to the TPA complex. EPR studies and MO calculations[22] on semiquinones have demonstrated substantial unpaired spin density at C-4 and C-5 and significantly smaller density at C-3 and C-6. Thus, the 5-*tert*-butyl exhibits a larger downfield shift relative to the 3-*tert*-butyl group, and the 4-H proton is significantly more upfield shifted than the 6-H proton. In the TPA complex, these effects are even more pronounced when compared to the other complexes. The greater semiquinone character in the TPA complex correlates well with its high reactivity toward O_2. These trends provide substantial support for the substrate activation mechanism we have proposed for the oxidative cleavage of catechols,[10] in which O_2 attack on the coordinated catecholate is facilitated by the enhanced radical character of the substrate (Scheme I). A peroxide complex is proposed to form subsequent to O_2 binding and then decomposes to the muconic anhydride. The recently reported crystal structure of the O_2 adduct of an Ir(III)–catecholate complex shows just such a peroxide moiety coordinated in a tridentate manner to the Ir center,[23] a result that lends further credence to the mechanism shown in Scheme I.

Acknowledgment. This research was supported by the National Institutes of Health Grants (GM-33162). We are grateful to Professor J. D. Britton for his expertise in the X-ray diffraction experiments.

Supplementary Material Available: Tables of atomic coordinates, thermal parameters, intermolecular distances, bond lengths, and bond angles for $[Fe^{III}(TPA)DBC]BPh_4$ (20 pages). Ordering information is given on any current masthead page.

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Generation and Characterization of Dimolybdenum Thiyl Radicals

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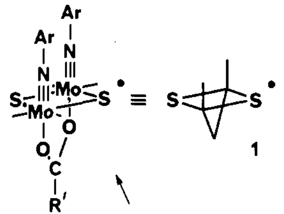
Abstract: Compounds of the type $[Mo_2(NC_6H_4CH_3)_2(S_2P(OC_2H_5)_2)_2S(O_2CCH_3)(SSR)]$, which contain RSS^- as Mo_2SSR units, and compounds of the type $[Mo_2(NC_6H_4R)_2(S_2P(OC_2H_5)_2)_2S_2(O_2CR')]_2$, which contain Mo_2SSMo_2 units, undergo photohomolysis with visible or ultraviolet light. Dimolybdothiyl radicals, $Mo_2S^\bullet$, are produced in all cases; these have been trapped and observed by EPR spectroscopy. Solvent reactions have shown that the radicals H abstract from tetrahydrofuran but not from chloroform nor from toluene. The radicals polymerize styrene and effect the cis–trans isomerization of 2-butene. A tetrasulfide derivative containing the $Mo_2SSSSMo_2$ unit also photolyzes to give polysulfides $Mo_2SSS_xSSMo_2$.

Introduction

While for some time there has been a great interest in syntheses and reactions of discrete metallosulfur complexes, there has also been within that general area a specific focus on sulfur-centered reactivity as opposed to, or in addition to, metal-centered reactivity. A wide variety of metallosulfur complexes have displayed sulfur-centered reactivity; among these, several systems have been particularly well developed, such as those of cyclopentadienylmetal and carbonyliron complexes.[1-4] Much of the interest in these systems has derived from the pivotal roles of metallosulfur systems in a variety of catalytic applications, and for which the question can therefore be posed as to whether the sulfur can interact with substrate in the catalytic mechanism.[1,2] Another interest lies in the similarity to organic sulfur chemistry which has been noted in many of the reactions. In such cases, sulfur ligands such as SH^-, S^{2-}, or S_2^{2-}, acting as terminal MS or bridge $M_2(\mu\text{-}S)$ units, showed parallel to thiol, thiolate and disulfide chemistry.[3-7] Noteworthy is that the bridge sulfur functionality is dicoordinate to metal and is therefore structurally similar to organic sulfides, R_2S, although in many cases its chemistry is distinctly thiolate in behavior.

Relative to organosulfur, one parallel in metallosulfur chemistry which has been less developed is sulfur-centered radical chemistry of a thiyl nature. This should not be too unexpected, however, since the metal itself within such a complex might accommodate the radical electron, thereby diminishing thiyl behavior.

One system which has displayed metallothiyl radical chemistry involves sulfidomolybdenum dimers of the type $[Mo_2(NAr)_2(S_2P(OEt)_2)_2(\mu\text{-}S)_2(\mu\text{-}O_2CR')]^\bullet$, **1** (for abbreviations, see note[8]), in which bridge sulfurs are the reactive species. The dimolybdothiyl complexes are not isolable per se but are instead generated in situ by photohomolysis of dimolybdenum(V) bisdimer disulfides $[Mo_2(NAr)_2(S_2P(OEt)_2)_2S_2(O_2CR')]_2$, **2**, or RSS-bridged dimers $[Mo_2(NAr)_2(S_2P(OEt)_2)_2S(O_2CR')(SSR)]$, **3** (eq 1). A number of reactions have been characterized for **1** in which



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(dithiophosphates not shown)

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[8] Abbreviations used in this paper: Me, methyl; Et, ethyl; Pr, *n*-propyl; Bz, benzyl; Ar, aryl; Ph, phenyl; To, *p*-tolyl; Xy, *m*-xylyl (3,5-dimethylphenyl); Cp, cyclopentadienyl.

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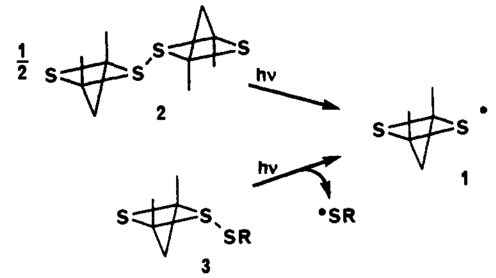


(1)

the dicoordinate bridge sulfur clearly demonstrated thiyl behavior.[9] While the overall chemistry thus appeared to be sulfur-based, interesting questions remained regarding the energetics and electronics of the system. Such considerations regarding the nature and generation of the dimer radical **1**, and further aspects of its reactivity, are discussed herein.

Experimental Section

Syntheses of most molybdenum complexes herein discussed have been previously described.[5,6,9,10] Reactions which were conducted under N_2 or vacuum used solvents which had been dried, vacuum transferred, and subsequently stored under N_2. $(EtO)_2PS_2H$ was vacuum distilled. XyN_3 was prepared by standard reaction of XyN_2^+ (from diazotization of $XyNH_2$) with N_3^- and was stored as a solution in c-C_6H_{12}. Other reagents were used as commercially available except where stated. Galbraith Laboratories (Knoxville, TN) performed the elemental analyses.

