have shown the trans NCH_2 to resonate downfield with respect to the cis NCH_2 nucleus. For 1, the assignment of the cis, trans NCH_2 pair C7, C17 is consistent with this observation; however, for the pair C12, C10 it is not. This may reflect the nonplanarity of the amide functions. We are, however, comparing carbons in a five-atom chain with those in an eight-atom chain, and hence, conformational effects may override the difference expected for a cis/trans disposition of the carbon atoms. Given the identity of the nuclei C10 and C17, examination of the 2-D COSY and $^{13}C-^{1}H$ correlation spectra permits assignment of the ^{13}C resonances associated with the nuclei C9 and C16, together with the A, B proton pairs for all four carbons. No method exists to differentiate firmly between the more and the less shielded nuclei within each of these A, B proton pairs. However, the assignments given in Table VI are based upon the likely correlations with protons in comparable structural sites in our earlier study of the related symmetric cryptand.[18] No method is available to distinguish precisely between the nuclei of the 14,15-positions.

The solution structure is consistent with the solid-state X-ray structure. This detailed knowledge of the NMR spectrum permits us to study in solution the structural conformations for host/guest complexes of macrocycles such as 1 with metal cations. This is particularly important for examining the relationship between macrocycle design and their physical properties and potential applications in the field of selective metal cation recognition. To date, despite strenuous efforts, no crystals of host/guest complexes have been grown where the host is a cryptandlike ferrocene-containing macrocycle.

Acknowledgment. We thank Fran Gallwey for collection of the NMR data and RTZ Chemicals Ltd. for financial support (N.W.S.).

Supplementary Material Available: A table of observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

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Reactions of a Sulfido-Bridged Dinuclear Molybdenum Complex with Nitriles and Isonitriles under Hydrogen: Facile C≡N Bond Cleavage

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The dinuclear complex $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SH)]^+X^-$ (X = SO_3CF_3, BF_4; Cp = C_5H_5; 1(X)) reacted with nitriles RCN under 1–2 atm of H_2 at 25–50 °C to form the new cationic complex $[CpMo(S_2CH_2)(S_2\overline{CR})MoCp]^+$ and ammonia. The reaction has been characterized for HCN as well as for a series of alkyl- and aryl-substituted nitriles. Complex 1 reacted with isonitriles (RNC) and hydrogen under similar conditions to form the cationic complex $[CpMo(S_2CH_2)(S_2\overline{CH})MoCp]^+$ and the primary amine RNH_2. The reactions were inhibited by excess acid. In order to probe the mechanisms of these reactions, the interactions of nitriles and isonitriles with 1 in the absence and presence of a protic acid and in the absence and presence of hydrogen have been studied. In the absence of hydrogen, 1 reacted with isonitriles to form $[(CpMo)_2(S_2CH_2)(S_2CNH(R))]^+$ (2), but no reaction of 1 with nitriles was detected spectroscopically. Under similar conditions in the presence of excess protic acid, 1 reacted with n-butyl isocyanide to form $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SCH{=}NHBu)]^{2+}$ (4) and with acetonitrile to form $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SC(CH_3){=}NH_2)]^{2+}$ (5). These S–H insertion products were identified by spectroscopic methods. The reaction of 4 and 5 with hydrogen appeared to involve carbon–sulfur bond hydrogenolysis; e.g., in the reaction of 5 with H_2, ethylammonium ion was identified as a product. The C–N bond cleavage reactions are proposed to involve the deprotonated forms of the insertion products 4 and 5, $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SCH{=}NBu)]^+$ and $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SC(CH_3){=}NH)]^+$. The former complex was tentatively identified by NMR spectroscopy. Reactions of these derivatives with hydrogen are proposed to lead to intramolecular S–H insertion products $[(CpMo)_2(S_2CH_2)(S_2CH(NH_2Bu))]^+$ (6) and $[(CpMo)_2(S_2CH_2)(S_2C(CH_3)NH_3)]^+$ (7). A precedent for this type of reaction has been characterized in a related molybdenum system. Complexes 6 and 7 are expected to eliminate $BuNH_2$ and NH_3, respectively, to form the final molybdenum products. The possible relevance of these reactions to the reductions of nitriles and isonitriles effected by the nitrogenase enzymes is discussed.

Introduction

We have been investigating the role of homogeneous molybdenum sulfido complexes in reactions that involve the activation of hydrogen and the reductions of carbon–heteroatom bonds. For example, a cyclopentadienylmolybdenum(IV) complex with nucleophilic μ-sulfide ligands, $(CpMo(\mu\text{-}S))_2S_2CH_2$, has been found to catalyze the hydrogenation of C=N bonds in imines, isocyanates, and isothiocyanates and of N=N bonds in azo compounds under 1–3 atm of H_2 at mild temperatures.[1] The active catalyst has been postulated to be a complex with one or two SH ligands, and a dinuclear Mo(III) complex with a μ-SH ligand was synthesized as a model for the catalyti-

