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Reactions at a Dimolybdenum(V) Sulfur Bridge: Metallothionitrites and the NO_2^-, NO, NO^+ Connection

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Nitrosation of a dimetal bridge sulfur was observed for reactions of dimolybdenum(V) anions of the general form $[Mo_2(NAr)_2(S_2P(OEt)_2)_2(\mu\text{-}S)_2(\mu\text{-}O_2CR)]^-$ with ClNO ($Cl^{15}NO$), NO^+, NO_2^- ($^{15}NO_2^-$), or *i*-$C_5H_{11}ONO$. The products were thionitrites containing the SNO^- bridge ligand. The compounds were very reactive and underwent rapid nitrosyl migration reactions even at low temperatures. The migration resulted in overall oxo-for-imido exchange, after which additional processes ensued.

Introduction

NO_2^-, NO, and NO^+ share close chemical connections, and studies of one frequently encounter another. Their simplicity belies their diversity in a myriad of chemical systems, both inorganic and organic. Even noxious NO is now under impressive scrutiny as an important biological messenger in humans and other animals.[1,2] This recent discovery of biotic NO and the well-known concerns for environmental NO contribute significantly to interest in nitro, nitroso, and related derivatives with regard to the precursors for biological NO production and also with regard to subsequent products of NO reactions. Nitrites, thionitrites, oximes, and even nitrates, both inorganic and organic, may play a role.[1−4]

Nitrosation chemistry in general has been extensively developed involving NO_2^-, NO, NO^+, and other reagents. Nitroso compounds of organic and of main group derivatives include a wide range of *C*-, *N*-, *O*-, and *S*-nitroso compounds;[5−7] transition metal derivatives abound as nitrosyl complexes containing linear and bent M−NO linkages.[8−11] These separate areas of organic, main group, and transition metal nitrosyl compounds are well developed; connections between the areas are not.

Nitrosyl derivatives of metal−sulfur complexes typically contain the metal−nitrosyl linkage, M−NO; representative and numerous examples are given by iron−sulfur−nitrosyl complexes and reactions.[12−14] This linkage, however, need not be an exclusive structural type. Considering the known background[6,15] of organic thionitrites (RSNO), the possibility for metallothionitrites, M_x(SNO), can be expected and would represent sulfur-bound NO. These complexes should be accessible by reactions of NO_2^-, NO, or NO^+ at reactive sulfur sites in metallosulfur complexes. The thionitrite ligand, −SNO, contrasts with thionyl imide (thiazate), −NSO, and with other "simple" N/S/O ligands which have been demonstrated for a variety of metal systems.[16−19]

The metallothionitrite prospect is a particularly important consideration for several areas of catalysis and biological studies. NO is a frequent probe of heterogeneous metal−sulfur catalysts, well exemplified by studies of hydrodesulfurization systems.[20−23] Although the hydrodesulfurization studies to date have only invoked metal-bound NO, sulfur-bound NO has indeed been proposed for ZnS and CdS catalysts in studies of alkene isomerization.[24] NO and NO_2^- have also been used as in vitro probes of biological metallosulfur studies; illustrative are the reactions of NO_2^- and NO with nitrogenase.[25,26] Furthermore, nitrosyl iron complexes are produced in vivo and in vitro from reactions with biological Fe−S systems.[2,11,12,27,28]

Organic thionitrites are readily prepared from thiolate sources and NO^+ equivalents such as NO_2^-, RONO, XNO (X = halogen), NO^+ salts, etc.[6,15] They are unstable to homolysis with formation of thiyl radicals and free NO (eq 1); this reaction

$$\mathrm{RSNO} \rightleftharpoons \mathrm{RS}^{\bullet} + {}^{\bullet}\mathrm{NO} \qquad (1)$$

can be photolytically or thermally initiated, and only several thionitrites are stable even at room temperature.[6,15] The reverse reaction of NO with RS• (photogenerated from RSSR) has also

