{15}), which contain the SMo_2SSMo_2S unit with an interdimer S_2^{2-} bridge, photolyze under fluorescent lighting to give products characteristic of S-S homolysis. Dimer radicals representable by $[SMo_2S]^\bullet$ were indicated but not directly observed. For R = aryl, SMo_2SSR quickly photolyzes and subsequently equilibrates with SMo_2SSMo_2S and RSSR; for R = alkyl, the photolysis is extremely slow. A mixture of SMo_2SSMo_2S compounds differing in their imido group and/or their carboxylate group also photoequilibrate to give scrambled disulfide products. Reactions of SMo_2SSMo_2S with $C_6H_5CH_2SH$, $(C_6H_5)_3P$, or $(C_2H_5O)_3P$ were also photolytic.

Introduction

Sulfide-disulfide-polysulfide ligand chemistry has drawn much attention of late for transition-metal chemistry in general and for molybdenum chemistry in particular.[1-3] Recent molybdenum studies amply demonstrate the chalcogen interconversions, frequently accompanied by formal metal redox processes involving Mo(VI), Mo(V), and Mo(IV).[4-10] Major interest in sulfido-molybdenum areas draws from interest in biomolybdenum enzymes[11-13] and industrial hydrodesulfurization,[14-16] both of which are believed to involve Mo-S sites.

Disulfide complexes of the general forms $[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SSR)]$ (**1**) and $[Mo_2(NAr)_2(S_2P(OEt)_2)_2S$-

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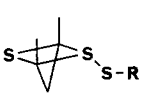
Table I. Photolysis Experiments

expt	reactants (mmol)
1	$[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SSTo)]$ (0.050)
2	$[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SSPh)]$ (0.050)
3	$[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SSBz)]$ (0.050)
4	$[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SSEt)]$ (0.050)
5	$[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)]_2S_2$ (0.025) + ToSSTo (0.025)
6	$[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)]_2S_2$ (0.025) + BzSSBz (0.025)
7	$[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)]_2S_2$ (0.025)
8	$[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)]_2S_2$ (0.025) + $[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CHp)]_2S_2$ (0.025)
9	$[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CHp)]_2S_2$ (0.025) + $[Mo_2(NPh)_2(S_2P(OEt)_2)_2S(O_2CMe)]_2S_2$ (0.025)
10	$[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)]_2S_2$ (0.025) + BzSH (0.102)
11	$[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)]_2S_2$ (0.025) + Ph_3P (0.050)
12	$[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)]_2S_2$ (0.025) + $(EtO)_3P$ (0.050)

$(O_2CR')]_2S_2$ (**2**)[17] are the subjects of the current study. Each consists of an imido(dithiophosphato)molybdenum(V) dimer wherein the metals are bridged by a carboxylate, a sulfide, and a disulfide.[18] Complexes **1** contain the monoorganyl disulfide



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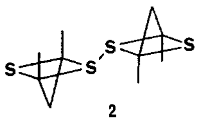

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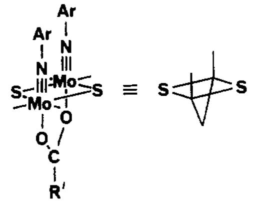

unit, RSS^-, bridging via its β-sulfur, representable as a dimer-organic disulfide, SMo_2SSR. Complexes **2** contain a disulfide linkage, S_2^{2-}, where each sulfur bridges individual dimers, representable as a bis(dimer) disulfide, SMo_2SSMo_2S. A curiosity of the monoorganyl disulfides for R = Ph or To was their solution photodecomposition under normal fluorescent lighting, while for R = Et or Bz photosensitivity was not seen. Studies of this photosensitivity, and also photolability in complexes **2**, are described herein.

Experimental Section

$[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SSR)]$ (R = Et, Bz, Ph, To),[18] $[Mo_2(NAr)_2(S_2P(OEt)_2)_2S(O_2CR')]_2S_2$ (Ar = Ph, R' = Me; Ar = To, R' = Me, Hp),[18] and $[Mo(NTo)(S_2P(OEt)_2)S]_4$[19] were prepared as previously described. *p*-Tolyl disulfide was prepared from thiocresol and iodine in ethanol.[20] Other reagents were used as commercially available.

$^{31}P\{^1H\}$ and ^1H NMR spectra were recorded in $CDCl_3$ on a Varian XL300 spectrometer at 121 and 300 MHz and are reported as downfield shifts from external 85% H_3PO_4 and internal Me_4Si, respectively. The IR spectrum was obtained as a KBr pellet on a Perkin-Elmer 283 spectrophotometer. Galbraith Laboratories, Inc. (Knoxville, TN) performed the elemental analyses.