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cally active species.[1,2] This derivative was found to stoichiometrically transfer a hydrogen atom from the SH ligand to azobenzene, suggesting a similar step in the catalytic reduction of this substrate. Our attempts to extend the hydrogenation activity of the molybdenum–sulfido catalyst to the carbon–nitrogen triple bond of nitriles were unsuccessful, however.[1]

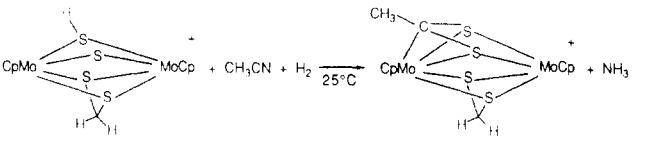
In our studies of a protonated form of the complex $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SH)]CF_3SO_3$ ($1(CF_3SO_3)$) we have observed reactions with additional unsaturated molecules.[3,4] Recently we have published a preliminary report that the reaction of 1 with acetonitrile and hydrogen at 25 °C resulted in the cleavage of the nitrile C≡N bond.[3] In more recent studies we have found that the C≡N bond of isonitriles is also reductively cleaved in reactions with 1 and hydrogen. The similarities in the two reactions and in the isolated products were somewhat surprising since, in the absence of hydrogen, the reactivity of 1 toward nitriles and isonitriles seemed to differ significantly. In this paper we report our investigations of the reactions of 1 with nitriles and isonitriles in both the absence and presence of hydrogen.

The nitrogenase enzymes are the most notable homogeneous catalysts for the reductive cleavage of the carbon–nitrogen triple bond in nitriles and isonitriles.[5,6] A molybdenum iron sulfide cluster is postulated to be the enzyme active site involved in the addition of 6 e^- and 6 H^+ to RCN or RNC to form ammonia and alkanes or amines and methane, respectively. Intriguing questions concerning the enzyme mechanism have led to the study of model metallosulfur complexes that mediate nitrile and isonitrile reduction by chemical or electrochemical reductants.[7-10]

The reduction of nitriles or isonitriles by hydrogen is promoted by relatively few soluble transition-metal complexes.[11-19] Amines are most often the products in these reactions. Heterogeneous catalyst systems have been found to hydrogenolyze the carbon–nitrogen bond of nitriles. For example, a surface composed of 30% Ni on Al_2O_3 catalyzed the reductive cleavage of aromatic and tertiary nitriles RCN to the methyl derivatives RCH_3.[20] MoS_2 and WS_2 surfaces have also been found to promote the hydrogenolysis of nitriles at temperatures above 240 and 360 °C, respectively.[21] The homogeneous reactions reported here provide an interesting model for intermediates formed on metal sulfide surfaces in that the cleaved hydrocarbon fragment of the substrate is stabilized by multisite coordination to metal and sulfide sites. The systems provide evidence for a joint role of metal and sulfide ligand in substrate cleavage that may be relevant to enzyme mechanisms as well.

Results and Discussion

Characterization of the Nitrile Cleavage Reactions. $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SH)]X$ (X = SO_3CF_3, BF_4) reacted with acetonitrile under a hydrogen atmosphere at room temperature as shown in eq 1. As ammonia was



1 (1)

produced in this reaction, it deprotonated the starting complex 1, and the reaction was terminated as the neutral derivative $(CpMo(\mu\text{-}S))_2S_2CH_2$ was formed. Product yields could be increased by adding an additional 1 equiv of acid to the reaction solution when the blue color of the deprotonated complex was apparent. However, the presence of excess acid in eq 1 resulted in additional chemistry, which is discussed below.

The ammonia produced in eq 1 was quantitatively identified by the colorimetric indophenol test,[22,23] and the organometallic product was isolated and characterized by spectroscopic data. In earlier work in our laboratory, the same cation was isolated from the reaction of $(CpMoS)_2S_2CH_2$, acetyl bromide, and H_2 and characterized by an X-ray diffraction study.[24] The product contained a hydrocarbon fragment coordinated to the structurally intact $Cp_2Mo_2S_4$ core of the dimer. The resulting new ligand was described as a planar dithioacetate molecule that was coordinated in an η^2 mode to one molybdenum ion and an η^3 fashion to the second metal ion. The molybdenum–carbon bond length of 2.22 Å was typical of a single bond between these atoms.[25] The distinctive NMR spectrum of the derivative, which shows two Cp singlets at 5.67 and 6.65 ppm and an AX pattern for the methanedithiolate protons, provides a facile identification of this structural type. The NMR spectrum was invariant up to 125 °C, and no fluxional properties for the product cation were observed.[24]

Reaction 1 involves a reduction by two electrons, which are provided by 1 mol of H_2. The formal oxidation states of the atoms in the nitrile molecule remain unchanged during the course of the reaction. The electron donation occurs within the dinuclear molybdenum complex, and *formal* oxidation states of +IV and +III can be assigned