^{31}P, ^1H, and ^{13}C NMR spectra were obtained on a Varian XL-300 spectrometer at 121, 300, and 75 MHz and are reported as downfield shifts from external 85% H_3PO_4 and internal Me_4Si; the solvent was $CDCl_3$ except where noted. UV–vis spectra were obtained on a Perkin-Elmer 330 spectrophotometer using spectral grade $CHCl_3$. All values for extinction coefficients are apparent ϵ values only (M^{-1} cm^{-1}).

In all studies employing compounds **2** or **3** (R = Ph or To only), the solutions were handled under red light conditions[5] except during actual irradiation or as noted below.

Studies of photolytic cutoffs were done using filtered light in an apparatus of local construction. The source was a 240-W Sylvania sunlamp, which was given a 10-min warm-up time prior to sample exposure. Corning band-pass filters 0-53 (279, 311), 0-52 (347, 370), 3-74 (412, 423), 3-71 (467, 497), 3-68 (530, 546), 2-63 (582, 602), and 2-58 (631, 650) were used for all compounds, as also was the ultraviolet-transmitting, visible-absorbing filter 7-54. For comparison purposes, the parenthetical values listed with the band-pass filters correspond to wavelengths (nm) for 10% and 80% transmittance relative to a 9-54 filter. Reactions were monitored by NMR, and the sample was photolyzed directly in the NMR tube at a distance of 30 cm from the lamp. All compounds used in the cutoff studies were tolylimido, acetate-bridged derivatives. For **2**, the reactions used 6.24–6.25 μmol of **2** and 25 μmol of BzSH in 0.50 mL of $CDCl_3$. For **3**, the reactions used 12.5 μmol of **3** in 0.50 mL of $CDCl_3$. For **3**, R = Et and Bz, the 9–54 filter was also used, and a quartz NMR tube was employed for all filters.

EPR spectra were obtained on a Varian E 109 spectrometer and were calibrated against DPPH. Samples were prepared by combining **2** (5.36 μmol) and trap (11.3 μmol) in 0.75 mL of CH_2Cl_2 on a vacuum line under N_2. Photolysis of the sample in the EPR cavity was done using a 650-W studio lamp (type DVY) or 240-W Sylvania sunlamp. Spectra were obtained at room temperature except where indicated. Simulations of the spectra were done using a modified version of a previously published program,[11] which allowed up to 75 points/G.

For solvent reaction studies, 4.5 μmol of **2** (Ar = Xy, R′ = Pr) and 0.75 mL of solvent were combined in an NMR tube under N_2. The tube was frozen (liquid N_2), evacuated, and flame-sealed. The sample was then photolyzed for 18 h in a light box of local construction using a 22-W, 8-in., circular, cool white fluorescent lamp. The NMR tube was held perpendicular to the lamp and such that the lamp and solution centers approximately coincided. The temperature during photolysis inside the box was ~26 °C. After photolysis, the NMR tube was then broken under vacuum and the volatile portion was vacuum transferred for 6 h. The nonvolatile residue was redissolved in $CDCl_3$, and NMR spectra were obtained.

For styrene polymerization studies, a sample procedure was as follows. Styrene (1.2 mmol), **2** (0.0122 mmol), and $CDCl_3$ (0.80 mL) were combined in an NMR tube under N_2. This was then frozen (liquid N_2), evacuated, and flame-sealed. The sample was photolyzed for 32 h using the light box described above. Under room lighting and open to air, the tube was broken and the solution was then stripped on a vacuum line overnight. The residue was thrice chased/stripped with 1,2-$C_6D_4Cl_2$ to promote removal of styrene monomer. After redissolving in $CDCl_3$, NMR spectra were obtained.

For butene isomerization studies, a typical procedure was as follows. In a septum-capped NMR tube under N_2, **2** (1.2 μmol) was dissolved in 1.0 mL of $CDCl_3$. After lowering the tube into a dry ice bath but prior to solvent freezing, *cis*-2-butene (120 μmol) was condensed into the solution. The sample was allowed to warm and then photolyzed using the light box described above. The reaction was monitored by NMR spectroscopy (^1H and ^{13}C).

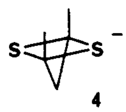
For photolysis of **3** (R = $PS(OEt)_2$) and of tetrasulfide, the procedure and quantities were identical to those as reported for prior photolysis experiments.[9] For photolyses of **2** with varying ratios of sulfur, **2** (12.5 μmol), the appropriate amount of 0.25 M sulfur in $CDCl_3$, and $CDCl_3$ (to bring to 1.0 mL) were combined and photolyzed for 24.0 h using the previously reported setup.[9]

$[Mo(NXy)(S_2P(OEt)_2)S]_4$, 7 (Ar = Xy). $Mo(CO)_6$ (3.28 g, 12.4 mmol), S (0.400 g, 12.5 mmol), $(EtO)_2PS_2H$ (3.2 mL, 20 mmol), and XyN_3 (10.0 mL of 2.11 M in c-C_6H_{12}, 21 mmol) were combined and purged with N_2 on a vacuum line. THF (~40 mL) was added, and the slurry was refluxed for 18 h under N_2. The pot was opened to air, and the contents were filtered and washed with THF. The dark red-green filtrate was stripped to an oil on a rotary evaporator and treated with MeOH (50 mL). Product was collected, washed (MeOH), and dried. Recrystallization from a CH_2Cl_2 filtrate (15 mL) with MeOH (60 mL) followed by collection, washing (MeOH), and drying gave a dark olive powder (32%). Anal. ($Mo_4C_{48}H_{72}N_4O_8P_4S_{12}$) C, H, N. ^{31}P NMR (ppm): 112.0. ^1H NMR (ppm): 6.31, s, Xy *p*-H; 6.00, s, Xy *o*-H; 4.66, m, 3.71, m, $POCH_2$; 1.84, s, Xy CH_3; 1.59, t, 0.83, t, $POCCH_3$.