Photolyses were performed directly in 5-mm NMR tubes by using a 12-in., 32-W General Electric Circline Cool White fluorescent lamp. The NMR tube was held perpendicular to the circular lamp, positioned so that the center points of the lamp and the solution approximately coincided. The same lamp was used throughout all experiments herein described.

The standard photolysis procedure involved dissolving the reagents in 2.0 mL of $CDCl_3$. The resulting homogeneous solution was evenly divided into two NMR tubes. One NMR sample was immediately wrapped in Al foil and then placed inside a cardboard tube subsequently sealed at both ends with black stoppers. This served as the dark control. The second sample was first analyzed by NMR to obtain a time zero spectrum and then photolyzed.

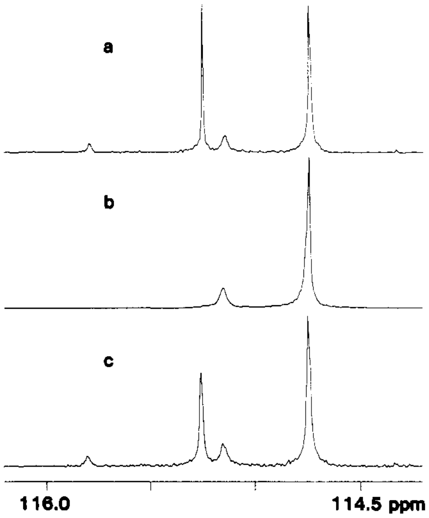

Figure 1. ^{31}P NMR spectra: (a) $[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SSTo)]$ after 60-min photolysis; (b) the dark control after 6 days; (c) $[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)]_2S_2$ + ToSSTo after 60-min photolysis.

All experimental preparations and manipulations were conducted under red light conditions[18] except during actual photolysis. The dark controls, although stored in the dark as described, were handled under red light conditions during NMR manipulations.

Experiments 1–11 in Table I were conducted by using the standard procedure. Experiment 12 was conducted under anhydrous conditions. For this experiment, the molybdenum reagent was dissolved in dry $CDCl_3$ (2.0 mL) under N_2 by using vacuum line techniques, followed by addition of $(EtO)_3P$. With a syringe, 0.8 mL of the resulting solution was put into each of two septum-capped NMR tubes previously purged with N_2. Some hydrolysis was nevertheless observed after several hours, but not at time zero. Use of excess phosphite allowed for completion of the photolytic reaction.

$[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SEt)]$. Synthesis of this compound followed that of the analogues.[18,21] A solution of $[Mo(NTo)(S_2P(OEt)_2)S]_4$ (0.2093 g, 0.125 mmol), $MeCO_2H$ (29 μL, 0.51 mmol), Et_3N (70 μL, 0.50 mmol), and EtBr (37 μL, 0.50 mmol) in C_6H_6 (2 mL) was stirred for 2 h, slowly giving a precipitate. Volatiles were removed by a rotary evaporator. A THF filtrate of the residue (2.5 mL) was slowly treated with 2/1 $EtOH/H_2O$ (5 mL). Filtration, washing (4/1 $EtOH/H_2O$), and vacuum drying gave an orange powder (0.1392 g, 60%). Anal. Calcd for $C_{26}H_{42}N_2O_6P_2S_6Mo_2$: C, 33.8; H, 4.6; S, 20.8. Found: C, 34.0; H, 4.4; S, 21.0. NMR data are as follows (ppm; minor isomer in parentheses, where distinguishable). ^{31}P: 115.3 (115.0). ^1H: (6.68 d, 6.58 d) 6.58 d, 6.47 d, To–H; 4.2–4.0 m, $POCH_2$; 3.18 q (2.41 q), SCH_2; (2.14 s) 2.08 s, To-CH_3; (1.85 t) 1.77 t, $SCCH_3$; 1.34–1.19 m, $POCCH_3$ + CH_3CO_2. All integrations were consistent. Selected IR bands (cm^{-1}): 1532 m, 1439 s, 1050 sh, 1008 vs, 960 vs, 818 s, 785 m.

Results

Photoequilibria. The SMo_2SSR compounds undergo photolysis in solution to an extent greatly dependent on the R group. Figure 1 shows some results for R = To (experiment 1). Both $[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SSTo)]$ (δ 115.2, 114.8) and $[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)]_2S_2$ (δ 115.8, 115.3) are clearly seen after photolysis. Each showed a major and a minor isomer related by inversion at the tricoordinate bridge sulfur, a phenomenon well characterized for these compounds.[18] ^1H NMR supported the ^{31}P NMR analysis and also clearly showed ToSSTo. The photolysis was complete after 15 min, with no further changes observed through 2-h total photolysis. The dark control, however, showed only starting material even after 6 days. The process was therefore photoequilibration (eq 1). The equilibrium could also

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[17] Abbreviations used in this paper: Me, methyl; Et, ethyl; Hp, *n*-heptyl; Ph, phenyl; To, *p*-tolyl; Bz, benzyl; Ar, aryl.

