effects. The structure was solved using Patterson and standard difference map techniques on a Data General NOVA 4 computer using SHELXTL.[37] Space group assignments were determined uniquely by systematic absences. Hydrogen atoms were included in calculated positions (d(C–H) = 0.96 Å; U_{iso}(H) = 1.2U_{iso}(C)).

For the impure complex "*cis-mer*-MoOCl$_2$(PMe$_3$)$_3$", high thermal motion of the carbon atoms of the PMe$_3$ ligand was evident, most probably due to rotational disorder. However, the immediate coordination environment about the molybdenum in both structures was well-defined.

The composite "atom" at the disordered site of the *mer*-MoO$_x$Cl$_{3-x}$-(PMe$_2$Ph)$_3$ series was modeled by refining each atom of the composite pair with a fixed isotropic thermal parameter (U = 0.05 Å^2) and the constraint that their positional parameters maintain common values. The site occupancies were allowed to refine subject to the constraint that their sum was 1.0. Although the compositions determined using this model are not identical to those determined by ^{1}H NMR analysis, the observed trend is unaffected.[38] Attempts to refine partial oxygen and chlorine

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(38) The composition as determined by refining site occupancies typically indicated slightly higher oxo contents than determined by ^{1}H NMR analysis of the bulk sample. The small discrepancy may be due to the possibility that the composition of the crystal selected for X-ray analysis was not representative of the bulk sample. Alternatively, the difference in compositions may be an artifact due to the fact that disorder model in which oxygen and chlorine are refined at the *same* site does not model well the true system in which these atoms are at different sites.

atoms at different distances from the molybdenum were unsuccessful, since the partial atoms converged to the same position (for other examples see ref 6c). Selected bond lengths and angles for the pure complexes *cis-mer*-MoOCl$_2$(PMe$_2$Ph)$_3$ and *mer*-MoCl$_3$(PMe$_2$Ph)$_3$ are given in Tables III–VI.

Complete tables of atomic coordinates, bond distances and angles, anisotropic displacement parameters, and ORTEP drawings for all structures are given in the supplementary material of ref 9.

The Dimolybdenum(V) Sulfur Bridge and Diazonium Ions: Formation of Dimolybdenum Diazosulfides

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Abstract: Arenediazonium ions, ArNN$^+$, bind to the sulfur bridge of the dimolybdenum anions [Mo$_2$(NAr′)$_2$(S$_2$P-(OC$_2$H$_5$)$_2$)$_2$(μ-S)$_2$(μ-O$_2$CR)]$^-$ to give dimolybdodiazosulfides [Mo$_2$(NAr′)$_2$(S$_2$P(OC$_2$H$_5$)$_2$)$_2$(μ-S)(μ-O$_2$CR)(μ-SNNAr)] containing the ArNNS$^-$ bridge ligand. The diazosulfides were reasonably stable at low temperatures, decomposing slowly to products characteristic of aryl radical intermediates, including H abstraction of solvent. An imido exchange reaction was observed between the metal imido groups and the arenediazo portion. Back-bridge attack was identified as a radical mechanistic step available to the Mo$_2$(μ-S)$_2$ core. Characterization methods included ^{15}N NMR spectroscopy, for which data for organic diazosulfides ArNNSR and imidomolybdenum dimers are reported.

Introduction

The reactions of arenediazonium ions with transition-metal systems have been of interest for some time in both organic and inorganic chemistry. Several well-developed organic synthetic schemes utilize the arenediazonium–transition-metal ion combination, although the exact intermediate involved is not necessarily understood.[1,2] Discrete metal–diazo complexes have been studied for some time as the products of reactions of transition-metal reagents with diazonium ions: common product types include metal–diazenido, M–NNAr, and metal–diazene, M–NHNAr, complexes.[3-5] Studies of these systems have been of particular interest as analogues of nitrosyl- and dinitrogen–metal systems,

including possible applications to mechanisms of dinitrogen fixation.[3,5,6]

In the diazenido and diazene complexes, the diazonium coordinates via nitrogen to the metal. A very different type of product is available for reaction of diazonium ions with sulfidometal systems. This reactivity is based on the organic chemistry of thiolate–diazonium ion reactions,[7] which yield diazosulfides directly (eq 1) or which lead overall to thiodediazoniation (eq 2). The latter provides a synthetic route to aryl sulfides.[7] Diazosulfides themselves have been of interest in photographic applications,[8] as sources of aryldiazenyl radicals,[9] and in synthetic applications.[10]

$$ArNN^+ + RS^- \rightleftharpoons ArNNSR \qquad (1)$$

$$ArNN^+ + RS^- \longrightarrow ArSR + N_2 \qquad (2)$$

(1) Zollinger, H. In *The Chemistry of Triple-Bonded Functional Groups, Part 1*; Patai, S., Rappoport, Z., Eds.; Wiley & Sons: Chichester, Great Britain, 1983; p 603.

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Formation of Dimolybdenum Diazosulfides

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Diazosulfide/thiodediazoniation chemistry is conceivably available to sulfidometal systems which display sulfur-centered reactivity. Reaction of the diazonium ions at the sulfur site can give metallodiazosulfides M$_x$SNNAr in parallel to eq 1. The "diazothiolate" ligand ArNNS$^-$ is not well known as an inorganic entity; somewhat related is the thionitrosamine ligand R$_2$NNS for which metal complexes have been definitively established.[11] The M$_x$SNNAr connection is a potentially very interesting linkage considering the known organic diazosulfide background. Furthermore, the linkage contains metallosulfur connected to a multiply bonded NN unit, which may represent new considerations in biological dinitrogen reduction mechanisms. An alternate metallodiazosulfide linkage, MNNSR, has been specifically attempted,[12] and a similar linkage has been discussed[13] in terms of relevance to biological nitrogen fixation.

Sulfidomolybdenum(V) dimer anions of the general formula [Mo$_2$(NAr')$_2$(S$_2$P(OEt)$_2$)$_2$(μ-S)$_2$(μ-O$_2$CR)]$^-$, **1**, (for abbreviations, see note[14]) possess a reactive sulfur bridge site and are thiolate analogues as has been previously demonstrated.[15,16] Reactions

(dithiophosphates not shown)
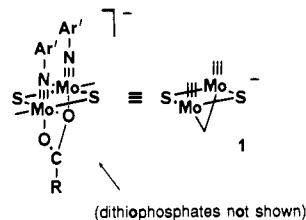
of the dimer anions with arenediazonium ions have been undertaken: these have produced dimolybdenum diazosulfides [Mo$_2$-(NAr')$_2$(S$_2$P(OEt)$_2$)$_2$(μ-S)(μ-O$_2$CR)(μ-SNNAr)], **2**. The reactions, product characterization, product decompositions, and a curious imido exchange reaction are presently described.