$[Mo_2(NXy)_2(S_2P(OEt)_2)_2S_2(O_2CPr)]_2$, 2 (Ar = Xy, R′ = Pr). Methanolic H_2O_2 was freshly prepared by diluting 0.112 mL of H_2O_2 (11%, 0.38 mmol) to 2.0 mL with MeOH. A portion (1.0 mL) was added to a slurry of $[Mo(NXy)(S_2P(OEt)_2)S]_4$ (0.432 g, 1.00 mmol), $PrCO_2H$ (92 μL, 1.0 mmol), CH_2Cl_2 (4.0 mL), and MeOH (8.0 mL). After stirring for 10 min, a second portion (0.5 mL) was added, followed by stirring for 5 min, addition of the remaining peroxide solution, and again stirring for 5 min. Volatiles were removed on a rotary evaporator. The solid was dissolved in CH_2Cl_2 and filtered; the filtrate (4.3 mL) was treated with MeOH (17.2 mL). The precipitate was collected, washed with MeOH, and vacuum dried to give maroon crystals (43%). Anal. ($Mo_4C_{56}H_{90}N_4O_{12}P_4S_{12}$) C, H, N. ^{31}P NMR (ppm): 116.2. ^1H NMR (ppm): 6.68, s, Xy *o*-H; 6.39, s, Xy *p*-H; 4.3–4.0, m, $POCH_2$; 1.80, s, Xy CH_3; 1.26, m, $POCCH_3$ + O_2CCH_2; 0.99, m, O_2CCCH_2; 0.58, t, O_2CCCCH_3.

Results

For clarification purposes, a number of abbrevations will be herein utilized. Abbreviations for organic groups have been footnoted.[8] General dimer groups $[Mo_2(NAr)_2(S_2P(OEt)_2)_2S_2(O_2CR')]$ will simply be designated Mo_2S, wherein the S represents a bridge sulfur; thus, bisdimer disulfides **2** and RSS-bridged dimers **3** are denoted Mo_2SSMo_2 and Mo_2SSR. Additional compound types necessary for current consideration are the dimer anion **4** (Mo_2S^-), S-derivatized dimers **5** (Mo_2SZ) and the bisdimer tetrasulfide **6** ($Mo_2SSSSMo_2$). It is noted that a key characteristic of the majority of these compounds[5,6,10] is the presence of sulfur invertomers in solution. These are illustrated for **5** and are labeled distal or proximal on the basis of the position of Z relative to the arylimido groups. While invertomer ratios do vary substantially, the major invertomers for **3**, **5**, and **6** are usually distal, while for **2** proximal is dominant. The cubane tetramer $[Mo(NAr)(S_2P(OEt)_2)(\mu_3\text{-}S)]_4$, **7**, is also related to the current study due to the



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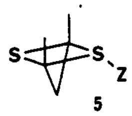
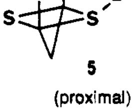


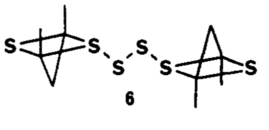
5

(distal)



5

(proximal)



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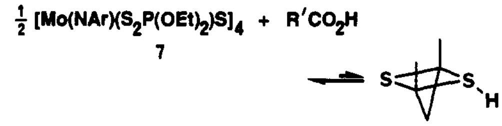
equilibria of eqs 2 and 3 with dimer anion and with the hydrosulfide-bridged dimer **5** (Z = H). The dimer anion is a thiolate analogue, and a number of nucleophilic substitutions and additions have been demonstrated. The equilibrium of eq 2 lies favorably to the right (>80%) under stoichiometric conditions, but fuller quantitation of the equilibrium is complicated by strong cation effects and by decomposition from solvent moisture or at high carboxylate ratios. Conversely, the hydrosulfide equilibrium (eq 3) is very unfavorable and no Mo_2SH is observable for unsubstituted carboxylic acids; α-halo acids, however, give observable Mo_2SH complexes.[12]

(2)

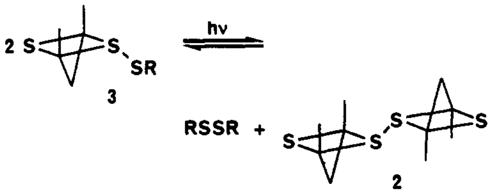


(3)

Unless otherwise specified, compounds are tolylimido, acetate-bridged derivatives (Ar = To; R' = Me). Where arylimido or carboxylate specification is desired, the designation will be of the type (Ar, R')Mo_2S.

Cutoffs and UV-Vis Spectra. It had been previously noted that Mo_2SSR compounds under fluorescent lighting displayed a great difference in reactivity between R = aryl and R = alkyl derivatives, such that photolysis of the former was facile while photolysis of the latter was almost insignificant.[9] This was believed due to very different wavelengths for photolysis bands. Reasonable parallel can be drawn to the differences in long-wavelength bands between unstrained dialkyl and diaryl disulfides; these bands are qualitatively of the $n(S) \rightarrow \sigma^*(S-S)$ type and can lead to S–S homolysis.[13-15] S–S bond energies of dialkyl and diaryl disulfides also differ substantially.[16,17] For the current dimer system, more specific information was therefore desired regarding the actual wavelengths of the photolysis bands of the different Mo_2SSR derivatives and also of the Mo_2SSMo_2 compounds. For this reason, filtered photolyses and UV-vis spectra were investigated.

For the filtered photolysis studies, two types of reactions were utilized. The approach to photoequilibrium (eq 4) was examined for Mo_2SSR, while for Mo_2SSMo_2 the extent of H abstraction from benzyl mercaptan (eq 5) was studied in its early stages. Both reactions have been previously characterized using unfiltered, fluorescent lamps.[9] Only qualitative interpretation of cutoff was presently intended, and quantitation was not appropriate in light of complications due to product photolysis, wavelength dependence of lamp output, etc.



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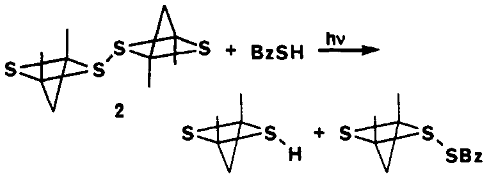

(5)

Table I. Selected UV-Vis Data[a]

	(Ar, R')Mo_2SSMo_2(Ar, R'), **2**		
Ar, R' = To, Me	∼506 (1820)	∼412 (13 700)	316 (49 500)
To, Pr	∼508 (1540)	∼409 (12 800)	∼310 (48 100)
To, Hp	∼510 (1620)	∼411 (12 700)	315 (48 800)
Ph, Me	∼504 (1530)	∼412 (11 900)	∼317 (45 000)
Xy, Pr	∼512 (1350)	∼412 (11 700)	∼310 (44 300)
	Mo_2SSR, **3**		
R = Et	502 (1480)	∼408 (6620)	311 (28 900)
Bz	502 (1520)	∼407 (6990)	310 (28 800)
Ph	504 (1440)	∼411 (7110)	314 (31 000)
To	502 (1440)	∼412 (7250)	312 (31 900)
$PS(OEt)_2$	502 (1530)	∼409 (6950)	306 (31 900)
	Mo_2SR, **5**		
R = Et	492 (1450)	∼406 (6720)	319 (27 900)
Bz	496 (1590)	∼410 (6510)	317 (27 000)
CH_2Cl	495 (1440)	∼408 (6430)	316 (28 300)
NH_2	500 (1600)	∼402 (7040)	314 (27 300)
	$Mo_2SSSSMo_2$, **6**		
	504 (2830)	∼407 (14 100)	308 (62 000)

[a] Values are wavelengths (nm) (ϵ (M^{-1} cm^{-1})). Compounds are tolylimido, acetate-bridged derivatives except as specified for **2**. The ∼ indicates shoulder.