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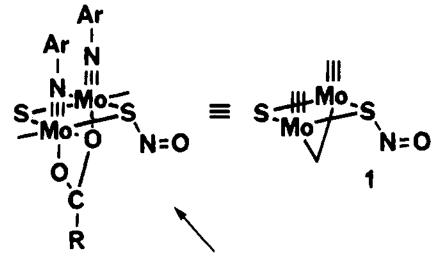
been shown.[29-31] With an intent to investigate metallothionitrite complexes, dimolybdenum complexes of the type $[Mo_2(NAr)_2(S_2P(OEt)_2)_2(\mu\text{-}S)_2(\mu\text{-}O_2CR)]$ seemed uniquely poised: these imido–dithiophosphato–carboxylato–sulfido dimers have separate thiolate anion and thiyl radical forms which have displayed clearly defined sulfur reactivity.[32-36] A dimolybdenum(V) thionitrite, $[Mo_2(NAr)_2(S_2P(OEt)_2)_2(\mu\text{-}S)(\mu\text{-}O_2CR)(\mu\text{-}SNO)]$, **1**, was therefore a reasonable candidate for the demonstration of sulfur-bound NO within a metallosulfur complex.



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(dithiophosphates not shown)

Experimental Section

Reactions which were conducted under N_2 or under vacuum used solvents which had been dried, vacuum transferred, and subsequently stored under N_2. $(EtO)_2PS_2H$ was vacuum distilled. Other commercial reagents were used as received. Syntheses of most molybdenum reagents herein utilized have been previously described.[32,37] Reactions conducted under red light followed prior methods.[32] XoN_3 (Xo = *o*-xylyl; all abbreviations are given in footnote 38) was prepared by the reaction of XoN_2^+ with N_3^-; XoN_2^+ was prepared by standard diazotization of $XoNH_2$. The XoN_3 was stored and used as a solution in c-C_6H_{12}. $PPN^+NO_2^-$ was prepared by a reported procedure;[39] labeled $PPN^{+15}NO_2^-$ was prepared similarly using $Na^{15}NO_2$. $PPN^+MeCO_2^-$ and $PPN^+PrCO_2^-$ were prepared as previously described;[36] $PPN^+Me^{13}CO_2^-$ was prepared by the method for $PPN^{+13}CH_3{}^{13}CO_2^-$.[36]

^{31}P, ^{15}N, ^1H, and ^{13}C NMR spectra were obtained as $CDCl_3$ solutions on a Varian XL300 spectrometer at 121, 30, 300, and 75 MHz. Peaks are reported as downfield shifts from external 85% H_3PO_4 (^{31}P), external neat $MeNO_2$ (^{15}N), and internal Me_4Si (^1H and ^{13}C). Low-temperature shifts are relative to ambient-temperature reference values. The infrared data were obtained as a KBr pellet using a Perkin-Elmer 283 spectrophotometer. Galbraith Laboratories, Inc., performed the elemental analyses.

$[Mo(NXo)(S_2P(OEt)_2)S]_4$. A slurry of $Mo(CO)_6$ (3.065 g, 0.0116 mol), S (0.375 g, 0.0117 mol), $(EtO)_2PS_2H$ (3.0 mL, 0.019 mol), XoN_3 (in c-C_6H_{12}, 7.6 mL total, 0.017 mol), and THF (~60 mL) was refluxed under N_2 for 18 h. The dark red-brown mixture was stripped on the vacuum line to a dark brown oil. The residue was stirred in petroleum ether/$CHCl_3$ (40 mL/5.0 mL) for 30 min and then filtered off and rinsed with petroleum ether. The filtrates were rotavapped to an oil. CH_2Cl_2 (6.0 mL) and MeOH (50 mL) gave a precipitate which was filtered off, washed (MeOH), and vacuum dried to yield a dark green solid (0.259 g, 5% yield). Anal. Calcd for $Mo_4C_{48}H_{76}N_4O_8P_4S_{12}$: C, 33.3; H, 4.4; N, 3.2. Found: C, 32.9; H, 4.4; N, 3.2. ^{31}P NMR (ppm): 112.6. ^1H NMR (ppm): 6.24 m, Xo–H; 4.66 m, 3.70 m, $POCH_2$; 2.19 s, Xo–CH_3; 1.53 t, 0.87 t, $POCCH_3$. Selected IR bands (cm^{-1}): 1459 m, 1290 m, 1027 vs, 956 vs, 769 s, 631 m.