Experimental Section

Procedures which were conducted under N$_2$ used solvents which had been dried, vacuum transferred, and subsequently stored under N$_2$. Red light conditions, where utilized, followed previous methods.[15]

[Mo(NAr')(S$_2$P(OEt)$_2$)S]$_4$ (Ar' = To, Ph) derivatives were prepared as previously described.[17,18] Arenediazonium tetrafluoroborate salts were prepared by standard diazotization methods. Labeled BF$_4^-$ salts of ToN^{15}N$^+$, *p*-O$_2$NC$_6$H$_4$N^{15}N$^+$, Ph^{15}NN$^+$, PhN^{15}N$^+$, and Ph^{15}N^{15}N$^+$ were prepared analogously, using Na^{15}NO$_2$ and Ph^{15}NH$_2$ as appropriate. Organic diazosulfides were prepared according to published methods,[8,19] using labeled diazonium ions as appropriate. The preparation of PPN$^+$MeCO$_2^-$ paralleled a prior synthesis,[20] but used NH$_4^+$MeCO$_2^-$ (from stoichiometric NH$_3$(aq) and MeCO$_2$H); purification was accomplished by dissolution in CHCl$_3$ to remove residual water, rotary evaporation of the separated solution, and final recrystallization from acetic anhydride/diethyl ether. The butyrate salt PPN$^+$PrCO$_2^-$ was prepared analogously, but was simply filtered from the original aqueous mixture, rinsed (cold H$_2$O), and vacuum dried. The PPN$^+$MeCO$_2^-$ and PPN$^+$-PrCO$_2^-$ salts were checked by NMR spectroscopy and by Ag$^+$(aq) tests which showed no Cl$^-$ contamination (from PPN$^+$Cl$^-$ reactant). Doubly labeled PPN$^+$ ^{13}CH$_3$^{13}CO$_2^-$ was prepared by mixing aqueous solutions of Ag$^+$ ^{13}CH$_3$^{13}CO$_2^-$ and PPN$^+$Cl$^-$, each at 60–70 °C, followed by rotary evaporation. The residue was extracted with CHCl$_3$, and this solution

was stripped to give the product, which was further dried under vacuum. Preparation of the Ag$^+$ ^{13}CH$_3$^{13}CO$_2^-$ for the above step followed that for Ag$^+$CH$_3$^{14}CO$_2^-$,[21] but used 95% EtOH, and the product was simply dried after centrifugation and EtOH washing.

Other reagents were used as commercially available.

^{31}P, ^{15}N, ^{1}H, and ^{13}C NMR spectra were obtained on a Varian XL300 spectrometer at 121, 30, 300, and 75 MHz. Peaks are reported as downfield shifts from external 85% H$_3$PO$_4$ (^{31}P), external MeNO$_2$ (^{15}N), and internal Me$_4$Si (^{1}H, ^{13}C); low-temperature shifts are relative to ambient temperature reference values. All coupling constants reported herein are absolute values only. The solvent was CDCl$_3$. Infrared spectra were obtained as evaporated smears on KBr plates using a Nicolet 7199 FTIR spectrometer. Elemental analyses were performed by Galbraith Laboratories (Knoxville, TN).

Studies of the dimolybdenum diazosulfides utilized a variety of different imidoaryl and carboxylate ligands within the molybdenum dimer, and also different diazonium aryl groups. A typical procedure was as follows. The solids [Mo(NTo)(S$_2$P(OEt)$_2$)S]$_4$ (0.033 56 g, 0.0201 mmol), PPN$^+$MeCO$_2^-$ (0.047 73 g, 0.0799 mmol), and ToN$_2^+$BF$_4^-$ (0.016 51 g, 0.0802 mmol) were combined in an NMR tube. Under N$_2$ and red light and with the tube immersed in liquid N$_2$, CDCl$_3$ (0.80 mL) was added. The tube was then flame-sealed under vacuum. The sample was placed in the NMR probe and held at –23 °C for the majority of the reaction; spectra were actually obtained at –23 or –45 °C, which gave enhanced resolution. Reported temperatures are ±2 °C. For experiments with ^{15}N-labeled diazonium salts, the concentrations of all reagents were generally doubled. For experiments over longer periods of time, the sample was kept in a freezer at –23 °C.

Studies of back-bridge attack were conducted as follows. Under N$_2$ and red light, a solution of bis-dimer disulfide [Mo$_2$(NTo)$_2$(S$_2$P-(OEt)$_2$)$_2$S$_2$(O$_2$CMe)]$_2$ (0.0186 g, 0.0115 mmol), MeCO$_2$H (3.0 μL, 0.052 mmol), and Et$_3$N (7.3 μL, 0.052 mmol) in 10 mL of solvent (CHCl$_3$ or CH$_2$Cl$_2$) was treated with ToN$_2^+$BF$_4^-$ (0.0108 g, 0.0524 mmol). After stirring for 4 h, the solution was stripped on the vacuum line. Open to air and normal lighting, the residue was dissolved in CDCl$_3$, and NMR spectra (^{31}P and ^{1}H) were obtained.