Qualitative results are briefly summarized. For Mo_2SSTo, Mo_2SSPh, and Mo_2SSMo_2, band-pass filters with cutoffs well into the visible were needed to produce a reduction in the extent of reaction. The results indicated that the photolysis wavelengths for the three derivatives were similar and in the region of 540–580 nm. Use of the ultraviolet-transmitting, visible-absorbing 7-54 filter showed some slow reaction for Mo_2SSMo_2; this suggested a possible minor contribution from a UV process. For Mo_2SSTo and Mo_2SSPh, the 7-54 filter allowed considerable reaction. These latter systems, however, were complicated by the presence of nascent ArSSAr, whose facile photolysis in the available UV range would have accelerated the overall equilibration.

For Mo_2SSBz and Mo_2SSEt, diminution of reaction was observed with ultraviolet-cutoff filters. Furthermore, the 7-54 filter allowed similar reaction as the low-wavelength band-pass filters. The general conclusions were that the two derivatives possessed photolysis bands in the 320–360-nm region, with Mo_2SSEt possibly red-shifted relative to Mo_2SSBz.

UV-vis spectra of a number of compounds have been examined, and some results are in Table I. The spectra are complex, and some features in addition to those listed in Table I can be observed. Colorwise, all compounds are orange in solution, although bisdimer disulfides are somewhat orange-brown. The data in Table I are meant to be illustrative of general trends and are not exhaustive for all features observed. A representative spectrum is shown in Figure 1. An obvious result from consideration of the spectra of Mo_2SSR and Mo_2SR compounds is that they are all very similar, regardless of whether the compound is photoactive. Similar peaks but different intensities are also found for the Mo_2SSMo_2 and $Mo_2SSSSMo_2$ derivatives.

The dominance in the spectra of gross general features which are the same for the different compounds precludes direct identification of photolysis bands even for those that are photolytic in the visible region. In further efforts, derivative spectra were examined for Mo_2SSTo, Mo_2SSBz, and Mo_2SSEt from first through fourth order from 450 to 800 nm, but these, too, were very similar. Difference spectra were also obtained in the range 450–800 nm for one Mo_2SSR versus another, utilizing all six permutations within the group of R = To, Ph, Bz, and Et, but the results were not definitive. Thus, it appeared that while cutoff studies indicated a photolysis band for Mo_2SSTo and Mo_2SSPh in the 540–580-nm range, the band was quite weak ($\epsilon < 25$) and buried under the tails from shorter wavelength absorptions. For comparison, the overall ϵ for the tail for Mo_2SSTo from 550 to 560 nm was 730–290.

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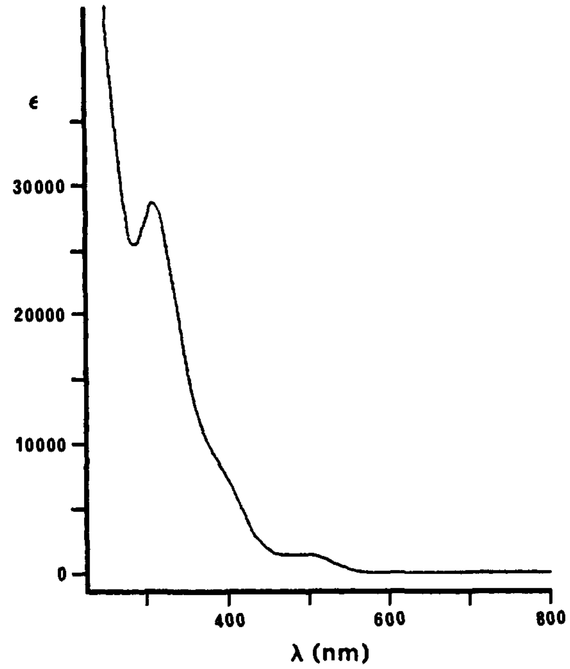


Figure 1. UV–vis spectrum of $\mathrm{Mo_2SSBz}$, **3** (R = Bz).

Despite gross similarities in all the spectra, a very interesting difference is apparent between bisdimer disulfides **2** and tetrasulfide **6**. For $\mathrm{Mo_2SSSSMo_2}$, the spectrum is essentially similar to that of $\mathrm{Mo_2SSR}$ or $\mathrm{Mo_2SR}$ except that the molar extinction coefficients are doubled; the dimer chromophores are therefore independent, and the $\mathrm{S_4}$ linkage is essentially insulating.[18] For the corresponding $\mathrm{Mo_2SSMo_2}$, the molar extinction is doubled only for the ~412-nm band, although it is also substantially increased for the 316-nm peak. The molar extinction for the ~510-nm band, however, is only modestly enhanced, and even this increase can be attributed to the doubling of the tails from shorter wavelength absorptions. Thus, the $\mathrm{S_2}$ linkage is not insulating for this long-wavelength feature.

A final consideration for the interpretation of the spectra is the question of the effect of invertomers. Since the different compounds per se give similar spectra, it is reasonable to expect the invertomers themselves have similar spectra. The question of invertomers may be very serious to photolysis, since the two isomers may have different photolytic bands and/or rates.

EPR Spectroscopy. While photochemical reactions clearly indicated the intermediacy of the dimolybdothiyl radical **1**, direct observation of the radical was desired. A number of organic thiyl radicals have been characterized by EPR spectroscopy either directly or as spin adducts.[19] EPR spectroscopy was therefore undertaken on samples of bisdimer disulfides during photolysis within the EPR cavity. Unfortunately, no spectrum was ever observed for radicals from a variety of $\mathrm{Mo_2SSMo_2}$ derivatives in solution or in frozen solution within a temperature range of 77–298 K.