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Table I. ^{1}H NMR Data[a] for $[CpMo(S_2CH_2)(S_2\overline{CR})MoCp]X$ Complexes[b]

nitrile reacted	C_5H_5[c] (solvent)	S_2CH_2[d] (J)	R (multiplicity, J) [assignt]
CH_3CN	6.66, 5.67 ($CDCl_3$)	6.70, 5.12 (9)	2.52 (s, CH_3)
CH_3CH_2-CN	6.61, 5.74 (CD_3CN)	6.68, 5.20 (8.7)	2.23 (q, 7.4) [CH_2CH_3] 1.41 (t, 7.4) [CH_2CH_3]
C_6H_5CN	6.29, 5.84 (CD_3CN)	6.62, 5.21 (8.7)	7.45 (m) [Ph]
$C_6H_5CH_2$-CN	6.71, 5.62 (CD_3CN)	6.69, 5.19 (8.7)	7.35 (s) [$CH_2C_6H_5$] 3.38 (s) [$CH_2C_6H_5$]
CH_3CH_2-O_2CCN	6.61, 5.82 (CD_3CN)	6.67, 5.13 (8.8)	4.25 (q, 7.6) [CH_2CH_3] 1.27 (t, 7.6) [CH_2CH_3]
$(CH_3)_2C$-HCN	6.59, 5.66 ($CDCl_3$)	6.88, 5.15 (8.7)	2.28 (sept, 6.4) [$CH(CH_3)_2$] 1.19 (d, 6.4) [$CH(CH_3)_2$]
HCN	6.67, 5.76 (CD_3CN)	6.84, 5.22 (8.7)	7.44 (s) [H]
$(C_6H_5)_2C$-HCN	6.49, 5.80 (CD_3CN)	6.62, 5.18 (8.7)	7.52–7.27 (m) [$CH(C_6H_5)_2$] 4.84 (s) [$CH(C_6H_5)_2$]

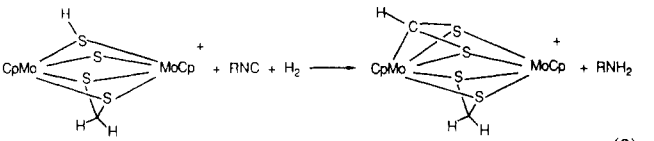
[a] In ppm relative to residual solvent protons, with J values in Hz. [b] X = BF_4 for R = CH_3, CH_3CH_2, C_6H_5; X = SO_3CF_3 for other R groups. [c] Singlets. [d] Doublets.

to the two molybdenum ions in the starting and product cations, respectively.

Scope of the Reaction. The protonated cation 1 reacted in a similar manner under hydrogen with a series of nitriles RCN, where R = H, CD_3, CH_3CH_2, $(CH_3)_2CH$, Ph, $PhCH_2$, Ph_2CH, and $CH_3CH_2O_2C$. In each case, a cationic derivative of the formula $[CpMo(S_2CH_2)(\mu\text{-}S_2\overline{CR})MoCp]^+$ was isolated and characterized by elemental analysis and spectroscopic data. ^{1}H NMR data for each of the organometallic products are given in Table I. Reaction temperatures ranged from 25 to 50 °C, and isolated yields ranged from 20 to 70%. Ammonia was detected as a product in each reaction in yields ranging from 30 to 80%. In the reaction of acrylonitrile with the protonated cation under hydrogen, an ammonia yield of 30% was observed. The NMR spectrum of the crude product mixture showed Cp resonances characteristic of the expected molybdenum cation, $[CpMo(S_2CH_2)(S_2\overline{CCH{=}CH_2})MoCp]^+$, as well as resonances for other cyclopentadienylmolybdenum products. However, we were not successful in separating this mixture or in definitively characterizing the dithioacrylate product. In the absence of hydrogen the protonated cation 1 is known to undergo S—H addition to the C=C bond of acrylonitrile.[4] This reaction as well as other unidentified processes appears to compete with the nitrile cleavage in this system. The nitrile cleavage reaction did not proceed with trimethylacetonitrile or with dibromoacetonitrile.

The effect of the substituent R on the rate of the nitrile cleavage reaction was studied by means of competition reactions. When 1 was reacted with an equimolar mixture of acetonitrile and ethyl cyanoformate under hydrogen in $CDCl_3$, greater than 90% of the product resulted from the cleavage of ethyl cyanoformate. However, competition reactions between nitriles with alkyl and aryl substituents did not show significant differences in rate. For example, the reactions of 1 with an equimolar mixture of $CH_3CN/(CH_3)_2CHCN$ (2 equiv each) and of CH_3CN/Ph_2CHCN showed by NMR spectroscopy that the two possible cationic products in each reaction were formed in approximately equal molar ratios. The reaction rate does not appear to be very sensitive to either electronic or steric effects within this range of variation.