[Mo$_2$(NTo)$_2$(S$_2$P(OEt)$_2$)$_2$S(O$_2$CMe)(SCCl$_3$)], **4** (Z = CCl$_3$). On a vacuum line under N$_2$, ToN$_2^+$BF$_4^-$ (0.1516 g, 0.736 mmol) was added to a solution of [Mo(NTo)(S$_2$P(OEt)$_2$)S]$_4$ (0.5131 g, 0.307 mmol) and PPN$^+$MeCO$_2^-$ (0.4398 g, 0.736 mmol) in CHCl$_3$ (10 mL). This mixture was stirred for 3 h, opened to air, and then stripped on a rotary evaporator. The residue was slurried with MeOH (5.0 mL), filtered, and washed (MeOH). The solid was extracted with C$_6$H$_6$ (10 mL), and the resulting solution was again stripped. The residue was dissolved in CH$_2$Cl$_2$ (1.5 mL) and treated with MeOH (3.0 mL). The precipitate was filtered, washed (MeOH), and vacuum dried, giving a red-orange crystalline solid (0.2225 g, 36%). Anal. (Mo$_2$C$_{25}$H$_{37}$Cl$_3$N$_2$O$_6$P$_2$S$_6$) C, H, N. ^{31}P NMR (ppm): 115.0. ^{1}H NMR (ppm): 7.05 d, 6.75 d, To H; 4.3–3.9 m, POCH$_2$; 2.20 s, To CH$_3$; 1.30 t, 1.21 t, POCCH$_3$; 1.25 s, O$_2$CCH$_3$. A trace of CH$_2$Cl$_2$ (<1%) tends to be retained and is evident in the ^{1}H NMR spectrum. Selected IR bands (cm^{-1}): 1537 m, 1449 s, 1052 m, 1007 vs, 963 vs, 822 s, 787 s, 740 m.

[Mo$_2$(NTo)$_2$(S$_2$P(OEt)$_2$)$_2$S(O$_2$CMe)(SCHCl$_2$)], **4** (Z = CHCl$_2$). On a vacuum line under N$_2$, ToN$_2^+$BF$_4^-$ (0.2361 g, 1.15 mmol) was added to a solution of [Mo(NTo)(S$_2$P(OEt)$_2$)S]$_4$ (0.8016 g, 0.479 mmol), MeCO$_2$H (0.065 mL, 1.1 mmol), and Et$_3$N (0.159 mL, 1.1 mmol) in CH$_2$Cl$_2$ (10 mL). After stirring for 4 h, the mixture was opened to air and stripped on a rotary evaporator. The residue was slurried with MeOH (9 mL) and then filtered. The insoluble portion was extracted with Me$_2$CO (200 mL), and this solution was then stripped. A CH$_2$Cl$_2$ filtrate (7 mL) of the residue was treated with MeOH (14 mL). Filtration, washing (MeOH), and vacuum drying afforded orange crystals (0.3171 g, 34%). Anal. (Mo$_2$C$_{25}$H$_{38}$Cl$_2$N$_2$O$_6$P$_2$S$_6$) H, N, C: calcd, 30.6; found, 31.1. ^{31}P NMR (ppm; minor invertomers are shown in parentheses where discernible): (115.1), 114.6. ^{1}H NMR (ppm; minor invertomers are shown in parentheses where discernible): 6.85 d, 6.62 d (6.50 d), To H; 6.07 s (5.87 s), SCHCl$_2$; 4.2–3.9 m, POCH$_2$; 2.16 s (2.10 s), To CH$_3$; 1.30 t, 1.20 t, POCCH$_3$; 1.23 s, O$_2$CCH$_3$. A trace of CH$_2$Cl$_2$ (<1%) tends to be retained and is evident in the ^{1}H NMR spectrum. Selected IR bands (cm^{-1}): 1528 m, 1441 s, 1052 m, 1011 vs, 974 vs, 824 s, 795 m, 761 m, 729 m.

[Mo$_2$(NTo)$_2$(S$_2$P(OEt)$_2$)$_2$S(O$_2$CMe)(SC$_4$H$_7$O)], **4** (Z = C$_4$H$_7$O). On a vacuum line under N$_2$, ToN$_2^+$BF$_4^-$ (0.3151 g, 1.53 mmol) was added to a solution of [Mo(NTo)(S$_2$P(OEt)$_2$)S]$_4$ (0.8018 g, 0.479 mmol), MeCO$_2$H (0.11 mL, 1.9 mmol), and Et$_3$N (0.266 mL, 1.9 mmol) in THF (10 mL). After stirring for 4 h, the mixture was opened to air and stripped on a rotary evaporator. The residue was slurried with MeOH

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(14) Abbreviations used in this paper: Me, methyl; Et, ethyl; Pr, *n*-propyl; Bu, *n*-butyl; Ar, aryl; Ph, phenyl; To, *p*-tolyl; PPN$^+$, Ph$_3$PNPPh$_3^+$.
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Table I. Selected NMR Data for (Ar', R)Mo$_2$SNNAr^a

	^{15}N^b	^{31}P	^{1}H^c	
			ArNNS	MoNAr
(To, Me)Mo$_2$SNNTo	β, 138.6 s (β, 138.4 s)	115.1 (115.0)	7.22 d (6.95 d) (6.78 d) (2.36 s), 2.34 s	(6.62 d), 6.59 d, 6.43 d, 2.12 s
(To, Pr)Mo$_2$SNNTo	β, 139.4 s (β, 138.2 s)	115.7, 115.6	7.21 d, 6.96 d, 6.80 d	6.60 m, 6.42 d
(To, Me)Mo$_2$SNNPh	(α, 150.8 d) (β, 145.1 d), β, 144.5 d; α, 141.5 d, $^1J_{NN}$ = 17 Hz (17 Hz)	115.1 (115.0)	7.14 m, 6.80 d	6.62 d, 6.59 d, 6.43 d, 2.11 s (2.07 s)
(Ph, Me)Mo$_2$SNNTo	β, 138.2 s (β, 137.1 s)	115.0 (115.0, 8 Hz upfield)	7.2–6.6 m	
(Ph, Me)Mo$_2$SNNPh	(α, 151.2 d), β, 144.2 d (β, 143.8 d), α, 141.4 d, $^1J_{NN}$ = 17 Hz (17 Hz)	115.0 (114.9)	7.2–6.6 m	