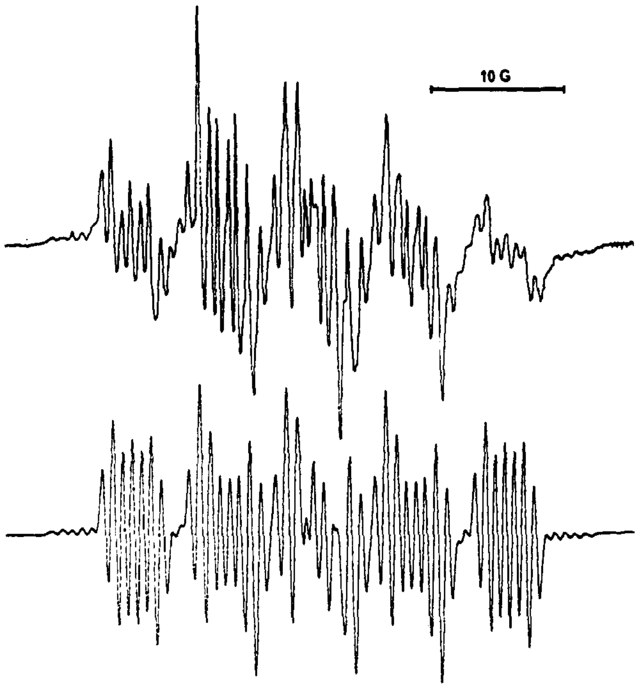
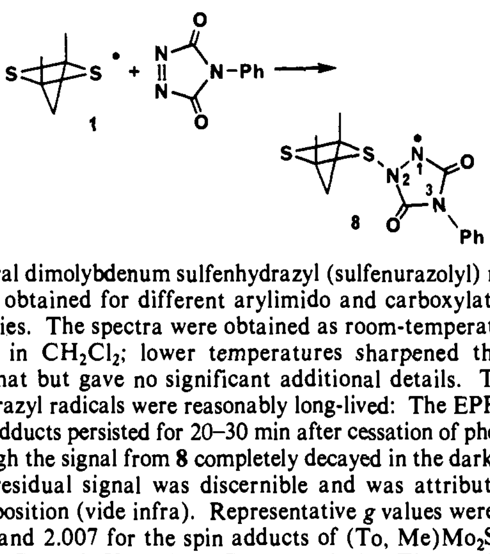


Figure 2. EPR spectrum of the triazolinedione spin adduct **8** with the (To, Hp)$\mathrm{Mo_2S^\bullet}$ radical (top) and a simulation of the spectrum (bottom).

Photolyses were then conducted for $\mathrm{Mo_2SSMo_2}$ in the presence of radical traps. Several traps, including 2-methyl-2-nitrosopropane, *N-tert*-butyl-α-phenylnitrone, and $\mathrm{Et_2S}$, which have been known to form organic thiyl spin adducts,[20–22] failed to produce an observable adduct with $\mathrm{Mo_2S^\bullet}$. Successful trapping was realized, however, with 4-phenyl-1,2,4-triazoline-3,5-dione; this reagent was shown to be an efficient trap for a variety of radicals including benzenethiyl, $\mathrm{PhS^\bullet}$.[23] Direct EPR observation of adduct formation (eq 6) was thus achieved, and different EPR spectra of several dimolybdenum sulfenhydrazyl (sulfenurazolyl) radicals **8** were obtained for different arylimido and carboxylate functionalities. The spectra were obtained as room-temperature solutions in $\mathrm{CH_2Cl_2}$; lower temperatures sharpened the lines somewhat but gave no significant additional details. The sulfenhydrazyl radicals were reasonably long-lived: The EPR signal of the adducts persisted for 20–30 min after cessation of photolysis. Although the signal from **8** completely decayed in the dark, a very small residual signal was discernible and was attributable to decomposition (vide infra). Representative *g* values were 2.006, 2.009, and 2.007 for the spin adducts of (To, Me)$\mathrm{Mo_2S^\bullet}$, (To, Hp)$\mathrm{Mo_2S^\bullet}$, and (Xy, Pr)$\mathrm{Mo_2S^\bullet}$, respectively. These values are higher than those of the previous urazolyl radicals, but are more consistent with acyl(sulfen)aminyl radicals RCON($^\bullet$)SR′, whose higher *g* values have been ascribed to significant delocalization onto sulfur.[24]



(6)

A spectrum for the adduct with (To, Hp)$\mathrm{Mo_2S^\bullet}$ is shown in Figure 2 and illustrates the general pattern found for all derivatives. Simulations were attempted, and a reasonably successful simulation for the spin adduct of (To, Hp)$\mathrm{Mo_2S^\bullet}$ was obtained; this is also shown in Figure 2. Simulation accounted for coupling to three inequivalent nitrogen atoms and two equivalent phosphorus atoms from the dithiophosphate ligands. Phosphorus coupling is well known for dithiophosphate metal complexes, including imidomolybdenum(V) monomers.[25] A second simulation component accounted for these and for coupling to a single magnetic

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molybdenum site (^{95,97}Mo, $I = {}^5/_2$, 25.4%) in the dimer. A complication to the simulation is the unknown contribution from a second sulfur invertomer. The orientation of the major invertomer is unknown, and its representation as distal in **8** is speculative. The spectrum of the spin adduct for (To, Me)$Mo_2S^•$ shows clear doubling of some peaks attributable to a much greater contribution from a minor invertomer. Due to uncertainties in the simulations, which are increased by the invertomer question, the *a* values from the simulation for the adduct with (To, Hp)-$Mo_2S^•$ are presumed to be representative for the adducts **8** in general, suitably estimated to be $a_{N1} = 7.2$ G, $a_{N2} = 6.3$ G, $a_{N3} = 1.4$ G, $a_P = 0.8$ G, and $a_{Mo} = 1.5$ G. The assignments of N1 and N2 couplings are based on considerations presented for the prior triazolinedione spin adducts[23] with due recognition for the possibility of their interchange. The current N1, N2, and N3 couplings are within the range of values in that prior work.

The simulations support the structure represented by **8** with the triazolinedione bound to bridge sulfur. The most reasonable alternate structure would involve the binding of the triazolinedione to molybdenum by displacement of carboxylate. Total carboxylate loss is excluded by the variations in the spectra with different carboxylate derivatives. Monodentate ligation of carboxylate to one molybdenum with triazolinedione bound to the second would destroy the symmetry of the adduct, giving inequivalent phosphorus and molybdenum coupling contributions. Simulations were attempted assuming inequivalent phosphorus sites: Using even small differences in phosphorus couplings gave significantly deleterious results.