Characterization of the Isonitrile Cleavage Reactions. The reaction of 1 with 1 equiv of isonitrile under 1–2 atm of hydrogen proceeded as shown in eq 2. The



(2)

reaction has been characterized for R = benzyl, *tert*-butyl, and *n*-butyl. The rate of the reaction with the benzyl derivative was the slowest, and reaction conditions of 50 °C for 5 days were employed. The other isonitriles reacted at ambient temperature over a period of 3–5 days. The cationic molybdenum product, which was isolated in yields of 35–60%, had been synthesized, as described above, from the reaction of 1 with HCN. The primary amine formed in reaction 2 was isolated as an ammonium salt and identified by NMR and mass spectroscopy. As the isonitrile cleavage proceeded, the product amine deprotonated 1, and the neutral derivative $(CpMo(\mu\text{-}S))_2S_2CH_2$ was identified by NMR spectroscopy in most product solutions. A third molybdenum product observed by NMR spectroscopy in the room-temperature reactions was $[(CpMo)_2(S_2CH_2)(S_2CNHR)]^+$ (2). The isolation and characterization of this product are discussed below. Reaction 2 did not occur in the presence of excess acid. Under these conditions, acid-catalyzed condensations of the isonitriles appeared to be promoted.[26] Excess acid also appeared to alter the reactivity of an intermediate in the reaction (vide infra).

Reactions of Molybdenum Complexes with Nitriles and Isonitriles in the Absence of Hydrogen. Studies of the reactivity of the protonated complex and of the corresponding deprotonated derivative with nitriles were carried out. When 1 was stirred in acetonitrile in the absence of hydrogen (under a nitrogen atmosphere), no reaction with the nitrile was observed by NMR or visible spectroscopy. It was also established that significant deprotonation did not occur; the pK_a of the triflate salt of 1 in this solvent was determined to be 8.3.[27] Similarly, the neutral derivative $(CpMo(\mu\text{-}S))_2S_2CH_2$ did not undergo a detectable reaction with the reactive nitrile EtO_2CCN under an atmosphere of nitrogen or hydrogen. NMR resonances of the complex remained unchanged.

Unlike nitriles, isonitriles underwent a rapid interaction with the molybdenum complex 1 as well as with its deprotonated analogue in the absence of hydrogen. Each of these reactions has been characterized. The neutral complex $(CpMo(\mu\text{-}S))_2S_2CH_2$ reacted rapidly with 1–2 equiv of isonitrile to form a neutral complex with a dithiocarbonimidate ligand (eq 3). This interaction is a reversible one. The equilibrium for the reaction with benzyl isocyanide lies to the right, and the complex with R = benzyl has been isolated and characterized by spectroscopic data[28] and by elemental analysis. However, the derivatives with R = *tert*-butyl and *n*-butyl in chloroform solution are in equilibrium with $(CpMo(\mu\text{-}S))_2S_2CH_2$ and free isonitrile. The equilibrium constant for the reaction with *tert*-butyl isocyanide was calculated to be 2.1×10^2 M^{-1} at 25 °C on

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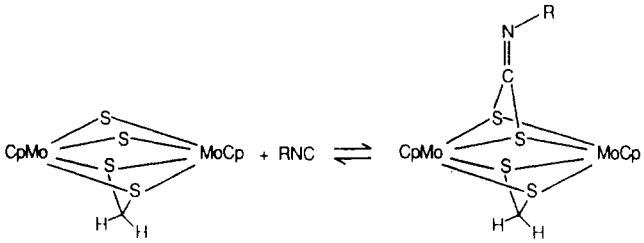
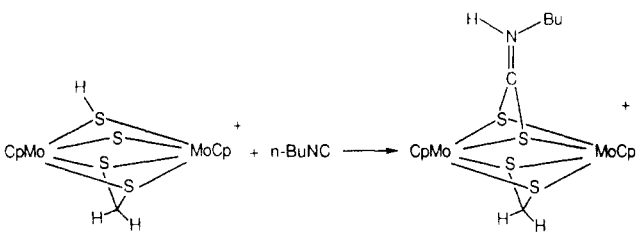


(3)

the basis of integrations of appropriate NMR resonances. Similar reversible reactions with isonitriles have been characterized for related $Cp_2Mo_2S_4$ complexes.[29]

The reaction of the protonated dimer **1** with 1 equiv of *n*-butyl isocyanide in the absence of hydrogen was monitored by NMR spectroscopy. At early reaction times (ca. 10 min) in CD_3CN, major product Cp resonances were observed at 7.2 and 5.8 ppm. The downfield chemical shift at 7.2 ppm is characteristic of Cp resonances of cationic species of the type $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SR)]^+$.[24,30] The resonance is tentatively assigned to a 1,1-insertion product of the formula $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SCH(=NR))]^+$. A singlet observed at 4.2 ppm is consistent with the S_2CH_2 protons in such a structure. The resonances associated with this product disappeared as the reaction proceeded (within 30 min), and the single major product that resulted from the reaction was the dimer with the Cp resonance at 5.8 ppm. This final product was isolated and characterized by spectroscopic techniques. The data are consistent with a dithiocarbonimidate complex protonated at the nitrogen atom (**2**; eq 4). For example, in the NMR