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$$[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)]_2S_2 + RSSR \overset{h\nu}{\rightleftharpoons} 2[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SSR)] \quad (1)$$

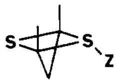
be approached from the left as aptly demonstrated by experiment 5, also partly shown in Figure 1. This photolysis was complete in 30–60 min, with no dark reaction observable at 24 h. The results of experiments 1 and 5 gave $K = 19 \pm 4$ for eq 1, R = To.

Similar results were obtained for $[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SSPh)]$ photolysis (experiment 2). Equilibration was complete after 30-min irradiation, but not at 15 min; starting material, $[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)]_2S_2$, and PhSSPh were clearly observed. No dark reaction was seen after 25 h. The NMR analyses gave $K = 10 \pm 3$ for eq 1, R = Ph.

The alkyl derivatives were tremendously slower to photolyze than the above aryl compounds. Photolysis of $[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SSBz)]$ (experiment 3) after 24 h showed only a trace of $[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)]_2S_2$; after 96-h irradiation this had increased slowly to ~9% with no evidence of full equilibration. The reverse photoprocess, $[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)]_2S_2$ + BzSSBz, was likewise very slow (experiment 6). Only a very gradual conversion was observed at 24-, 48-, and 96-h photolysis, but this was complicated by decomposition of the bis(dimer) disulfide under prolonged irradiation (see below). Again, full equilibration was not evident. For experiments 3 and 6, 24-h dark controls showed no reaction.

$[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SSEt)]$ photolysis (experiment 4) was also slow, progressing from 4% photoconversion to the bis(dimer) disulfide at 24 h to 12% at 144 h, again with no evidence of attaining equilibrium. The 24-h dark control showed no reaction.

Prolonged photolysis of SMo_2SSMo_2S complexes in $CDCl_3$ were found to give substantial side reactions, the first of which involved solvent. For $[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)]_2S_2$ (experiment 7), 4-h photolysis gave 6% loss of starting material by ^{31}P NMR, which showed $[Mo(NTo)(S_2P(OEt)_2)S]_4$ and a product at δ 114.4 of similar integrations. At 8-h photolysis, 91% of the starting material was observed, but at 24 h, still other products were noticeable and further photolysis gave a complex mixture. The 25-h dark control showed no reaction. The $[Mo(NTo)(S_2P(OEt)_2)S]_4$ was readily explainable by deuterium abstraction from solvent to initially give $[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SD)]$ (3, Z = D), which equilibrates to the observed product. Previous studies have shown the equilibrium (eq 2) to lie far to the left,



3

$$[Mo(NTo)(S_2P(OEt)_2)S]_4 + 2MeCO_2H \rightleftharpoons 2[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SH)] \quad (2)$$

as written, in CH_2Cl_2.[19,22] The δ 114.4 peak was proposed to be due to $[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SCCl_3)]$ (3, Z = CCl_3), containing a trichloromethanethiolate bridge; the overall reaction was eq 3.

$$2[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)]_2S_2 + 2CDCl_3 \xrightarrow{h\nu} [Mo(NTo)(S_2P(OEt)_2)S]_4 + 2MeCO_2D + 2[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SCCl_3)] \quad (3)$$

Photoexchange of the SMo_2SSMo_2S complexes themselves was demonstrated by experiments 8 and 9, which involved the use of bis(dimer) disulfide compounds varying in their carboxylate and imido functionalities. Some results for experiment 8 are shown in Figure 2. A shorthand notation is adopted for simplification: each individual dimer fragment itself is indicated first by its imido functions then by its carboxylate bridge, so that ToMe·ToMe = $[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)]_2S_2$, ToHp·ToHp = $[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CHp)]_2S_2$, and ToHp·ToMe = $[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CHp)]SS[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)]$.

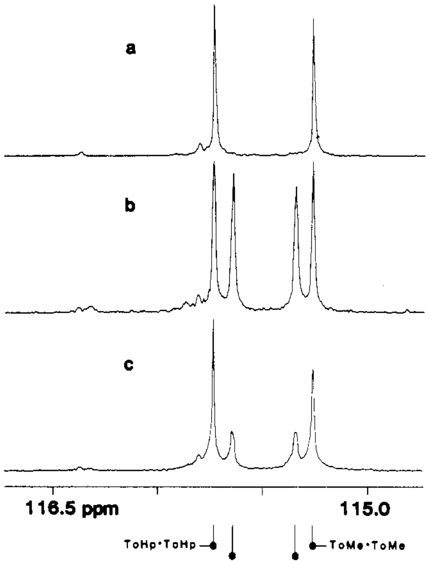


Figure 2. ^{31}P NMR spectra of ToHp·ToHp + ToMe·ToMe: (a) time zero; (b) 120-min photolysis; (c) 24-h dark control. Labels are shown for the major invertomers.