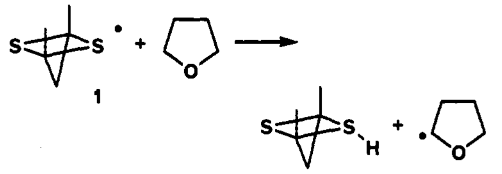
While the binding of triazolinedione to sulfur is thus well supported, triazole–metal complexes in general are indeed known with ligation to metal via nitrogen.[26,27] Interestingly, however, the reaction of 4-phenyl-1,2,4-triazoline-3,5-dione with $(MeCp)_2V_2(\mu\text{-}S_2)(\mu\text{-}S_2)$ resulted in partial sulfur loss and the binding of the triazolinedione as a bridge to the two vanadium atoms.[28] Presumably the reaction did not involve a radical mechanism, but attack by the triazolinedione on a sulfide bridge was specifically proposed.

Solvent Reactions. In earlier work,[9] the photolysis of disulfide Mo_2SSMo_2 was reported to give a slow reaction observable upon prolonged illumination, ultimately leading to decomposition. Initially observed products were the tetramer **7** and a product believed to be derived from solvent. The slow reaction was ascribed to H(D) abstraction from chloroform solvent, giving tetramer **7** (via hydrosulfide, eq 3) and a trichloromethanethiolate-bridged dimer, Mo_2SCCl_3 (**5**, Z = CCl_3). That conclusion has since proven to be incorrect, but it prompted further study of solvent abstraction reactions using tetrahydrofuran and toluene in addition to chloroform.

Due to solubility problems, tolylimido and phenylimido disulfides Mo_2SSMo_2 were not suited for THF or toluene. The xylylimido/butyrate derivative (Xy, Pr)Mo_2SSMo_2(Xy, Pr) was prepared and characterized since it proved to be of greatly enhanced solubility. Its preparation parallels that of other derivatives.[5] Although most disulfides **2** show invertomers in solution, (Xy, Pr)Mo_2SSMo_2(Xy, Pr) shows only one isomer which is assigned the proximal orientation.

Photolysis of (Xy, Pr)Mo_2SSMo_2(Xy, Pr) was conducted for 18 h in each of the three solvents. To facilitate referencing in NMR spectra, the sample tubes for all solvents were broken in vacuo after photolysis, volatiles were stripped, and the residues were then each redissolved in $CDCl_3$. For photolysis in $CDCl_3$, ^{31}P NMR spectra showed 73% unreacted disulfide **2**, 14% tetramer **7**, 10% at 114.9 ppm, and several minor products; this paralleled, but was slightly faster than, the previous results for (To, Me)-Mo_2SSMo_2(To, Me) in this solvent. In $C_6D_5CD_3$, ^{31}P NMR spectra showed 65% unreacted **2**, 21% tetramer **7**, 10% at 114.9 ppm, and several minor products. In C_4D_8O, ^{31}P NMR spectra showed ~1% disulfide **2**, no significant 114.9 ppm product, 93% tetramer, and several minor products. In all cases, the percentages for the products are relative to observable dimer products plus tetramer **7**.

The results showed that photoreduction occurred cleanly in the case of THF to give tetramer as the ultimate reduction product (via eq 3). The proposed mechanism involves H(D) abstraction from solvent (eq 7). The fate of the 2-tetrahydrofuryl radical was not determined, but coupling products and oligomers have been noted in prior studies.[29,30] There was no strong evidence for a similar reaction in the cases of the other solvents. Instead, initial products were tetramer and $Mo_2SSPS(OEt)_2$, which is a mixed disulfide of dimer with a dithiophosphate, **3** (R = PS-$(OEt)_2$). The (To, Me)$Mo_2SSPS(OEt)_2$ derivative has been separately prepared and fully characterized,[10] and its identification as the photodecomposition product from (To, Me)Mo_2SSMo_2(To, Me) in $CDCl_3$ is definitive. This nullifies the previous conclusion[9] that Mo_2SCCl_3 was one of the slow photolysis products. The current 114.9 ppm product by analogy is assigned to (Xy, Pr)-$Mo_2SSPS(OEt)_2$.



(7)

The generation of tetramer and $Mo_2SSPS(OEt)_2$ as a slow step in photolyses is curious. A plausible mechanism for Mo_2SSPS-$(OEt)_2$ formation would involve nascent $(EtO)_2PS_2^•$ radicals from decomposing $Mo_2S^•$ radicals. Extensive mechanistic details are difficult to garner from the available data, since loss of dithiophosphate ligands suggests gross decomposition of some dimer fragments; these may be unobserved in NMR spectra due to loss of organic ligands or due to resultant paramagnetism. Such decompositions could, however, provide the reducing equivalents for tetramer formation.

As an additional complication, photolysis of $Mo_2SSPS(OEt)_2$ itself can be considered. This was investigated in a manner parallel to photolyses of prior Mo_2SSR **3** derivatives.[9] Photolysis gave the disulfide scramble of eq 4 (R = $PS(OEt)_2$), but was quite slow: After 24 h, only 7% Mo_2SSMo_2 was observed; this increased to 26% at 144 h, but decomposition by then was substantial and equilibrium had not been attained. At 24 h, ~2% tetramer was already observable. Overall the dimer–dithiophosphate disulfide was only slightly faster at photolysis than alkyl Mo_2SSR **3** (R = Et or Bz only).

Other Reactions. In addition to previously characterized photochemical reactions using dimer radical $Mo_2S^•$, two further reactions were of interest. These were the addition of dimer radicals to alkenes and alkynes, and the photolysis of the tetrasulfide $Mo_2SSSSMo_2$.