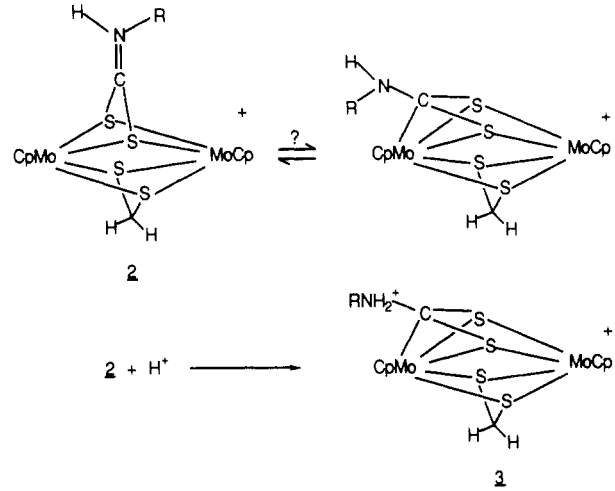


1 **2**

(4)

spectrum of the product, a broad resonance observed at 8.79 ppm was assigned to the NH proton; the coupling pattern was better resolved for the methylene group adjacent to the nitrogen, and the apparent quartet at 3.19 ppm was attributed to coupling of these methylene protons to an adjacent CH_2 and to the N–H proton with similar coupling constants. The resonances of the room-temperature NMR spectrum did not change as the temperature was decreased to −90 °C. The spectrum therefore provided no evidence for the presence at room temperature of rapid solution equilibria involving **2**, e.g. eq 5. Complex **2** was found to rearrange, however, upon the addition of excess acid. Low-temperature NMR data for the new dication **3** are given in the Experimental Section. A direct protonation of **2** may precede this rearrangement, or, as suggested by a reviewer, the protonation could involve the equilibrium shown in eq 5 (*K* being very small).

The mechanism of the formation of **2** in eq 4 was of interest, since electrophilic molecules generally react with isonitriles by 1,1-addition to the electronegative carbon atom.[31,32] Such 1,1-insertions of isonitriles have been



2

3

(5)

identified previously in reactions with H_2S and thiols[32] as well as with metal hydrides.[33] While such an insertion may occur in the reaction of *n*-butyl isocyanide with **1**, the product appears to be of low stability relative to that of **2**. We reasoned that the formation of **2** may involve an initial interaction of the isocyanide with a trace amount of the neutral complex $(CpMo(\mu\text{-}S))_2S_2CH_2$ followed by proton transfer from **1**. In fact, when eq 4 was carried out in the presence of a small amount (0.3 equiv) of excess triflic acid, the formation of **2** was completely inhibited, and a new product was formed, which is discussed below.

Neither the isolated neutral dithiocarbonimidate complex nor its protonated forms, **2** and **3**, underwent a further reaction with hydrogen at room temperature. The addition of $(CpMo(\mu\text{-}S))_2S_2CH_2$ or of **1** to the reaction solutions did not alter the observed stability of the isonitrile complexes toward hydrogen. We conclude that these complexes are not mechanistically involved in the isonitrile cleavage reaction (eq 2). The formation of **2** in the reactions under hydrogen appears to be an independent side reaction.

Reactions of 1 with Nitriles and Isonitriles in the Presence of Excess Acid. We mentioned above that when the reaction of **1** with *n*-BuN≡C was monitored by NMR spectroscopy, a derivative of low stability was observed and tentatively assigned to the 1,1-insertion product. When this reaction was repeated with excess acid, we observed by NMR spectra that this reactive insertion product appeared to be stabilized by protonation as shown in Scheme I (reaction a). The reaction with excess acid was not particularly clean. Evidence for other molybdenum products and for possible isonitrile condensation products[26] in solution was observed in the NMR spectrum, and solids were also present in the tube. We were not successful in isolating **4** in pure form. Nevertheless, **4** was the major product, present in a significant concentration in these solutions (see Figure 1), and in a sealed NMR tube it persisted in solution for >24 h. We were therefore able to carry out homonuclear decoupling experiments on this product in order to support our structural assignment.

Single Cp and methanedithiolate resonances were observed at 7.19 and 4.45 ppm, respectively. A doublet (*J*