The time zero spectrum clearly showed ToMe·ToMe at δ 115.3 and ToHp·ToHp at δ 115.7 with their respective minor invertomers at δ 115.8 and 116.4. Photolysis generated new peaks assignable to ToHp·ToMe at δ 115.6 and 115.4 with minor invertomers at δ 116.3 and 115.9; two peaks for each invertomer are observed due to the different dimer fragments within ToHp·ToMe. Photoequilibration was complete in 60–120 min, giving 50% ToHp·ToMe, fully consistent with a statistical distribution of components (eq 4). Prolonged photolysis through 18 h gave no further net ToHp·ToMe but slowly gave some decomposition as noted for $CDCl_3$ solutions.

$$\text{ToHp·ToHp} + \text{ToMe·ToMe} \overset{h\nu}{\rightleftharpoons} 2\text{ToHp·ToMe} \quad (4)$$

A dark reaction was observed for this system, with a trace of exchange observable after only 2 h. At 24 h, 32% ToHp·ToMe was found, increasing to 45% at 48 h and 50% at 72 h, consistent with the photolytic process but much slower. None of the characteristic solvent reaction peaks were observed even after 72 h in the dark.

To assist the characterization of the dark reaction in experiment 8, photolysis of a solution of $[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CHp)]_2S_2$ (ToHp·ToHp) + $[Mo_2(NPh)_2(S_2P(OEt)_2)_2S(O_2CMe)]_2S_2$ (PhMe·PhMe) was conducted (experiment 9). If complete scramble via carboxylate exchange and S-S cleavage between dimer fragments was allowed, 10 products were possible, totaling 16 major invertomer ^{31}P NMR peaks, as listed.

ToHp·ToHp
ToHp·PhHp
ToHp·ToMe
ToHp·PhMe
PhHp·PhHp
PhHp·ToMe
PhHp·PhMe
ToMe·ToMe
ToMe·PhMe
PhMe·PhMe

The imido groups do not exchange under these conditions, thus tagging the individual dimer fragments. Some results for experiment 9 are shown in Figure 3.

The spectra were quite complex with considerable peak overlap and obvious asymmetry in some of the peaks. Only major invertomers are herein considered. Assignments were based on the following data. ToHp·ToHp, ToMe·ToMe, and PhMe·PhMe were known compounds. ToHp·ToMe was known from experiment 8; its appearance in the 24-h dark control required the other two new peaks to be PhHp·PhMe. On the basis of experiment 8, the first expected photolysis product was ToHp·PhMe, clearly seen

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[22] Recent measurements by visible spectroscopy have given $K = 0.04 \pm 0.02$ for eq 2 in CH_2Cl_2 at 27 °C. Gültekin, E. K.; Noble, M. E., unpublished results.

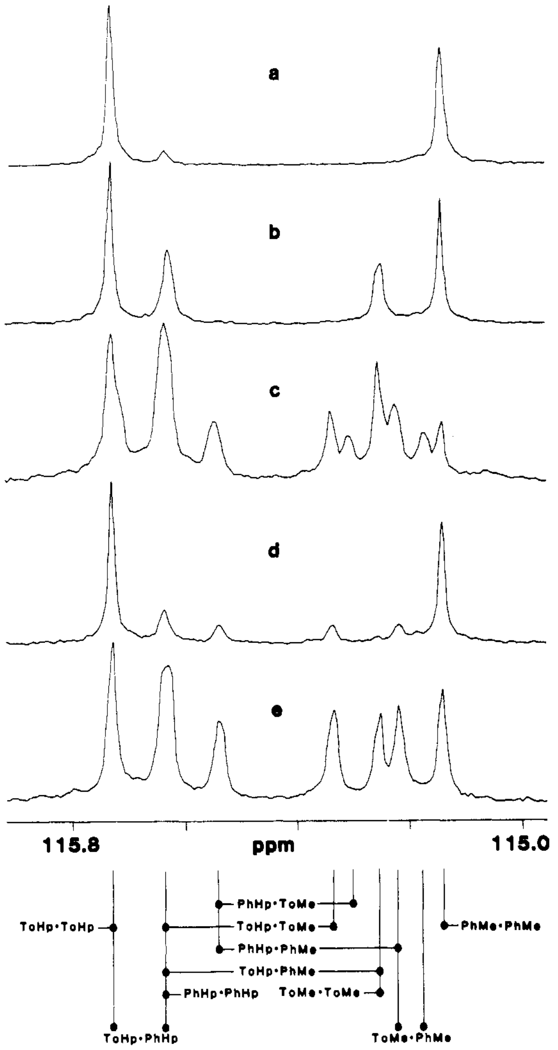

Figure 3. ^{31}P NMR spectra of ToHp·ToHp + PhMe·PhMe: (a) time zero; (b) 30-min photolysis; (c) 21-h photolysis; (d) 24-h dark control; (e) 6-day dark control. Labels are shown for the major invertomers.

at 30 min. The remaining four possible products were then assigned on the basis of their sequence of appearance and on known correlations of phenylimido vs. tolylimido dimer shifts and of acetate vs. octanoate dimer shifts. Assignments are included in Figure 3.