The interaction of organic thiyl radicals with alkenes and alkynes has been long studied, particularly with respect to polymerization initiation.[13,31-34] Reactions of Mo_2SSMo_2 were attempted with a variety of alkenes and alkynes under fluorescent lighting. General results with different substrates indicated that polymerization had occurred for some (for example, styrene and methyl propynoate) but not for others (for example, phenylacetylene, diphenylacetylene, dimethyl 2-butynedioate, ethylene,

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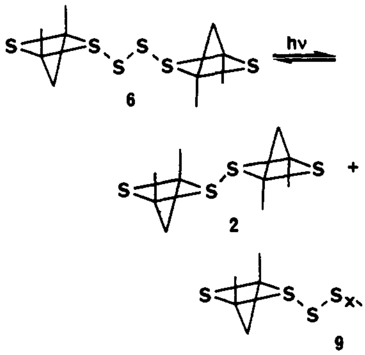
and butene). Styrene was most studied: As an example, after 32 h of photolysis of Mo_2SSMo_2 with 100-fold styrene followed by stripping of all volatiles (including excess styrene monomer), NMR spectra were consistent with a mixture of α,ω-bisdimer polystyryl chains $Mo_2S(CH_2CHPh)_xSMo_2$, although a small amount of tetramer **7** (7%) was also observed. The bisdimer oligomers were evident as broad peaks in the spectra: The ^{31}P NMR spectrum was dominated by a reasonably narrow envelope at 115.0 ppm; the ^1H NMR spectrum showed a broad Ph band at 7.10 ppm, broad areas in the saturated alkyl region, and dimer envelopes. Integrations indicated an average chain length, x, of 19 ± 1. Reaction with 2-butene was also studied: This gave cis–trans isomerization but no permanent addition or polymerization product. For example, photolysis of Mo_2SSMo_2 with 100-fold *cis*-2-butene gave cis–trans equilibration within 1–2 h of photolysis, indicating reversible addition of the $Mo_2S^{\bullet}$ radical to the butene. In addition to organic sulfur systems, the isomerization of 2-butene has been photocatalyzed by CdS and ZnS, and thiyl radicals were also involved therein.[35]

The photolysis of tetrasulfide $Mo_2SSSSMo_2$ was investigated to determine if it was indeed photohomolytic and also to establish the existence of bisdimer polysulfide ($Mo_2SSS_xSSMo_2$, **9**) dissociative equilibria (eq 8). The equilibria were investigated from two directions: by photolysis of $Mo_2SSSSMo_2$ individually and by photolysis of mixtures of Mo_2SSMo_2 with elemental sulfur.



(8)

The tetrasulfide **6** was indeed photolytic under fluorescent lighting, equilibrating in approximately 24 h. ^{31}P NMR spectra revealed a variety of peaks, including that of tetrasulfide (114.8 ppm). Short-term photolysis revealed the initial products to be disulfide **2** (115.2 ppm), and compounds represented by ^{31}P NMR peaks at 114.6, 114.5, and 114.4 ppm, in decreasing quantity, which were believed to be the bisdimer polysulfides **9**. Additional peaks were seen at longer times, including some attributable to decomposition. The photolysis of Mo_2SSMo_2 with 2 equiv of S after 24 h gave the same spectra as the photolysis of $Mo_2SSSSMo_2$ alone. At equilibrium, ^{31}P NMR spectra revealed 47% Mo_2SSMo_2, 25% $Mo_2SSSSMo_2$, 4% for the product at 114.6 ppm, 2% for each of the products at 114.5 and 114.4 ppm, and other minor components. With higher ratios of S to Mo_2SSMo_2 (8-fold and 20-fold), the amount of remaining disulfide decreased, the amount of tetrasulfide remained nearly the same, and the other products increased. The presence of free sulfur at equilibrium could not be determined in any case, and its quantitative significance was unknown. The exact form of sulfur was also unknown, and it is simply represented as S in eq 8. Free sulfur has been suggested to be involved in organic polysulfide photolysis.[16,36] The current results fully support the mixed polysulfide equilibrium of eq 8. Interestingly, a trisulfide, Mo_2SSSMo_2, was not indicated as a major product, since the major products increased, relative to tetrasulfide, with higher S ratios. The lack of a trisulfide contrasts with the $[CpFe(CO)_2]_2(\mu\text{-}S_x)$ system, for which a trisulfide was indeed the preferred species within the group $x = 1\text{–}4$,[37] although these were not indicated to be interconvertible photolytically.

Discussion

While undoubtedly some of the extensive chemistry of metallosulfur compounds may involve thiyl reactivity, this has not been well defined. Metallosulfur radicals per se are known, but sulfur-based radical chemistry is not therefore guaranteed. An example is given by the Mo(III)–Mo(IV) radical $[(MeCp)_2Mo_2(\mu\text{-}S_2CH_2)(\mu\text{-}SMe)(\mu\text{-}S)]$: This compound failed to H abstract from THF, and failed to react with a number of alkenes or alkynes,[38] indicating insufficient localization of the radical electron on the bridge sulfur. Curiously, it was reported to undergo light-induced coupling,[39] presumably to give a bisdimer disulfide product. This suggests that thiyl-type behavior may be realized by sulfur-to-metal charge transfer, in addition to S–S homolysis.

One factor to consider regarding metallothiyl character is single-sulfur-site reactivity within a given metal–sulfur fragment. While there exists a very rich sulfur-based chemistry for metallosulfur systems in general, many of these involve compounds with multiple-sulfur-site reactivity, wherein more than one sulfur is chemically active within a given metal–sulfur unit. Multiple-sulfur-site reactivity can squelch sulfur-based radical chemistry by formation of intrafragment disulfide bonds; this process may also involve redox at the metal center. With only single-sulfur-site reactivity, interfragment disulfide bonds can instead be realized, along with the potential for photohomolytic behavior. The dimolybdenum system currently described, although possessing equivalent sulfur bridge sites in radical **1** or anion **4**, does in fact display single-sulfur-site reactivity, and the chemistry is dominated by facile reaction at one bridge sulfur concomitant with passivation of the second. Multiple-sulfur-site systems are not totally excluded from this chemistry: $[Fe_2(CO)_6(\mu\text{-}S)_2]_2(\mu\text{-}S_2)^{2-}$[40] and $[Cp_2Mo_2(\mu\text{-}S_2CH_2)(\mu\text{-}S)]_2(\mu\text{-}S_2)^{2+}$[41] contain interdimer disulfide linkages although the parent $M_2(\mu\text{-}S)_2$ cores have a well-developed multiple-sulfur-site reactivity.