$Cl^{15}NO$. Under N_2, Bu_3SiCl (61 μL, 0.23 mmol) was added to $PPN^{+15}NO_2^-$ (0.6280 g, 0.107 mmol) in $CDCl_3$ (0.30 mL), giving an immediate yellow color. After stirring for several minutes, the volatile product solution was vacuum transferred directly into the reaction tube (below). Unlabeled ClNO was prepared similarly. Me_3SiCl can also be used, but $Me_3SiOSiMe_3$ is carried with the volatile portion.

$[Mo_2(NAr)_2(S_2P(OEt)_2)_2S(O_2CR)(SNO)]$, 1. Several arylimide (ArN) and carboxylate combinations (RCO_2) were utilized in this study. A typical procedure is as follows. $[Mo(NXo)(S_2P(OEt)_2)S]_4$ (0.06574 g, 0.0380 mmol), $PPN^+MeCO_2^-$ (0.05469 g, 0.0915 mmol), and $CDCl_3$ (0.50 mL) were combined in an NMR tube under N_2 and then frozen (liquid N_2). $Cl^{15}NO/CDCl_3$ (above) was vacuum transferred into the NMR tube and frozen therein. The tube was evacuated and flame sealed under red light. The sample was kept frozen until placement into the NMR probe at −60 °C. Handling was done under red light or with the tube wrapped in Al foil.

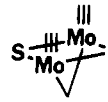
Alternative nitrosating reagents instead of ClNO were also examined. These included $NO^+BF_4^-$; $PPN^+NO_2^-$ with $MeCO_2H$; and *i*-$C_5H_{11}ONO$ with $MeCO_2H$. In all cases, both $[Mo(NAr)(S_2P(OEt)_2)S]_4$ and $PPN^+MeCO_2^-$ were present. Solid reagents were placed in the NMR tube prior to any liquids; liquid reagents were added after at least some solvent had been placed in the NMR tube.

Results

For simplicity, $[Mo_2(NAr)_2(S_2P(OEt)_2)_2S_2(O_2CR)]$ dimer groups are designated Mo_2S, wherein the S represents one sulfur bridge. Where a distinction is necessary for a specific arylimide (ArN) or carboxylate (RCO_2) functionality, the designation is (Ar, R)Mo_2S. Abbreviations for organic groups have been footnoted.[38]

For the present studies, the dimer anion Mo_2S^-, **2**, was generated in situ by the favorable equilibrium between the cubane tetramer $[Mo(NAr)(S_2P(OEt)_2)S]_4$, **3**, and carboxylate anion, eq 2; this method has been extensively used previously.[32,34,36] The carboxylate anion was provided as the PPN^+ salt in slight (~20%) excess. Synthesis of the *o*-xylylimido tetramer used in the current work followed methods for other arylimido derivatives;[35-37] the yield, however, was very poor, and this was attributed to steric problems of adjacent *o*-xylylimido groups.

$$\underset{\mathbf{3}}{\tfrac{1}{2}\,[Mo(NAr)(S_2P(OEt)_2)S]_4} + RCO_2^- \rightleftharpoons$$



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For the present study, ClNO was generated as needed by the reaction of R_3SiCl (R = Me, Bu) with $PPN^+NO_2^-$ in $CDCl_3$, eq 3. A related route has been reported[40] and involved the heterogeneous reaction of Me_3SiCl and $NaNO_2$ in CCl_4 (to give ClNO + NaCl + $Me_3SiOSiMe_3$). The present use of $PPN^+NO_2^-$ provided complete homogeneity in $CDCl_3$; immediate reaction and completion within minutes were thus obtained. The reaction of RONO with Me_3SiCl (to give ClNO + $ROSiMe_3$) in CH_2Cl_2 has also been reported[41] and is likewise a homogeneous preparation. Nevertheless, with an ultimate preference for ^{15}N

$$2\,R_3SiCl + PPN^+NO_2^- \longrightarrow ClNO + PPN^+Cl^- + R_3SiOSiR_3 \quad (3)$$