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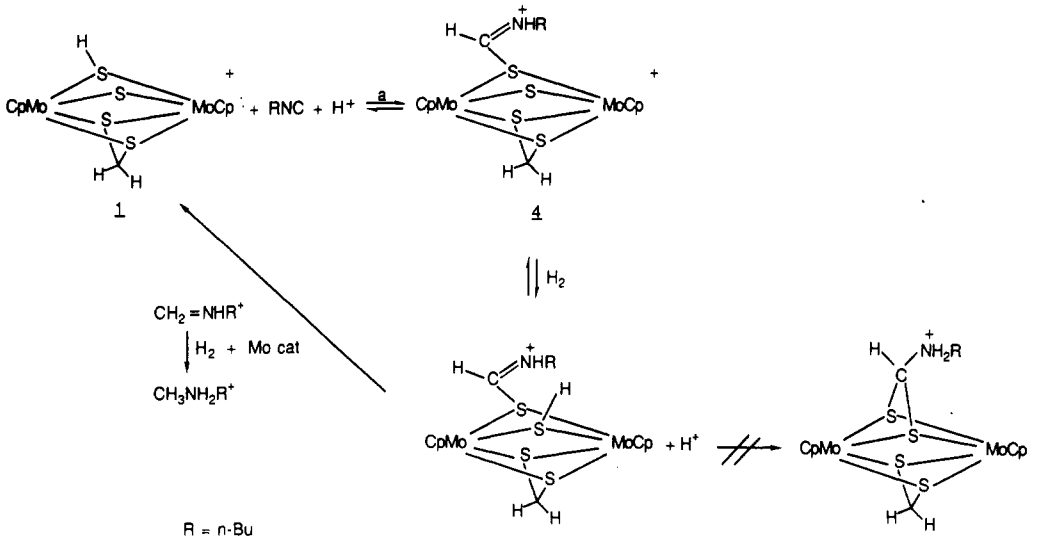
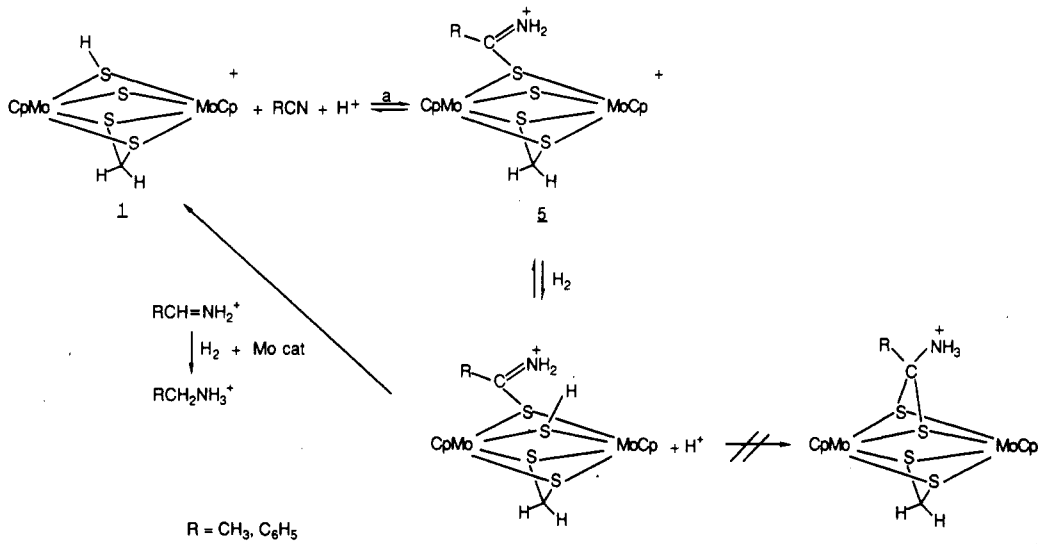
Scheme I



Scheme II



= 15.2 Hz) at 8.58 ppm was assigned to the imino CH, and a broad resonance at 13.2 ppm was assigned to the NH proton. The methylene group adjacent to the nitrogen appeared as an apparent quartet at 3.74 ppm. When the NH resonance at 13.2 ppm was irradiated, the =CH doublet collapsed to a singlet and the methylene resonance became a triplet. The coupling constant for the imino CH group is similar to those observed in organic aldimines[34] and N-substituted secondary carbenes coordinated to transition metals.[35]

The reaction of 1 with acetonitrile in the presence of excess acid also resulted in the formation of a new product, which was isolated in good yield. Spectroscopic data (see Experimental Section and Figure 2) are consistent with the structure of 5 shown in Scheme II (reaction a). When an isolated sample of 5 was dissolved in CD_3CN, exchange between complexed and free acetonitrile was found by NMR studies to be complete in 4 h.

The tendency for nitriles to undergo 1,2-addition reactions as opposed to the 1,1-additions to isonitriles has been well established and attributed to the different electronic features of the two structures.[36] The 1,2-addition of the S—H group in H_2S and thiols to the C≡N bond in nitriles