^{a} Chemical shifts were obtained at –45 °C. Where minor isomers are clearly discernible, these are shown in parentheses. ^{b} ^{15}N shifts are listed for Mo$_2$SN$_\beta$N$_\alpha$Ar resonances, obtained with singly (Ar = To) or doubly (Ar = Ph) labeled compounds. ^{c} Only aryl group resonances are listed. Others include POCH$_2$ (4.25–3.85 m) and POCCH$_3$ + RCO$_2$ (1.5–0.3 m). Chemical shifts greater than 7.25 ppm are excluded due to concealment by PPN$^+$ resonances.
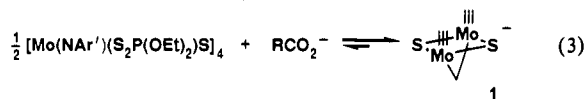
(20 mL) and then filtered. The solid, after suction drying, was extracted five times with C$_6$H$_6$ (3 mL each). The soluble portion was then stripped. A CH$_2$Cl$_2$ filtrate (4 mL) of the residue was treated with MeOH (8 mL). Filtration, washing (MeOH), and vacuum drying afforded orange crystals (0.1491 g, 16%). Anal. (Mo$_2$C$_{28}$H$_{44}$N$_2$O$_7$P$_2$S$_6$) C, H, N. ^{31}P NMR (ppm; minor invertomers are shown in parentheses where discernible): 115.5 (115.3) (115.3, 7 Hz upfield from prior peak), 114.7. ^{1}H NMR (ppm; minor invertomers are shown in parentheses where discernible): 6.95 d, 6.65 d (6.57 d), 6.52 d (6.46 d), To H; 5.02 d, 4.60 m, 3.08 m, 2.62 m, 2.24 m, ~2.1 m, C$_4$H$_7$O; 4.2–3.9 m, POCH$_2$; 2.16 s, 2.10 s, To CH$_3$; 1.30 t, 1.29 t, 1.26 t, 1.16 t, POCCH$_3$; 1.20 s, O$_2$CCH$_3$. Selected IR bands (cm^{-1}): 1545 m, 1446 s, 1080 w, 1055 m, 1013 vs, 964 vs, 822 s, 798 m.

[Mo$_2$(NTo)$_2$(S$_2$P(OEt)$_2$)$_2$S(O$_2$CMe)(STo)], 4 (Z = To). On a vacuum line under N$_2$, ToN$_2$$^+BF_4$$^-$ (0.5354 g, 2.60 mmol) was slowly added to a solution of [Mo(NTo)(S$_2$P(OEt)$_2$)S]$_4$ (1.6734 g, 1.00 mmol), MeCO$_2$H (0.15 mL, 2.6 mmol) and Et$_3$N (0.36 mL, 2.6 mmol) in THF (6 mL). The mixture was stirred for 75 min, followed by stripping on the vacuum line. The residue was opened to air, and Et$_2$O (24 mL) was added. This slurry was stirred for 4.5 h, and then filtered and rinsed (Et$_2$O). The very deep red-orange filtrates were stripped, and the residue was stirred with MeOH (7 mL) for 18 h. This was filtered and washed to give a dull orange powder after drying. The solid was dissolved in THF and filtered; the filtrate (1.8 mL) was treated dropwise with 4:1 EtOH/H$_2$O (3 mL). The precipitate was collected, washed (EtOH), and dried to give a red-orange powder. This solid was dissolved in C$_6$H$_6$ and filtered. The filtrate (4 mL) was evaporated gently under a N$_2$ stream to a volume of 0.9 mL. MeOH (0.3 mL) was added, and this solution was then placed in an ice bath, followed by the addition of more (1.7 mL) MeOH. The resulting precipitate was filtered cold, washed (MeOH), and dried to give an orange solid. This was recrystallized from THF (1.0 mL) and 4:1 EtOH/H$_2$O (2.0 mL). A final recrystallization from C$_6$H$_6$ (1.0 mL) and MeOH (2.5 mL) was conducted after cooling in an ice bath. Vacuum drying for 15 h gave the pure product as an orange powder (0.1514 g, 8%). Anal. (Mo$_2$C$_{31}$H$_{44}$N$_2$O$_6$P$_2$S$_6$) C, H, N. ^{31}P NMR (ppm; minor invertomers are shown in parentheses where discernible): (115.2), 115.0. ^{1}H NMR (ppm; minor invertomers are shown in parentheses where discernible): 8.09 d (7.81 d) (7.06 d), 7.02 d, STo H; (6.64 d) (6.49 d), 6.32 d, 6.16 d, NTo H; 4.3–4.0 m, POCH$_2$; 2.31 s, STo CH$_3$; (2.10 s), 2.03 s, NTo CH$_3$; 1.34 t, 1.27 t (1.23 t), POCCH$_3$; 1.27 s (0.81 s), O$_2$CCH$_3$. Selected IR bands (cm^{-1}): 1544 m, 1447 s, 1015 vs, 986 vs, 823 s, 796 m.

Results

For simplicity, general dimer groups [Mo$_2$(NAr')$_2$(S$_2$P-(OEt)$_2$)$_2$S$_2$(O$_2$CR)] will be hereafter designated Mo$_2$S, wherein the S represents one bridge sulfur. Unless otherwise specified, tolylimido (Ar' = To) and acetate-bridged (R = Me) derivatives are implied. When a distinction is required for a specific imidoaryl (NAr') or carboxylate (RCO$_2$) dimer, the designation will be (Ar', R)Mo$_2$S. Organic group abbreviations have been footnoted.[14]
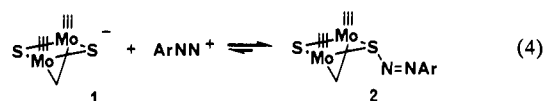
For the current series of reactions, the dimer anion Mo$_2$S$^-$, 1, was generated in situ by the reaction of a carboxylate ion with the cubane tetramer [Mo(NAr')(S$_2$P(OEt)$_2$)S]$_4$, 3, in the favorable equilibrium shown by eq 3. The carboxylate sources in

$$\frac{1}{2}\,[\text{Mo(NAr')}(\text{S}_2\text{P(OEt)}_2)\text{S}]_4 \;+\; \text{RCO}_2^- \;\rightleftharpoons\; \text{S}\overset{\text{III}}{\underset{\text{Mo}}{-}}\text{Mo}^-\text{S} \quad (3)$$

1

the current study were primarily PPN$^+$RCO$_2$$^-$ salts. Bu$_4$P$^+$-MeCO$_2$$^-$ and Bu$_4$N$^+$MeCO$_2$$^-$ gave similar results as PPN$^+$-MeCO$_2$$^-$ and allowed clarification of the aryl region in ^{1}H NMR spectra when needed. The combination RCO$_2$H + Et$_3$N, extensively used in earlier syntheses,[15,16,22] was less favorable for detailed reaction studies in the current work due to poor equilibrium at lower temperatures.

Reactions were primarily conducted in CDCl$_3$; reactions done in other solvents are specifically noted as such.