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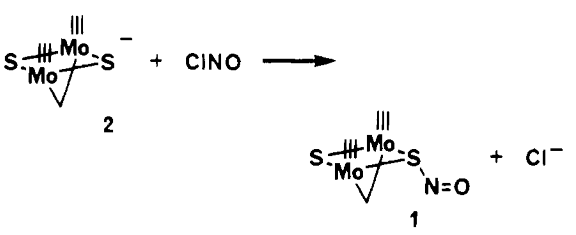
labeling via PPN$^+$^{15}NO$_2^-$ instead of RO^{15}NO, the present route was chosen and developed. In this procedure, vacuum transfer effectively eliminates PPN$^+$Cl$^-$ byproduct, but Me$_3$SiOSiMe$_3$ transfers when Me$_3$SiCl is employed. The presence of volatile siloxane can be eliminated from the product solution by the use of Bu$_3$SiCl (see Experimental Section). Overall this method has proven to be very convenient and is very amenable to the generation of labeled Cl^{15}NO.



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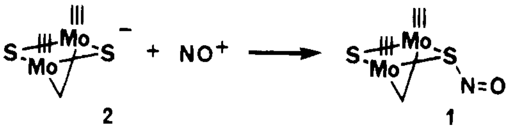

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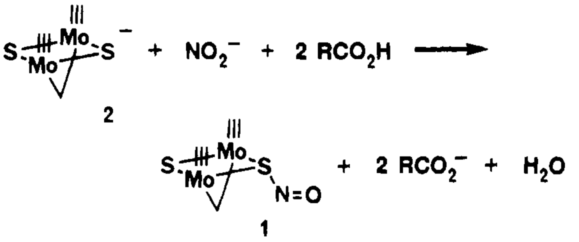

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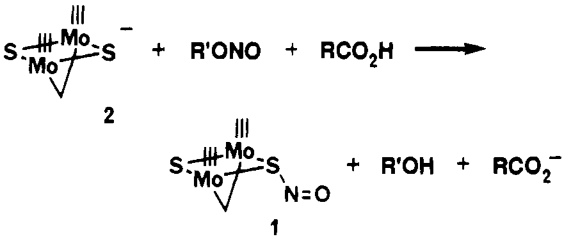

(7)

Reactions of the dimer anion Mo$_2$S$^-$, **2**, with several different nitrosating reagents readily produces thionitrites Mo$_2$SNO, **1**, via the reactions of eqs 4–7. Although the thionitrites could be thus prepared, they rapidly underwent subsequent reactions even at low temperature, as described below. ClNO was the overall fastest nitrosation reagent, and the *o*-xylylimido Mo$_2$SNO derivatives were the slowest to decompose; thus, the combination of ClNO and (Xo, R)Mo$_2$S$^-$ provided the best conditions for study. Reactions were typically conducted in CDCl$_3$ at −60 °C using excess ClNO, and solution yields of ~73–79% for (Xo, Me)Mo$_2$SNO were obtainable within 15–40 min although decomposition was also evident by then. Reactions were monitored by multinuclear NMR spectroscopy at −60 °C, primarily utilizing ^{1}H, ^{31}P, and ^{15}N.