Again, photolysis proceeded readily and a full equilibration was realized after 21-h irradiation. A dark reaction was also again observed at a much slower pace. All 10 possible scramble products could be assigned in the photolysis spectra. Such was not the case for the dark controls, which showed notable absences of peaks attributable to S–S cleavage and subsequent scramble. These included ToHp·PhHp, ToHp·PhMe, PhHp·ToMe, and ToMe·PhMe, wherein a tolylimido dimer fragment was bound via the disulfide bridge to a phenylimido dimer fragment. Thus, all dark products in both experiments 8 and 9 were explicable by simple, slow carboxylate ligand exchange, while the light reactions involved a faster scramble via S–S cleavage and re-formation, accompanied by the slower carboxylate exchange.

Photoreductions. Reduction of the bis(dimer) disulfide, $[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)]_2S_2$, by several reagents was investigated. For benzyl mercaptan (experiment 10) after 15-min photolysis, 10% conversion was realized, giving a 2-fold mole ratio of $[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SSBz)]$:$[Mo(NTo)(S_2P(OEt)_2)S]_4$. This slowly progressed through 32-h photolysis, at which time only a trace of starting material was still observed but with a similar ratio of products. At 96-h photolysis, however, all $[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)]_2S_2$ was gone, and the mole ratio of $[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SSBz)]$:$[Mo(NTo)(S_2P(OEt)_2)S]_4$ had decreased to 0.7. The 24-h dark control showed no reaction. The spectral results were fully consistent with a two-step photoreduction, eq 5 and 6, the latter becoming important at long photolysis times.

$$2[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)]_2S_2 + 2BzSH \xrightarrow{h\nu} 2[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SSBz)] + [Mo(NTo)(S_2P(OEt)_2)S]_4 + 2MeCO_2H \quad (5)$$

$$2[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SSBz)] + 2BzSH \xrightarrow{h\nu} 2BzSSBz + [Mo(NTo)(S_2P(OEt)_2)S]_4 + 2MeCO_2H \quad (6)$$

All components in eq 5 and 6 were verified by ^{1}H NMR spectra. Inherent to $[Mo(NTo)(S_2P(OEt)_2)S]_4$ genesis was again the equilibrium of eq 2.

Photolysis of $[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)]_2S_2$ in the presence of excess triphenylphosphine (experiment 11) within 30 min gave 12% conversion to $[Mo(NTo)(S_2P(OEt)_2)S]_4$ but was not fully completed until 16–24 h of irradiation. Ph_3PO was the phosphine product. $[Mo(NTo)(S_2P(OEt)_2)S]_4$ remained the major product, but traces of $[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SCOMe)]$ (**3**, Z = COMe) were also seen. The ^{1}H NMR spectra showed the molybdenum products, Ph_3P, Ph_3PO, $MeCO_2H$, and $(MeCO)_2O$. The *S*-thioacetate-bridged dimer has been previously demonstrated to equilibrate in solution (eq 7).[18]

$$[Mo(NTo)(S_2P(OEt)_2)S]_4 + 2(MeCO)_2O \rightleftharpoons 2[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SCOMe)] \quad (7)$$

The overall reaction was therefore reduction with substantial hydrolysis due to adventitious moisture (eq 8 and 9). No dark

$$[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)]_2S_2 + Ph_3P \xrightarrow{h\nu} [Mo(NTo)(S_2P(OEt)_2)S]_4 + Ph_3PO + (MeCO)_2O \quad (8)$$

$$[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)]_2S_2 + Ph_3P + H_2O \xrightarrow{h\nu} [Mo(NTo)(S_2P(OEt)_2)S]_4 + Ph_3PO + 2MeCO_2H \quad (9)$$

reaction was observed for $[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)]_2S_2$ in this experiment through 96 h. A very slow oxidation of Ph_3P did occur, however, giving small quantities of Ph_3PO. This was presumed due to aerial O_2 and was not considered signficant.