The dimer anion Mo$_2$S$^-$, 1, was found to react very readily with arenediazonium ions to produce dimolybdodiazosulfides Mo$_2$SN-NAr, 2 (eq 4). Although their synthesis was quite facile, the diazosulfides were thermally unstable in the reaction mixture.

$$\text{S}\overset{\text{III}}{\underset{\text{Mo}}{-}}\text{Mo}^-\text{S} \;+\; \text{ArNN}^+ \;\rightleftharpoons\; \text{S}\overset{\text{III}}{\underset{\text{Mo}}{-}}\text{Mo}^-\text{S}\underset{\text{N=NAr}}{\diagdown} \quad (4)$$

1   2

Fairly good stability was obtained at low temperatures, and reactions were generally conducted at –23 °C. The reactions were studied by multinuclear NMR spectroscopy, utilizing compounds at natural abundance for their observed nuclei and also compounds with selective labels; the latter included singly (α or β) and doubly labeled [^{15}N]diazonium salts, and doubly labeled [^{13}C]acetate. Spectra were usually obtained after lowering the temperature to –45 °C due to improved resolution at the lower temperature.

At –23 °C, the formation of the diazosulfide 2 occurred readily: for example, with 2-fold acetate and diazonium ion, product was observable within minutes, and was maximized within 30 min. Presumably the poor solubility of the diazonium salt in the organic solvent was a limiting factor in the speed of the reaction. Although the reaction producing the diazosulfide was favorable and Mo$_2$-SNNAr complexes were the initial dimer products, their syntheses were complicated by equilibria and side reactions; these are described below. Typical solution yields of Mo$_2$SNNAr observed at low temperatures were ~70% at stoichiometric ratios of reactants.

Characterization of the product diazosulfides was done by NMR spectroscopy. A substantial number of diazosulfides Mo$_2$SNNAr were thus prepared, utilizing a number of permutations involving different imidoaryl, carboxylate, and diazonium aryl groups. Representative data for several are given in Table I. Variations in the spectra with different imidoaryl or carboxylate or diazonium aryl groups clearly showed that a covalent product was obtained which contained the molybdenum dimer fragment and ArNN. The spectra were fully consistent with the formulation of the products specifically as the diazosulfides Mo$_2$SNNAr. Thus, the NMR spectra showed normal dimer resonances for compounds of the type Mo$_2$SZ, 4, which contain a derivatized sulfur bridge. This included preservation of mirror symmetry within the dimer fragment, which controverted the possibility that ArNN binds

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Formation of Dimolybdenum Diazosulfides

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Table II. ^{15}N NMR Data for Organic Diazosulfides

ArN$_\alpha$N$_\beta$SR	con-figuration	α	[1]J_{NN}	β
ToNNSC$_6$H$_4$-*p*-OMe[a]	E	105.3		134.9
p-O$_2$NC$_6$H$_4$NNSC$_6$H$_4$-*p*-OMe[a]	E	97.3		154.9
p-O$_2$NC$_6$H$_4$NNSCMe$_3$[b]	E	99.1		164.9
	Z	109.4		137.1
PhNNSCMe$_3$[a,c]	E	104.9	15 Hz	147.0
	Z	114.9	18 Hz	126.8

[a] Assignments for α and β resonances are based on selective labeling. [b] Assignments for α and β resonances are based on analogy to other members of the table. [c] [1]J_{NN} values are derived from doubly labeled samples.

to one metal while the second metal binds a monodentate carboxylate.

4
(distal)

4
(proximal)
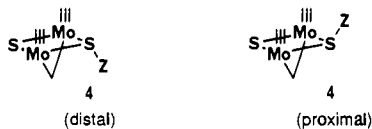
Additional substantiation as the diazosulfides was obtained from ^{15}N NMR spectra of the products: chemical shifts of 137.1–151.2 ppm were observed for both the α and β resonances of the diazosulfide linkage. (The α and β designations follow Mo$_2$SN$_\beta$N$_\alpha$Ar, preserving the labels of the original diazonium ion.) ^{15}N NMR data for organic diazosulfides could not be located in the literature for comparison; values for these were therefore measured for the current work and are presented in Table II. The chemical shifts fall within the range for azo compounds, but the sizeable upfield shift of the α-relative to the β-nitrogen parallels results for triazenes, albeit to a substantially lesser extent.[23] Shifts in triazenes have been attributed to conjugation of lone pair and π electrons.[23,24] Conjugation can be considered for diazosulfides, and calculations have indeed indicated S–N π interaction.[25] The chemical shifts for β-nitrogens in the dimolybdodiazosulfides (Table I) fall within the range for those of the organic derivatives; α resonances, however, are relatively downfield. This may actually be due to loss of the usual conjugative effects, since the capability of the tricoordinate bridge sulfur in Mo$_2$SNNAr to engage in π bonding will be much less than that of the dicoordinate sulfur of the organic RSNNAr derivatives.

The various NMR spectra of the dimolybdodiazosulfides indicated the presence of two isomers, for which coalescence could be observed at 0 °C. There were two possibilities for the observed isomerization. Mo$_2$SZ compounds typically show the presence of sulfur invertomers in solution;[15,16,22] these are illustrated above for **4** and are labeled as distal or proximal on the basis of the position of substituent Z relative to the arylimido groups. In addition, organic diazosulfides ArNNSR can show E and Z configurations which are in some cases separately isolable.[8,26,27] The two isomers are related by thermal and photochemical processes.[19,27–30] The Z configuration, which is produced initially (eq 1), thermally isomerizes to the E configuration. This is generally quite facile at normal temperatures, and isolable (Z)-ArNNSR are primarily known only for R = CMe$_3$ or CPh$_3$ unless low temperatures are employed.[27] Photoconversions of the two isomers can occur in either direction. The current dimolybdodiazosulfide products were thus capable of four isomers, but only two were observed. Although the ^{31}P and ^{1}H NMR spectra could not distinguish between sulfur invertomers or azo isomers as being present, the ^{15}N NMR spectra suggested the

former, on the basis of coupling constants for the doubly labeled Mo$_2$SNNPh derivatives. Azo-type compounds in general show distinct differences in N=N couplings between their E and Z isomers, with [1]J_{NN}(Z) > [1]J_{NN}(E).[31–34] This is maintained for *tert*-butyl phenyldiazosulfide, PhNNSCMe$_3$, whose [1]J_{NN} values were measured to be 18 Hz (Z) and 15 Hz (E) as given in Table II. Currently, for two Mo$_2$SNNPh derivatives (Table I), [1]J_{NN} values were consistently 17 Hz for both isomers. This suggests that the isomers are not due to different azo configurations; therefore, the observed isomers are tentatively assigned to different sulfur invertomers. The specific assignment for each of the two observed isomers as distal and proximal sulfur invertomers is not possible using the usual ^{1}H NMR spectroscopic methods[15] due to the overlap in the spectra. Even the measurement of invertomer ratios (distal/proximal) was difficult for the different Mo$_2$SNNAr derivatives, but overall these appeared to fall in the range of 0.5–2.