Representative ^{31}P and ^{15}N NMR data (ppm) for three derivatives prepared via eq 4 are as follows: (Xo, Me)Mo$_2$SNO, 114.4 (^{31}P) and 439.8 (^{15}N); (To, Me)Mo$_2$SNO, 114.7 (^{31}P) and 438.8 (^{15}N); (Xo, Pr)Mo$_2$SNO, 115.0 (^{31}P) and 439.8 (^{15}N). The variations of the spectral parameters indicated that a covalent product was obtained involving imido–dithiophosphato–carboxylato–molybdenum dimers and the ^{15}N label. The ^{1}H NMR spectra showed much overlap and were poorly resolved, but collectively the ^{31}P and ^{1}H NMR shifts were completely consistent with binding at the sulfur bridge, on the basis of a range of Mo$_2$(μ-S–Z) compounds which have been previously described.[32,34,36,42,43] Most (but not all) such prior compounds had displayed two sulfur inversion isomers in solution, but these were not definitive for the thionitrites. This isomer uncertainty resulted primarily from the presence of decomposition products which were clearly evident in ^{31}P NMR spectra. Thus, inversion isomers may indeed have been present, but with a minor isomer in only small amount. The depiction of a specific sulfur invertomer in the structure diagrams for Mo$_2$SNO (**1**) is illustrative only.

The present NMR data are not consistent with lost coligands and alternate binding modes of a ClNO-derived group. To wit, arylimido ^{1}H and dithiophosphate ^{31}P and ^{1}H NMR shifts are normal for Mo$_2$(μ-S–Z) compounds and these groups have not been displaced or modified. Diagnostic[32,34,36,42,43] α-CH resonances of bridge carboxylate groups were not distinguishable in ^{1}H NMR spectra due to overlap and inadequate resolution. (Typically these lie upfield, within dithiophosphate POCCH$_3$ triplets.) Bound acetate was directly observed in ^{13}C NMR spectra when Me^{13}CO$_2^-$ was employed, and bound carboxylates were indirectly observed by the obvious ^{31}P NMR shift difference noted for (Xo, Me)Mo$_2$SNO vs (Xo, Pr)Mo$_2$SNO. The possibility of a monodentate carboxylate at one metal and a ClNO-derived nitrogen ligand at the other metal is further eliminated by the symmetry demanded by the spectra. The ^{15}N NMR data fully substantiate the thionitrite formulation: the currently observed shifts of 438.8–439.8 ppm are within the range 333–452 ppm for ^{15}N and ^{14}N NMR shifts of organic thionitrites, RSNO.[44-47] Although these ^{15}N NMR shifts fall in the range for bent M–NO,[10,11] this linkage is controverted by the other NMR data as noted.

While ClNO proved the most effective reagent for study, others also showed some reactivity. The reaction of NO$^+$BF$_4^-$ with (Xo, Me)Mo$_2$S$^-$, eq 5, at −60 °C typically produced 46% (solution yield) (Xo, Me)Mo$_2$SNO, while yet showing 45% total of unreacted (Xo, Me)Mo$_2$S$^-$ and [Mo(NXo)(S$_2$P(OEt)$_2$)S]$_4$. The observable yields were smaller than those with ClNO; this was believed to be a result of the requirement to first dissolve at low temperature. Nitrosations were also obtained with PPN$^+$NO$_2^-$, eq 6, and isoamyl nitrite, *i*-C$_5$H$_{11}$ONO, eq 7, but the results with these were significantly poorer. The reagents themselves result in reactions that are distinctly slower and complicated by the inclusion of a protic reagent which disturbs the dimer anion equilibrium, eq 2: typically, RCO$_2^-$/RCO$_2$H mixtures shift the equilibrium left relative to RCO$_2^-$ alone. The actual reactions of (Xo, Me)Mo$_2$S$^-$ with PPN$^+$NO$_2^-$ and MeCO$_2$H (eq 6) and separately with *i*-C$_5$H$_{11}$ONO and MeCO$_2$H (eq 7) were quite slow and typically showed less than 10% (Xo, Me)Mo$_2$SNO while also showing significant amounts of (Xo, Me)Mo$_2$S$^-$, [Mo(NXo)(S$_2$P(OEt)$_2$)S]$_4$, and, decomposition products.