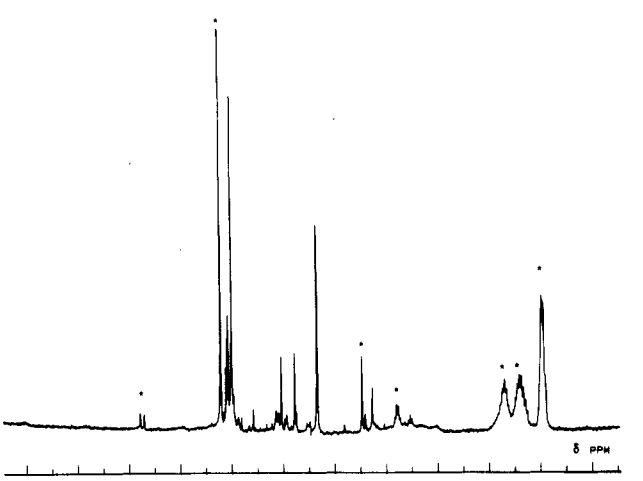


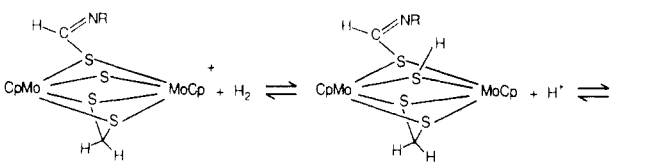
Figure 1. ^1H NMR spectrum (200 MHz) of the product mixture from the reaction of 1 with 0.3 equiv of triflic acid and 1 equiv of *n*-butyl isocyanide in CD_2Cl_2. Resonances marked with an asterisk are associated with $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SCH{=}NHBu)]^{2+}$ (4). A broad weak resonance at 13.2 ppm is not shown. Assignments are given in the Experimental Section, and results of decoupling experiments are given in the Results and Discussion.

(34) Boyd, D. R.; Hamilton, R.; Thompson, N. T.; Stubbs, M. E. *Tetrahedron Lett.* **1979**, 3201.

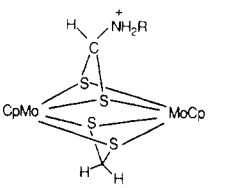
(35) (a) Christian, D. F.; Roper, W. R. *J. Organomet. Chem.* **1974**, *80*, C35. (b) Christian, D. F.; Clark, H. C.; Stepaniak, R. F. *J. Organomet. Chem.* **1976**, *112*, 227.

has been characterized previously.[37] Those reactions involved nucleophilic attack by sulfide and were promoted by triethylamine. In the present system, we propose that **1** undergoes a reversible electrophilic addition to the nitrile and that the excess acid stabilizes the product. Reversible insertions of alkenes into the S—H bond of **1** have been characterized previously, and the unusual mechanistic features for these electrophilic additions have been discussed.[4] We believe that the trapping of the S—H insertion products with excess acid and the identification of **4** and **5** is an important result because the insertion products are believed to the key intermediates in the nitrile and isonitrile cleavage by hydrogen.

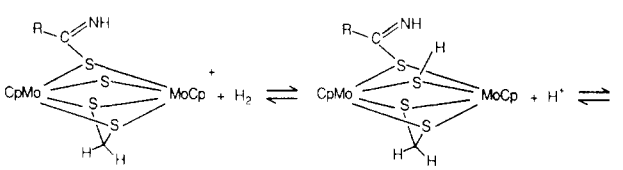
Proposed Mechanism of C≡N Bond Cleavage. Although excess acid helped to stabilize the insertion products of nitriles and isonitriles with **1**, the C≡N bond cleavage reactions did not occur in the presence of excess acid. In considering the mechanism for this cleavage reaction, therefore, we return to conditions in which no excess acid is present. In the reaction of **1** with *n*-butyl isocyanide under nitrogen, the 1,1-insertion product was tentatively identified by NMR spectroscopy (see above), but this intermediate was not detected when the reaction was carried out under hydrogen. We propose that this intermediate, as well as the nitrile insertion product, reacts with hydrogen as shown in eqs 6 and 7. A similar net



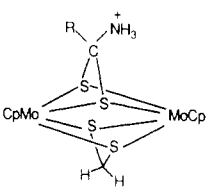
(6)



6



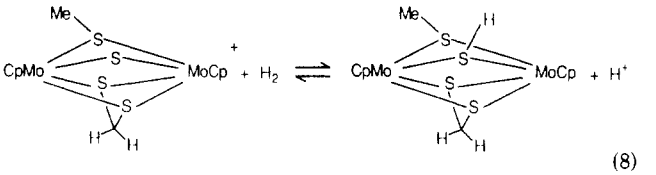
(7)



7

heterolytic activation of hydrogen has been characterized previously (eq 8),[38] and the reversibility of this reaction has been demonstrated.[2]

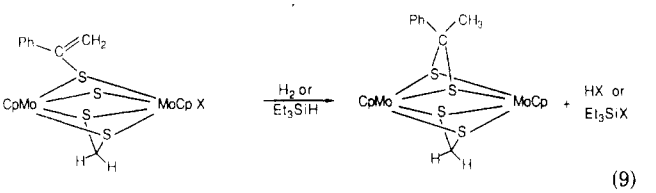
In these reactions the addition of hydrogen across a molybdenum–sulfide bond may produce a transient molybdenum hydride intermediate, but this species has not been detected spectroscopically. Although most molybdenum hydrides are not strongly acidic,[39] the positive



(8)

charge as well as the high coordination number about molybdenum in such an intermediate may favor proton dissociation. Alternatively, a pathway for this hydrogen activation process that involves only sulfur ligands could be proposed; further clarification may result from ongoing studies in our laboratory.