The complications in the chemistry of the solutions containing the diazosulfides involved both equilibrium processes and irreversible decompositions. The dimer anion equilibrium of eq 3 was reasonably favorable: under stoichiometric conditions using [Mo(NTo)(S$_2$P(OEt)$_2$)S]$_4$ and PPN$^+$MeCO$_2^-$, the dimer anion/tetramer ratio was 7.3 at –30 °C; this was the same within error at –50 °C. This equilibrium is seriously offset by acidic sources, however, and the protonated form of eq 3, which involves a hydrosulfide dimer Mo$_2$SH, **4** (Z = H), instead of dimer anion **1** lies completely to the left for acetic acid.[17] The dimolybdodiazosulfide formation reaction, eq 4, was also an equilibrium, and therefore parallels organic diazosulfide equilibria, eq 1, which are fast and highly favorable.[8,28,29] The equilibrium nature of eq 4 was supported by observations that an excess of carboxylate and diazonium ions drastically increased Mo$_2$SNNAr formation and that the amount of diazosulfide was affected also by overall concentrations of all components. Another factor in the equilibrium was the poor solubility of the diazonium salt in the organic solvent. Free diazonium salt was in fact not seen in the NMR spectra (^{1}H and ^{15}N, if so labeled) due to very low solubility, especially at low temperature. The reaction has been studied with the inclusion of 18-crown-6 (2-fold relative to diazonium ion), which rendered the diazonium ion soluble due to complexation.[1] Under these conditions, the complexed diazonium ion was indeed observed in the reaction solution. For example, ToN[15]N$^+$ with 18-crown-6 was clearly seen in ^{15}N NMR spectra at –63.2 ppm at –45 °C, thus confirming the availability of that reagent. While the crown ether rendered the diazonium ion observable, the complexation was in fact an additional equilibrium to consider. Since it failed to produce significantly beneficial results overall, most reactions were conducted without crown ether present.

Generally in the reactions examined, tetramer **3** was observed and was frequently in excess of dimer anion **1**. This required consumption of carboxylate ion, on the basis of the dimer anion equilibrium of eq 3. This could have occurred by simple protonation, or by an additional equilibrium or side reaction. In reactions using acetate, especially as [13]CH$_3$[13]CO$_2^-$, ^{1}H and ^{13}C NMR spectra did show an additional acetate resonance whose position was sometimes variable: the resonance fell between peak positions for MeCO$_2$H and MeCO$_2^-$, as determined by reference spectra at the applicable temperatures; this was consistent with a MeCO$_2$H/MeCO$_2^-$ equilibrium. Regardless of the identity of the additional species involved, the ^{31}P and ^{1}H NMR spectra clearly showed that a molybdenum dimer compound was not a component of that additional pathway.

Subsequent Reactions. The solutions containing the dimolybdodiazosulfides Mo$_2$SNNAr were unstable, and the products decomposed within 1 h at room temperature or within several days at –23 °C. Solutions for reaction studies were handled under red

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light conditions[15] specifically to avoid photohomolytic processes established for organic diazosulfides[30] and also for some molybdenum dimer compounds.[35] Thus, decompositions were thermal and were not photoinitiated. Decomposition produced a number of molybdenum dimer products, the relative quantities of which depended on reactant ratios, total reactant concentrations, temperature, and atmosphere (air or N_2). Tetramer **3** was sometimes observed, also dependent on the exact conditions. The primary molybdenum dimer products included the bis-dimer disulfide **5**, Mo_2SSMo_2, which consists of two dimers joined by a disulfide
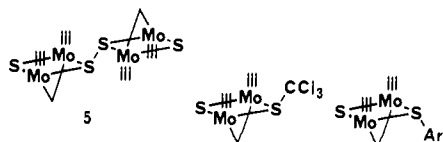
linkage, a trichloromethanethiolate-bridged dimer, Mo_2SCCl_3, **4** (Z = CCl_3), and an arenethiolate-bridged dimer, Mo_2SAr, **4** (Z = Ar), wherein Ar was derived from the arenediazonium ion. The bis-dimer disulfide **5** has been previously characterized.[15] The Mo_2SCCl_3 product was derived from H abstraction from chloroform solvent, and its identification is definitive on the basis of complete isolation and characterization of the (To, Me)Mo_2SCCl_3 derivative from larger scale reactions conducted at room temperature. Furthermore, analogous solvent products Mo_2SCHCl_2 and $Mo_2SC_4H_7O$ (C_4H_7O = 2-tetrahydrofuryl) have been fully isolated and characterized from preparatory scale reactions in CH_2Cl_2 and THF, respectively. The three solvent-derived

products were characterized by elemental analyses and by NMR and IR spectroscopies. The NMR spectra showed the usual dimer resonances and the sulfur substituent. For $Mo_2SC_4H_7O$, the spectra were complicated by the asymmetry of the 2-tetrahydrofuryl substituent and the concomitant loss of mirror symmetry within the dimer fragment. For tetrahydrofuryl ring protons, six multiplets were observable from 5.0 to 2.1 ppm in the ^1H NMR spectrum, and the seventh was buried under dithiophosphate CH_2 multiplets. In addition to the usual dimer absorptions, the IR spectra showed bands assignable to ν(C–Cl) at 740 cm^{-1} in Mo_2SCCl_3 and at 761 and 729 cm^{-1} in Mo_2SCHCl_2, and a band for an ether ν(C–O) at 1080 cm^{-1} in $Mo_2SC_4H_7O$. Invertomer ratios (distal/proximal) were 0.088 for Mo_2SCHCl_2 and 0.06 for $Mo_2SC_4H_7O$; for Mo_2SCCl_3, only one invertomer was seen, and it was assigned the proximal configuration. The trichloro, Mo_2SCCl_3, and dichloro, Mo_2SCHCl_2, compounds can be compared to the monochloro derivative Mo_2SCH_2Cl, **4** (Z = CH_2Cl), which was previously reported as the product of nucleophilic substitution by dimer anion Mo_2S^-, **1**, on CH_2Cl_2 solvent.[16] Some parallel is also noted for $Mo_2SC_4H_7O$ with organic 2-tetrahydrofuryl sulfides RSC_4H_7O[36] and with $Mo_2(C_5H_5)_2(C$-$O)_4(SC_4H_6O)$ which contains a 2-tetrahydrofuranthiolate bridge but also with a Mo–C(2) bond.[37]