Reaction of $[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)]_2S_2$ with excess triethyl phosphite was conducted under anhydrous conditions to avoid phosphite hydrolysis to $(EtO)_2PHO$ (experiment 12). Photolysis after 8 h left only a trace of the bis(dimer) disulfide, which was then totally gone at 20-h irradiation. The ^{31}P NMR spectrum at that time revealed, of the molybdenum products, 51% $[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SEt)]$ (**3**, Z = Et), 38% as δ 115.9 (minor) + 115.2 (major) invertomers, 4% as a δ 112.8 product, and 7% $[Mo(NTo)(S_2P(OEt)_2)S]_4$. No $(EtO)_3P$ was seen: this had been converted to $(EtO)_2PHO$, a product at δ 25.3, and minor components. Obviously some hydrolysis had slowly occurred, presumably due to the use of a septum cap since the time zero spectrum showed no trace of hydrolysis.

The second major molybdenum product was tentatively identified as $[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SPO(OEt)_2)]$ (**3**, Z = $PO(OEt)_2$), containing an *O,O'*-diethyl thiophosphate unit bridging via its sulfur. ^{31}P NMR assignments of the major invertomer were δ 115.2 for the two bidentate dithiophosphates and δ 25.3 for the bridge monothiophosphate. The δ 115.9 peak was assigned to the minor invertomer (isomer ratio 12:1) for the dithiophosphates; a minor invertomer for the monothiophosphate could not be assigned with a high certainty. Several pieces of evidence supported the tentative identification of this compound. The δ 115.2 peak always integrated 2-fold to δ 25.3. The δ 25.3 peak was in an agreeable ^{31}P NMR range for $(EtO)_2PO(SR)$ compounds.[23] The ^{1}H-coupled ^{31}P NMR spectrum of this compound gave a quintet for δ 25.3, clearly indicative of only two ethyl groups. Unfortunately, this compound has eluded synthetic efforts

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[23] Mark, V.; Dungan, C. H.; Crutchfield, M. M.; Van Wazer, J. R. *Top. Phosphorus Chem.* **1967**, *5*, 227.

toward its full characterization. The phosphite reaction is therefore tentatively described by eq 10.

$$[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)]_2S_2 + (EtO)_3P \xrightarrow{h\nu} [Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SEt)] + [Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SPO(OEt)_2)] \tag{10}$$

While the monothiophosphate-bridged dimer integrates slightly low, decomposition (e.g., acetate interaction with the bridge monothiophosphate) would be expected to give the observed $[Mo(NTo)(S_2P(OEt)_2)S]_4$.

The 24-h dark control showed no molybdenum-involved reaction but again only partial hydrolysis of $(EtO)_3P$.

$[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SEt)]$. This compound was prepared simply to verify assignments in the $(EtO)_3P$ photolysis reaction. Its preparation and properties are similar to those of prior analogues.[18,21] The ethanethiolate-bridged dimer showed an invertomer ratio of 1.2 in $CDCl_3$.

Discussion

All results from the current study are readily explained by S–S photohomolysis, a process so well established for diorganyl disulfides, RSSR,[20,24–27] but for which one or both sulfur sites now bridge two molybdenum centers. The photolysis produces thiyl radicals (eq 11–13), which are then capable of further reaction;

$$RSSR \xrightarrow{h\nu} 2RS^\bullet \tag{11}$$

$$[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SSR)] \xrightarrow{h\nu} [Mo_2(NTo)_2(S_2P(OEt)_2)_2S_2(O_2CMe)]^\bullet + RS^\bullet \tag{12}$$

$$[Mo_2(NAr)_2(S_2P(OEt)_2)_2S(O_2CR')]_2S_2 \xrightarrow{h\nu} 2[Mo_2(NAr)_2(S_2P(OEt)_2)_2S_2(O_2CR')]^\bullet \tag{13}$$

those herein described involve simple recombination, homolytic substitution, H(D) abstraction, and reaction with organophosphorus compounds.

Photolytic scramble of diorganyl disulfides (eq 14) has been well studied; the mechanism involves S_H2 and recombination steps as exemplified by, but not limited to, eq 15 and 16.[26,28–30]

$$RSSR + R'SSR' \overset{h\nu}{\rightleftharpoons} 2RSSR' \tag{14}$$

$$RS^\bullet + R'SSR' \rightarrow RSSR' + R'S^\bullet \tag{15}$$

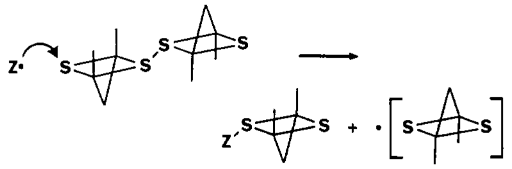
$$RS^\bullet + R'S^\bullet \rightarrow RSSR' \tag{16}$$