There were several considerations relevant to the reactions of eqs 4–7 worth noting. The protic reactions of eqs 6 and 7 may have involved acid catalysis, nascent HNO$_2$, or other species.[7,48,49] For all reactions, there was the possibility for the existence of some RCO$_2$NO. Acyl nitrites have been invoked

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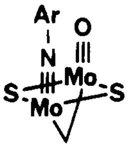
in some nitrosation studies but these are unstable species.[7,50,51] It was believed that their involvement herein was not significant, particularly in the reactions of eqs 4 and 5, which were expected to be inherently facile.

Although the binding of the NO group to the bridge sulfur was clearly demonstrated, the binding of nitrite to metal was also investigated as a possible side reaction. The reaction of $[Mo(NAr)(S_2P(OEt)_2)S]_4$ (Ar = Xo, To) with $PPN^{+15}NO_2^-$ in $CDCl_3$ at −60 °C was studied, and the results indicated the binding of NO_2^- to give a product tentatively assigned as a dianion, $[Mo_2(NAr)_2(S_2P(OEt)_2)_2S_2(NO_2)_2]^{2-}$. These dianions were characterized by ^{31}P NMR peaks at 117.3 (Xo) and 117.4 (To) ppm, ^{15}N NMR peaks at 196.3 (Xo) and 195.4 (To) ppm, and ^1H NMR peaks appropriate for the arylimido and dithiophosphate ligands. The ^{15}N NMR shifts are downfield from those reported for $M-NO_2$ complexes[44,52] and are more consistent with *O*-ligation.[53] These compounds were not observed in the thionitrite reactions.

Subsequent Reactions. All thionitrites produced in the current study readily underwent further reaction even at low temperatures; the initial step involved migration of the nitrosyl group from bridge sulfur to imido nitrogen. This reaction was rapid even at −60 °C for almost all (Ar, Me)Mo_2SNO derivatives which were investigated, regardless of the method of preparation (eqs 4−7). Once the nature of this reaction was realized, a reactant with ortho-substituted arylimido groups was chosen for study with the expectation that steric inhibition would slow the migration. For this reason the (Xo, R)Mo_2SNO derivatives were prepared and indeed proved to be the most stable as noted.

The migration itself was studied at low temperature by ^1H, ^{31}P, and ^{15}N NMR spectroscopy, primarily using the *p*-tolylimido variant (To, Me)Mo_2SNO. The initial products included the oxo−imido dimer anion $[Mo_2(NTo)O(S_2P(OEt)_2)_2S_2(O_2CMe)]^-$, **4**, and the dimolybdenum diazosulfide (To, Me)Mo_2SNNTo, **5**. The identification of the oxo−imido dimer anion was confirmed by an independent reaction of $[Mo_2(NTo)O(S_2P(OEt)_2)_2S_2]_x$ (x = 1, 2)[54] with $PPN^+MeCO_2^-$ in $CDCl_3$ at low temperature; this is analogous to the present bis(imido) dimer anion **2**, and it involves an equilibrium analogous to that of eq 2. The identification of the diazosulfide **5** was definitive on the basis of its prior characterization.[36]



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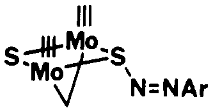

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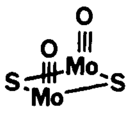

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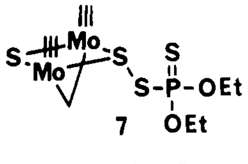

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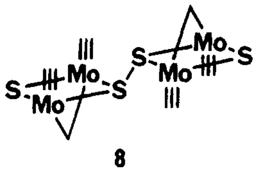

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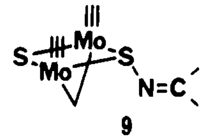
Following the formation of these products, the chemistry becomes rampantly complex and a very large number of additional compounds are ultimately evident by NMR spectroscopy. Those which can be identified include the dioxo dimer $[Mo_2O_2(S_2P(OEt)_2)_2S_2]$, **6**, the dithiophosphate−disulfide dimer (To, Me)$Mo_2SSPS(OEt)_2$, **7**, and the bis(dimer) disulfide (To, Me)Mo_2SSMo_2(To, Me), **8**. These identifications are definitive on the basis of their prior characterizations.[32,43,55] The formation of these compounds testifies to the complexity of the bulk decomposition. Consistent with formation of the diazosulfides and their known reactivity, N_2 is observed in the ^{15}N NMR spectrum of decomposed, labeled reaction products.