Identification of Mo_2SAr products in the decompositions of the dimolybdodiazosulfides was based on successful isolation and characterization of (To, Me)Mo_2STo. This compound itself was obtained pure from room temperature reactions in THF, although ultimate yields were lower than even solvent-derived products due to the tedious workup involved. As an example of actual product distribution, for one such preparatory reaction conducted similarly to that described for Mo_2STo in the Experimental Section, a ^{31}P NMR spectrum of the entire product mixture indicated 44%

Table III. ^{15}N NMR Data for Arylimido Groups[a]

[Mo(NTo)(S$_2$P(OEt)$_2$)S]$_4$, **3**		40.8
[Mo(NPh)(S$_2$P(OEt)$_2$)S]$_4$, **3**		41.7
(To, Me)Mo_2SNH_2, **4** (Z = NH_2)	distal	18.0
(To, Me)Mo_2SCH_2Cl, **4** (Z = CH_2Cl)	distal	10.2
	proximal	5.1
(To, Me)Mo_2SEt, **4** (Z = Et)	distal	16.1
	proximal	12.4
(Ph, Me)Mo_2SCCl_3, **4** (Z = CCl_3)	proximal	20.7
(Ph, Me)Mo_2SSMo_2(Ph, Me), **5**	proximal	21.7

[a] All values were obtained at natural abundance using high concentrations. Distal and proximal refer to sulfur invertomer configuration.

$Mo_2SC_4H_7O$, 27% Mo_2STo, and 10% bis-dimer disulfide **5** as major products. Isolated Mo_2STo was characterized by elemental analyses and by NMR and IR spectroscopies. The NMR spectra showed the invertomer ratio (distal/proximal) to be 2.2.

Although the above products were only isolated for tolylimido derivatives, two phenylimido variants, (Ph, Me)Mo_2SCCl_3 and (Ph, Me)Mo_2SPh, were characterized spectroscopically (NMR) in mixtures obtained from preparatory scale reactions in $CHCl_3$ directed toward their syntheses. Neither compound was obtained pure despite reasonable efforts; nevertheless, their identification was considered definitive by analogy to the isolated tolyl derivatives.

In addition to the identification of Mo_2SAr, Mo_2SSMo_2, and solvent-derived products in subsequent reactions of the dimolybdodiazosulfides, it was also observed that arene hydrocarbons were produced in the reactions. For example, in the decomposition of solutions of (To, Me)Mo_2SNNTo or of (Ph, Me)Mo_2SNNPh, toluene or benzene, respectively, was observed. Interestingly, when imidoaryl and diazonium aryl groups differed, hydrocarbons from both aryl groups were found. Thus, in separate decompositions of solutions of (To, Me)Mo_2SNNPh or of (Ph, Me)Mo_2SNNTo, both toluene and benzene were observed in both cases. This was distinctly curious, since it implied an exchange of ArN functions between the imido and diazo portions. This was supported by ^{31}P NMR spectra which showed additional peaks when the imidoaryl and diazonium aryl groups differed: the additional peaks could be attributed to mixed imidoaryl dimer products. The exchange was indeed confirmed using ^{15}N labeling. With only β-labeled $ToN^{15}N^+$, the only significant product in the ^{15}N NMR spectra after decomposition was N_2. With doubly labeled $Ph^{15}N^{15}N^+$, in addition to N_2, several peaks were observed in the ^{15}N NMR spectra in the arylimido region. The ^{15}N arylimido region itself, although previously identified for other imidometal systems,[38] was specifically determined for sample compounds related to the current work, and representative shifts are given in Table III. Peaks corresponding to phenylimido resonances of Mo_2SCCl_3 and Mo_2SSMo_2 were indeed observed in the ^{15}N NMR spectra of the decomposed solutions of (Ph, Me)$Mo_2S^{15}N^{15}NPh$. The exchange was also monitored over a longer period of time at –23 °C prior to total decomposition. The ^{15}N NMR spectra showed that the α resonance of $Mo_2S^{15}N^{15}NPh$ declined while an uncoupled β resonance appeared: this indicated the production of singly labeled $Mo_2S^{15}NNPh$. Thus, the ArN exchange was definitive and represented a unique thermal process independent of gross decomposition pathways, although both occurred slowly at –23 °C.

Back-Bridge Attack. The radical character of much of the chemistry of diazonium ions[1,2] provided an opportunity to study a mechanistic step previously proposed for bis-dimer disulfides Mo_2SSMo_2, **5**.[35] Although not related to the dimolybdodiazosulfides, this work is presented here due to its mechanistic relationship. The chemistry of Mo_2SSMo_2 includes S–S homolysis[35] which yields dimolybdenum thiyl radicals, $Mo_2S^•$, **6**, and a number of thiyl-type reactions have been described. Radical reactions with organic disulfides RSSR include propagation steps involving S_H2 attack on the unhindered disulfide bond.[39,40] This propagation

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step is unavailable to Mo_2SSMo_2 reactions, however, since the disulfide linkage is buried. This was indicated by the failure of typical nucleophilic reagents (e.g., BzSH, Ph_3P, and $(EtO)_3P$) to effect reduction of Mo_2SSMo_2 although these reagents do indeed react with $Mo_2S^\bullet$ photogenerated therefrom. It had been proposed earlier that an alternative propagation step for Mo_2SSMo_2 chemistry might involve "back-bridge" attack, by which radical attack occurs at the opposite bridge sulfur and is then followed by S–S homolysis (eq 5). The ability to generate radicals from


(5)
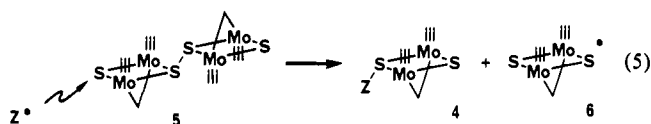
diazonium ion reactions allowed for probing this mechanistic step. Room temperature reaction of ToN_2^+ with $MeCO_2H/Et_3N$ in $CHCl_3$ in the presence of Mo_2SSMo_2 gave a significant (26%) amount of Mo_2SCCl_3 and a trace of Mo_2STo, although much Mo_2SSMo_2 remained unreacted. Similar reaction in CH_2Cl_2 yielded 10% Mo_2SCHCl_2. The reactions were conducted under red light specifically to avoid photohomolytic processes. The observation of Mo_2STo and of solvent-derived dimer products did indeed suggest back-bridge attack as a propagation step. In this case, tolyl radicals or dehydrosolvent radicals $^\bullet CCl_3$ or $^\bullet CHCl_2$ were the attacking species, Z in eq 5, on Mo_2SSMo_2, 5.