Presumably, the current dimer–organic disulfides, SMo_2SSR, react similarly following the photohomolytic initiation step (eq 12). For R = To and Ph, equilibria were readily achieved, giving somewhat similar equilibrium constants. Dialkyl disulfides give nearly statistical distributions with $K = 4$ (eq 14) except when *tert*-butyl groups are involved, for which $K \sim 25$.[28,29] The high values herein observed are attributable to steric constraints imposed by the bulky dimer fragment. Equilibrium was never attained in the allotted times for the SMo_2SSR, R = Et and Bz, derivatives. These results are consistent with established organic thiyl chemistry for which aryl precursors are notably more reactive than alkyl.[31–33] Presumably more intense, shorter wavelength irradiation is required for faster rates of photolysis of SMo_2SSR, R = Et and Bz. This marked difference in photolability accounts for the ease of preparation of the alkyl derivatives under normal lighting, while aryl analogues required diminished lighting as had been previously reported.[18]

Notably, the reaction of $[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)]_2S_2$ and BzSSBz (experiment 6) was also extremely slow although solvent reactions were similar to those of experiment 7. Photohomolysis was therefore occurring to give the dimer radicals $[Mo_2(NTo)_2(S_2P(OEt)_2)_2S_2(O_2CMe)]^\bullet$, but these were inadequate in providing fast homolytic substitution rates on BzSSBz although reaction with ToSSTo had been very facile (experiment 5). An additional consideration in this comparison, however, was possible contribution by RSSR photohomolysis (eq 11) for R = To but much less likely for R = Bz. Diarly disulfides are known to homolyze under fluorescent irradiation.[34]

That the bis(dimer) disulfides themselves were actually photolabile was substantiated by the photoexchange experiments 8 and 9. Irradiation gave homolysis (eq 13) with ultimately full exchange. Carboxylate exchange also occurred, but this was shown to be a dark reaction. Generation of the dimer radicals $[SMo_2S]^\bullet$ was therefore strictly photolytic in these and all experiments described herein.

The nature of the dimer radical cannot be deduced by data thus described, except to say there is substantial contribution of an electronic structure involving localization of the odd electron on a bridge sulfur. Delocalization within the SMo_2S framework would introduce Mo(V)–Mo(VI) contributions and would also allow communication of the radical to the opposite bridge sulfur position. An interesting mechanism of reaction might also exist for the bis(dimer) disulfides toward an attacking radical that is not available to diorganyl disulfides. Typically, radicals attack unhindered RSSR compounds primarily at the sulfur in a backside, S_H2 fashion.[20,33] This is not expected to be available in the bis(dimer) disulfides since the actual disulfide linkage is notably buried, a result borne out by reduction reactions. There does exist, however, the possibility for "back-bridge" attack involving radical attack on the opposite bridge followed by disulfide homolysis (eq 17). The data is presently insufficient to fully substantiate this possible mechanistic step.



(17)

Although the dimer radicals were not directly examined, several reactions were observed characteristic of thiyl radical chemistry. Hydrogen abstraction by $RS^\bullet$ is well established: the H donor can be mercaptan, solvent, or other substrate.[31,32,34] A slow photoreduction of $[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)]_2S_2$ was observed in the presence of benzyl mercaptan, indicative of dimer radical abstraction of the thiol hydrogen (eq 5, 6). Prolonged photolysis in $CDCl_3$ gave products consistent with deuterium abstraction from solvent (eq 3), although further decomposition was also noted. While solvent reaction may have been an interference in some experiments, it did provide a consistent internal marker for homolysis.

Photoreactions with organophosphorus reagents were also examined. While triphenylphosphine reactions of SMo_2SSR complexes had been previously demonstrated and discussed in terms of classical nucleophilic mechanisms,[18] the bis(dimer) disulfide $[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)]_2S_2$ was here shown to react with Ph_3P or $(EtO)_3P$ only upon irradiation. The lack of any dark reaction was consistent with great steric hindrance precluding attack by phosphorus on a disulfide sulfur site. This was particularly true for triethyl phosphite since it reacts with a wide variety of diorganyl disulfides by simple nucleophilic attack, albeit commonly followed by Arbusov rearrangement.[35–37]

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Reactions of thiyl radicals with phosphines or phosphites produce initially a phosphoranyl radical (eq 18, Z = R′ or OR′),

$$\mathrm{RS^{\bullet} + Z_3P \rightarrow (Z_3PSR)^{\bullet}} \qquad (18)$$

generally followed by C–S homolysis to give an organophosphorus sulfide and an organic radical (eq 19).[35-39] This latter step was

$$\mathrm{(Z_3PSR)^{\bullet} \rightarrow Z_3PS + R^{\bullet}} \qquad (19)$$

not observed for the current system, however, as it required sulfur abstraction from a bridge. Alternative modes of decomposition of the presumed dimer–phosphoranyl radical intermediate $[\mathrm{SMo_2SPZ_3}]^{\bullet}$ were therefore found. For triethyl phosphite, C–O fission gave the observed ethanethiolate-bridged dimer and the proposed (*O,O′*-diethyl thiophosphato-*S*)-bridged dimer (eq 10). C–O homolysis is indeed known for thiyl–phosphite systems as an alternative to eq 19, but it is a relatively minor pathway.[39-41] For triphenylphosphine the overall reaction, eq 8, resembled previous nucleophilic reductions,[18] but the radical mechanism here was not clearly discernible. There may have been direct acetate involvement with the radical site to account for the observed products.