Discussion

The dimolybdenum thionitrites $Mo_2SN{=}O$, **1**, are isoelectronic and isostructural with previously characterized dimolybdenum sulfenimines[42] $Mo_2SN{=}CH_2$, $Mo_2SN{=}CHR$, and $Mo_2SN{=}CR_2$, **9**, and with the aforementioned dimolybdenum diazosulfides[36] $Mo_2SN{=}NAr$, **5**. The sulfenimines were fully stable, fully isolable compounds and have been characterized crystallographically. The diazosulfides were thermally unstable and were characterized in solution at −23 to −45 °C. The present thionitrites were the least stable and required even lower temperatures for study.



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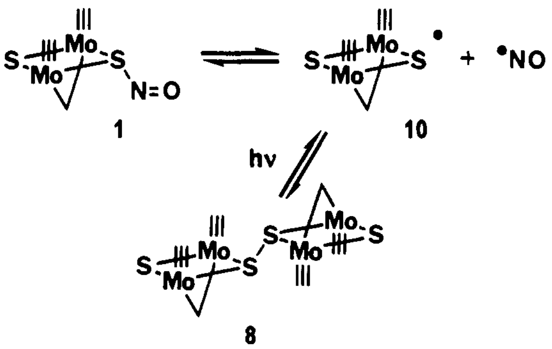
The primary reactions observed for the thionitrites were not the typical homolytic decompositions as established for organic thionitrites (eq 1). The parallel reaction would be the dissociation shown by eq 8, which would have produced the known dimolybdenum thiyl radical $Mo_2S^\bullet$, **10**, and subsequent disulfide, **8**.[33,35] Instead, migration occurred more quickly, and the initial products were oxo−imido dimer anion **4** and diazosulfide **5**. While at first considered unusual, these reactions are in direct parallel to the reactions of the dimolybdenum diazosulfides;[36] the strong parallel reflects the isoelectronic relationship between NO^+ and $ArNN^+$. Migration of the electrophilic "NO^+" functionality from electron-rich sulfur to electron-rich imido nitrogen gives a diazoate ligand, $ArNNO^-$ (eq 9); this step is



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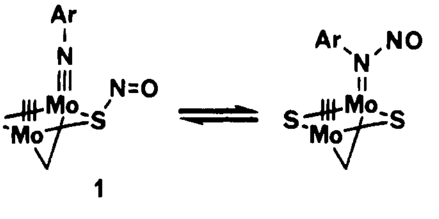

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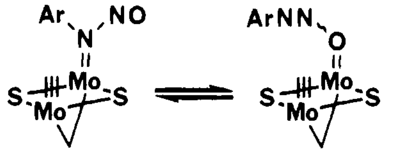
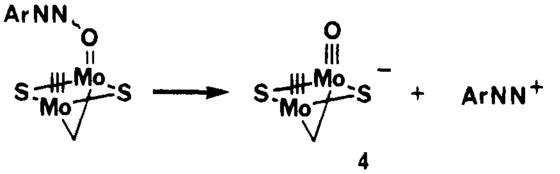
facilitated for the sulfur inversion isomer shown in eq 9. (Only one of the two initial imido groups is depicted in these diagrams for illustration purposes.) After a 1,3-shift from *N*- to *O*-bound diazoate (eq 10), the diazonium group is labilized (eq 11) either



(10)



(11)