Discussion

The current work illustrates a very different avenue of reactivity for metallosulfur systems. While the reactivity is of little "inorganic" precedent, dimolybdodiazosulfide formation is quite consistent with organic diazosulfide chemistry. Even the decomposition reactions, while at first seemingly complex, well reflect thiodediazoniation reactions and the chemistry of diazonium ions in general. The ability of the present molybdenum dimer system to closely parallel the organic chemistry is a result of not only the thiolate-type nucleophilicity of the dimer anion Mo_2S^- but also of the thiyl-type characteristics of the dimer radical $Mo_2S^\bullet$.

Relevant mechanistic steps for the decompositions of the dimolybdodiazosulfides are presented in eqs 6–10. Thermal homolysis of Mo_2SNNAr can give $Mo_2S^\bullet$, 6, and aryldiazenyl, $ArNN^\bullet$, radicals (eq 6). The latter, which have been shown to have a reasonable lifetime at low temperature,[9] decompose to give aryl radicals, $Ar^\bullet$ (eq 7). Hydrogen abstraction from solvent gives

(6)

$$ArNN^\bullet \longrightarrow Ar^\bullet + N_2 \qquad (7)$$

$$Ar^\bullet + HCCl_3 \longrightarrow ArH + CCl_3^\bullet \qquad (8)$$

(9)

(10)
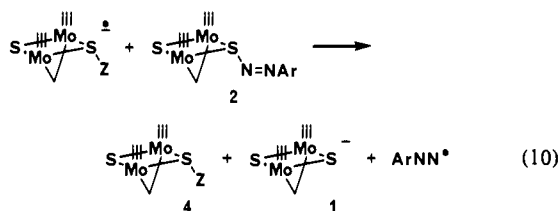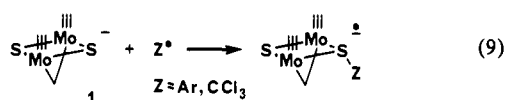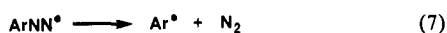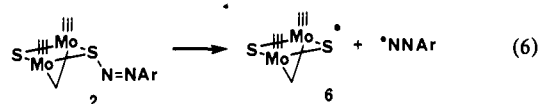
dehydrosolvent radicals, illustrated using $CHCl_3$ in eq 8 (and 9). The propagation steps of eqs 9 and 10 account for solvent-derived

Scheme I

DECOMPOSITION PRODUCTS
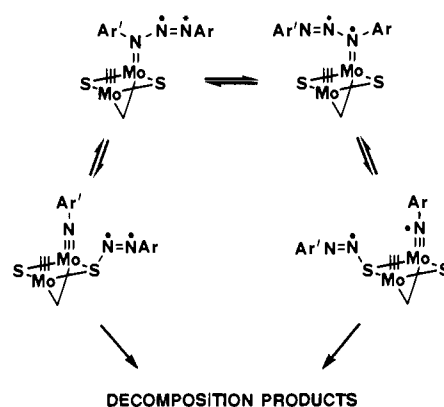
products and for Mo_2SAr. The reactions of eqs 6, 7, 9, and 10 are direct analogues of the mechanistic steps for thiodediazoniations,[7] and Mo_2SAr is in fact the normal thiodediazoniation product. Production of Mo_2SSMo_2 disulfides can be accommodated by recombinations of $Mo_2S^\bullet$. Other mechanistic steps can also be incorporated.

There are, in fact, numerous other radical steps possible in the current chemistry due to the coincidental requirement for carboxylate ions in the presence of diazonium ions. The well-established chemistry[1,2,41] of diazonium carboxylates and the associated acylarylnitrosoamines allows for production of aryl radicals and also allows for possible complications in dimolybdodiazosulfide production. Radicals generated by such side reactions may contribute to the decomposition of Mo_2SNNAr. Consistent with the known organic chemistry, carboxyl radicals were not evident in the current work: this was indicated in reactions using $^{13}CH_3{}^{13}CO_2^-$ which showed no CO_2 production and in which all labeled products retained $^1J_{CC}$.

The production of aryl radicals via diazonium decomposition did allow the demonstration herein of back-bridge attack on Mo_2SSMo_2 disulfides. The mechanism involved eqs 7 and 8, and then eq 5. Formation of aryldiazenyl, $ArNN^\bullet$, under the conditions utilized could have proceeded by reaction of the diazonium ion with $MeCO_2^-$ or with Et_3N.[1]

The imido exchange reaction via diazonium ion is distinctly peculiar. In fact, despite the extensive chemistry of imidometal systems,[38] imido exchange reactions at metal centers are not well known.[42] A proposed mechanism for the current reaction is given in Scheme I, wherein one imido group is included for illustration. Intramolecular migration of diazo nitrogen from bridge sulfur to imido nitrogen occurs, tantamount to exchange of an electrophilic group between electron-rich sites. The process is facilitated by the close juxtaposition of the groups when in proximal configuration. The intermediate triazene then undergoes a 1,3-shift, a process well established for triazene ligands.[43] Migration of Ar'NN back to bridge sulfur gives diazosulfide. This mechanism accounts for the ^{15}N NMR spectral data associated with labeled diazonium positions, which are represented by asterisks in Scheme I.

The demonstration of the dimolybdodiazosulfides herein introduces an additional example toward the consideration of sulfur involvement in biological nitrogen fixation mechanisms, a notion which has been previously addressed.[22] The present compounds represent metallosulfur bound to a N=N linkage. Of further interest is the proposed imido exchange mechanism, since this represents NN bond making and breaking as effected jointly by both metal and sulfur.

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