Other Systems. The chemistry herein described, while an obvious mimicry of diorganyl disulfide chemistry, knows a limited parallel in metal–sulfur systems. Photochemistry of such compounds has, of course, been investigated, but not so much in terms of S–S photohomolysis.[42] Photochemical reactions of metal complexes with diorganyl disulfides are known to give metal thiolates[43] or, for organocobaloximes, thioethers;[44] these therefore do not involve new S–S bonds in the products. An increasing variety of disulfide complexes are known,[45] but the majority of these involve bidentate disulfide, or the disulfide is one component of a multiply bridged oligomer. S–S photolability would be expected to be less demonstrable, albeit not impossible, in these types and more readily observable in systems wherein a single S–S linkage bridges two fragments capable of at least a transitory existence.

Several examples of photolabile metal S–S compounds are noted. S–S photohomolysis has been reported for dithionite bridges in $[(\mathrm{C_5H_5})\mathrm{Fe(CO)_2SO_2}]_2$ and $[\mathrm{Mn(CO)_5SO_2}]_2$.[46] Monomeric, radical intermediates were implicated. $[(\mathrm{H_2NC_2H_4NH_2})_2\mathrm{Co(OH_2)(S_2O_3)}]^+$, containing a Co–S(S)–$\mathrm{SO_3}$ unit, has demonstrated photosensitivity to fluorescent lighting, although S–S cleavage was not explicitly indicated.[47] $[(\mathrm{C_5H_5})\mathrm{Fe(CO)_2}]_2\mathrm{S_3}$, a trisulfide-bridged iron dimer, was also reported to be light sensitive in solution, but again the nature of the photolability was not indicated.[48] Photoisomerization has been observed for the $[(\mathrm{Me_5C_5})\mathrm{MoS_2}]_2$ system and involves sulfide–disulfide interconversions.[49] One component of that process actually has a multiple bridge involving disulfide and sulfide sites, but presumably dimer dissociation does not occur and radical monomers are not involved.

Acknowledgment. This work was supported by Research Awards from the Graduate School and from the College of Arts and Sciences of the University of Louisville.

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Synthesis and Electropolymerization of Distyrylbipyridine and Methyldistyrylbipyridine Complexes of Iron, Ruthenium, Osmium, Rhenium, and Cobalt

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Received June 25, 1986

Several dozen Fe, Ru, Os, Re, and Co complexes containing the ligands 4,4′-distyryl-2,2′-bipyridine (DSB) and 4,4′-bis(*p*-methylstyryl)-2,2′-bipyridine (MeDSB) have been prepared. The ligands undergo coupling reactions when the complexes are reduced electrochemically, resulting in the formation of smooth and adherent electroactive polymeric films on Pt electrodes. Evaluation of the relative rates of electropolymerization for selected metal complex monomers shows that the DSB and MeDSB ligands lead to slower electropolymerizations than do the related ligands vbpy (4-vinyl-4′-methyl-2,2′-bipyridine) and vpy (4-vinylpyridine) in analogous complexes. The stability of the DSB and MeDSB ligands was helpful in the synthesis of novel electropolymerizable monomers such as $[\mathrm{Os(DSB)_3}]^{2+}$, $[\mathrm{Os(MeDSB)_3}]^{2+}$, $[\mathrm{(DSB)_2M(CO)Cl}]^+$ (M = Ru, Os), and $[\mathrm{(DSB)Re(CO)_3X}]$. The last complex is a $\mathrm{CO_2}$ reduction catalyst. Correlations between monomer composition and polymer characteristics were revealing, showing, for example, that poly-$[\mathrm{(MeDSB)_3M}]^{2+}$ films exhibit faster electron transport and are more permeable than previously studied poly-$[\mathrm{Ru(vbpy)_3}]^{2+}$ films.

The realization that electrocatalysis with chemically modified electrodes should be most effective with an electroactive polymer film catalyst possessing an accessible interior and fast electron transport has been one of several factors behind the development of electroactive polymer coatings for electrodes.[1,2] The most common types of coatings are polymers with covalently attached redox sites and ion-exchange polymers with electroactive counterions. Ion-exchange polymers[3-17] are attractive in that a given

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