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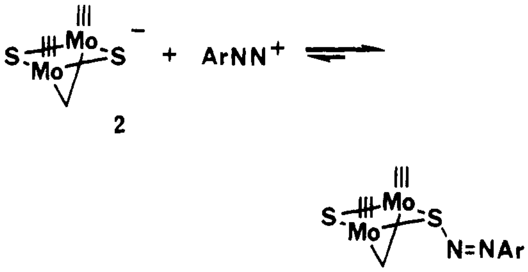
in a direct way or after migration to sulfur. Reaction of diazonium ion with available Mo_2S^- yields the observed diazosulfide (eq 12). Equation 9 is the key step which is



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(12)

5

sterically slowed by the use of *o*-xylylimido derivatives. Equation 12 has been previously established, and eqs 9−11 are analogous to the chemistry of the diazosulfides;[36] the migration intermediate therein involved a triazenide $ArNNNAr^-$, instead of the current, isoelectronic diazoate $ArNNO^-$. Together, these reactions constitute oxo-for-imido and imido-for-imido substitution processes which are very different from most previous exchange types.[56,57] Furthermore, the derivation of an oxo group from a S−NO function can be compared to other systems for which oxo groups were derived from M−NO units.[56,58]

Migration reactions of NO^+ units have been observed in other nitrosation reactions involving sulfur, but these are primarily non-metal systems.[7,59,60] In these, as in the current dimolybdenum thionitrites, the sulfur sites provide a kinetically very accessible point of attachment for incoming substrate and allow for subsequent, facile migration. In essence, the sulfurs are intramolecular catalysts for net nitrosation of another site in the compound. Sulfur compounds can also act intermolecularly as nitrosation catalysts for other compounds.[7]

The chemistry herein conclusively demonstrates the nitrosation of a sulfur site within a metallosulfur complex using covalent nitrites, nitrosonium ion, and nitrite ion. This establishes the pathway for reactions of such reagents with metal−sulfur compounds. The reaction of NO directly with photogenerated thiyl radical $Mo_2S^\bullet$, **10**, was also attempted (the reverse of eq 8), but failed; this was somewhat expected due to the known thermal and photolytic instability of the S−NO[15] linkage and the known photolytic instability of many Mo_2S−Z compounds.[33,35] Nevertheless, the observation of the direct reaction of NO at other metal−sulfur sites, including radical[24] or nucleophilic sites, remains a reasonable expectation. Inorganic, non-metal, anionic sulfur systems undergo reaction with NO to produce $-SN(O)NO^-$ ("*S*-NONOate") anions and other products;[61−63] some such reactions may have environmental consequences. The converse of the reaction of anionic sulfur with NO is the reaction of sulfur with anionic nitrite; this yields a variety of intermediates and products.[64]

There may be additional relevance of the present chemistry to specific aspects of metal−sulfur compounds. NO^+ is a common oxidant, and its reactions with a number of sulfidometal compounds have been reported.[65−69] Direct attack at sulfur to produce an initial thionitrite is reasonable albeit speculative; homolysis can provide NO and an oxidized sulfur site. A simple, overall one-electron oxidation can thereby occur,[68] or additional reactions can ensue. In some cases, a M−NO product can be obtained via S → M migration.[68] The fate of the sulfur can vary: S−S coupling to give a disulfide complex[66] (cf. eq 8) and loss of sulfur[67] are possible examples. Reactions of NO^+ with thiolate−metal complexes have demonstrated similar chemistry.[70−73] Some such studies[71,72] have invoked the intermediacy of a *S*-bound organic thionitrite ligand, M(RSNO), which then isomerizes (S → M nitrosyl migration) to M(NO)(SR). Nitrite is capable of related chemistry,[68,74] and this aspect may be of importance in the bioproduction of iron nitrosyl complexes from reactions of iron−sulfur protein units with exogenous nitrite. Another compound of biological interest may be nitrogenase, which has been probed by NO_2^- and by NO;[25,26] in addition to metal and sulfide sites, this enzyme also contains an intercluster disulfide linkage[75] which may allow for thiyl behavior and additional nitrosation vulnerability thereby (cf. eq 8).

While these aspects for thionitrite involvement are speculative, they suggest reasonable pathways which are supported by the extremely fast kinetics of *S*-nitrosation chemistry in general.[5−7]

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