Facile S–S photohomolysis between metal fragments which are linked by a single di- or polysulfide chain can reasonably be expected when the resultant metal–sulfur radical fragments are capable of at least a transitory existence, and even more so when the radical units per se are more stable. This is in direct parallel to organic di- and polysulfide photohomolysis. A number of metal–sulfur systems which contain a bisfragment disulfide, $L_xM_ySSM_yL_x$, or higher polysulfide, $L_xM_ySS_zSM_yL_x$, structural unit have been characterized[2,37,40–45] in addition to the currently described system **2** (or related **3**) and **6**. Of these, $[CpFe(CO)_2]_2(\mu\text{-}S_3)$ was reported to be light-sensitive,[37] although S–S photohomolysis was not specified. $[Fe_2(CO)_6(\mu\text{-}S)_2]_2(\mu\text{-}S_2)^{2-}$ was reported to be unstable in solution in the absence of oxygen;[40] light sensitivity was not indicated, but this is an interesting possibility. Considering the elaborate chemistry of Cp–Mo–S systems,[1] compounds such as $[Cp_2Mo_2(\mu\text{-}S_2CH_2)(\mu\text{-}S)]_2(\mu\text{-}S_2)^{2+}$[41] may also prove to be of photolytic behavior.

While the currently described disulfides Mo_2SSMo_2 and Mo_2SSR have shown qualitative similarities to organic disulfides, the former remain distinctly different electronically due to the dimetal framework. For the current Mo_2S systems in general, the lowest unoccupied molecular orbitals will include orbitals of predominantly Mo–L π^* character and one of Mo–Mo σ^* character. The highest occupied orbitals will be composed of Mo–Mo σ and one or two S p out-of-plane (the Mo_2S_2 plane)

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contributions; the latter type can be mixed with Mo d out-of-plane orbitals to give Mo–S π character as has been described for other $M_2(\mu\text{-}S)_2$ systems.[2,46–50] Two such Mo–S π interactions are allowed for radical $Mo_2S^\bullet$ and anion Mo_2S^-, which would allow an average π bond order of 0.5. That the chemistry is primarily sulfur-based in $Mo_2S^\bullet$ and in Mo_2S^- suggests that one of the S p (Mo–S π) orbitals may be the SOMO or HOMO therein; for $Mo_2S^\bullet$ this results in a diminished π interaction. A π-type radical has been described for the sulfur bridge of $[M_2(CO)_{10}S]^-$ (M = Cr, W).[51] When one bridge sulfur is bonded to a third atom in the Mo_2SZ compounds, the energy of its S p orbital is altered due to involvement in σ bond formation and the π participation is lost; the Mo–S π interaction at the second sulfur is concomitantly strengthened. This is supported by crystal structure results for several derivatives: Mo–S(dicoordinate) and Mo–S(tricoordinate) bridge bond distances differ by 0.09–0.11 Å.[12,52–54] The strengthening of the Mo–S(dicoordinate) π interaction accounts for the effective passivation of the second sulfur site. Similar descriptions have been expressed for other metallosulfur dimers.[2,48] For current derivatives with a tricoordinate bridge, the Mo–Mo σ orbital may then be the HOMO.

The high-wavelength S–S photohomolysis of Mo_2SSMo_2 and Mo_2SSR (R = aryl) suggests that the S–S σ^* may be the LUMO in these specific compounds, closely followed then by the aforementioned Mo–L π^* and Mo–Mo σ^* orbitals. The transition involved in the photohomolysis may then involve Mo–Mo $\sigma \rightarrow$ S–S σ^*. For Mo_2SSR (R = alkyl) derivatives, the stronger S–S bond leads to a substantially higher S–S σ^* orbital energy and a photolysis transition in the ultraviolet. The overall picture suggests that the Mo_2S–S bond is lower in energy than organic RS–S bonds for R = alkyl; for R = aryl, the comparison is ambiguous. The corollary is that $Mo_2S^\bullet$ is a more stabilized radical than $RS^\bullet$, R = alkyl.

These considerations are of interesting consequence to the tetrasulfide $Mo_2SSSSMo_2$. Alkyl tetrasulfides are more homolytically sensitive at internal RSS–SSR bonds than at RS–SSSR bonds, due again to differences in bond energies.[13,33,34,55] Presently, however, the decreased energy of Mo_2S–S bonds is proposed to reverse that behavior, such that Mo_2S–$SSSMo_2$ bonds are a weaker link than the Mo_2SS–$SSMo_2$ bonds. Preferential photohomolysis of Mo_2S–$SSSMo_2$ over Mo_2SS–$SSMo_2$ bonds would indeed account for the observed production of Mo_2SSMo_2 and the absence of trisulfide Mo_2SSSMo_2. This would also suggest that the observed polysulfides $Mo_2SSS_xSSMo_2$, at least initially, are of even-numbered sulfur chains, since these result from combination of two odd-numbered sulfur chain radicals.

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Rotational Isomerism and Fluxional Behavior of Bis(carbon dioxide) Adducts of Molybdenum

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Abstract: The exchange reactions involving the bis(carbon dioxide) complex *trans*-$Mo(CO_2)_2(PMe_3)_4$ (**1**) and chelating phosphines P–P ($Me_2PCH_2PMe_2$, dmpm; $Me_2PCH_2CH_2PMe_2$, dmpe; $Et_2PCH_2CH_2PEt_2$, depe; and $Ph_2PCH_2CH_2PPh_2$, dppe) and isocyanides, CNR, provide efficient routes to the new $(CO_2)_2$ adducts *trans*-$Mo(CO_2)_2(P\text{–}P)(PMe_3)_2$ (P–P = dmpe (**3a**), depe (**3b**), dmpm (**3c**), dppe (**3d**)), *trans*-$Mo(CO_2)_2(P\text{–}P)_2$ (P–P = dmpe (**4a**), depe (**4b**)), and *trans*-$Mo(CO_2)_2(depe)(PMe_3)(CNR)$ (R = Bu^t (**5a**), Cy (**5b**)). Due to the asymmetric nature of the coordinated CO_2 groups and to the existence of different ligands (PMe_3, P–P, CNR) in the plane perpendicular to the O_2C–Mo–CO_2 bond axis, several isomers arising from the different conformations of the CO_2 ligands are possible for each of the above type of complex. Their existence has been demonstrated by variable-temperature NMR spectroscopy, and they have furthermore been shown to interconvert in solution. Four nondissociative mechanisms have been considered for this exchange process, of which one that involves exchange of the coordinated and free oxygen atoms of one of the CO_2 ligands has been shown to be inoperative. Two rotational mechanisms, namely an independent rotation and a disrotatory motion, have also been excluded. A concerted rotation of the CO_2 groups in which both molecules rotate in the same direction is in accord with all the experimental results.

Carbon dioxide activation by transition-metal compounds continues to attract considerable attention.[2] An important part of these studies is the synthesis and characterization of M–CO_2 complexes that can be used as models for relevant steps in the

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