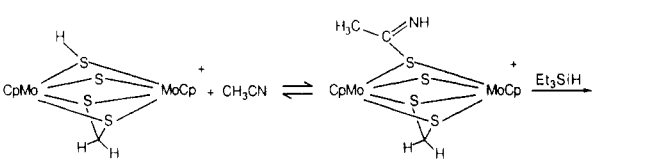
The intramolecular S–H addition reactions that give the final products of eqs 6 and 7 also have a precedent in the previous chemistry of these molybdenum systems in the reductions of ethenethiolate cations:[38] In the latter system



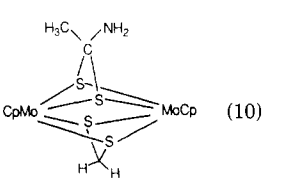
(9)

an intermediate with an S–H ligand was not detected. However, the hydride donor Et_3SiH used in the place of H_2 was found to effect the same transformation, and this provided further support for the net heterolytic cleavage of hydrogen proposed for these systems. The protonated forms of the amino-substituted 1,1-dithiolate ligands in **6** and **7** provide good leaving groups, and displacement of ammonia or amine by formation of a Mo–C bond would yield the final observed products.

Attempts To Synthesize a Proposed Intermediate. In our earlier work we found that the product of eq 9 was quite stable, and we therefore believed that the structurally related neutral forms of **6** and **7** would be stable, isolable complexes. The protonation of these complexes is proposed to result from heterolytic hydrogen activation (see eq 6). In order to prepare the neutral derivative $(CpMo)_2(S_2CH_2)(S_2C(CH_3)NH_2)$ (**8**), we attempted to carry out the reaction of **1** with acetonitrile using Et_3SiH rather than molecular hydrogen (eq 10). However, the reaction



(10)



8

proceeded to form the product cation $[(CpMo)(S_2CH_2)(S_2\overline{CCH_3})MoCp]^+$, as well as the deprotonated form of the starting material $(CpMo(\mu\text{-}S))_2S_2CH_2$. It appears that the presence of significant amounts of

(36) Green, J. A., II; Hoffmann, P. T. In *Isonitrile Chemistry*; Ugi, I., Ed.; Academic Press: New York, 1971; p 1.
(37) Gilbert, E. E.; Rumanowski, E. J.; Newallis, P. E. *J. Chem. Eng. Data* **1968**, *13*, 130.
(38) Laurie, J. C. V.; Duncan, L.; Haltiwanger, R. C.; Weberg, R. T.; Rakowski DuBois, M. *J. Am. Chem. Soc.* **1986**, *108*, 6234.
(39) (a) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley: New York, 1988; p 1103. (b) Moore, E. J.; Sullivan, J. M.; Norton, J. R. *J. Am. Chem. Soc.* **1986**, *108*, 2257.

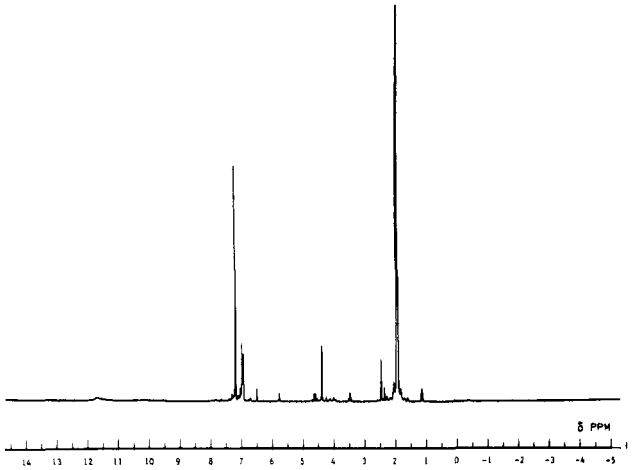
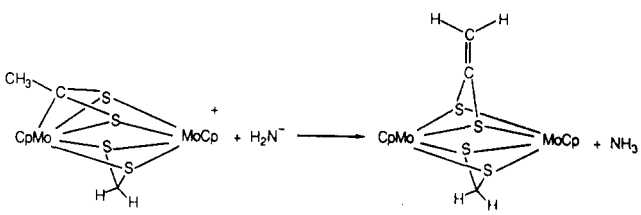


Figure 2. ^1H NMR spectrum (200 MHz) of $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SC(CH_3)=NH_2)]^{2+}$ (5) in CD_3CN. Singlets at 7.19, 4.38, and 2.45 ppm are assigned to Cp, S_2CH_2, and CH_3 protons, respectively. The broad NH_2 resonance at 11.70 ppm is barely observable in this spectrum. Resonances at 7, 4.6, and 2.3 ppm are always observed in spectra of 5; these appear to be associated with an unidentified isomer of 5. Multiplets at 1.2 and 3.4 ppm are due to diethyl ether; the resonance at 1.9 ppm is due to solvent.

unreacted 1 in the solution provided a proton source for promoting the cleavage of the C–N bond in 8 in the absence of additional acid.[40]

We were interested in several aspects of the reactivity of 8, and therefore, alternate procedures for its synthesis were investigated. For example, the susceptibility of the Mo–C bond to nucleophilic attack in the cation $[(CpMo)(S_2CH_2)(S_2\overline{CCH_3})(MoCp)]^+$ was studied by carrying out a reaction of the cation with sodium or lithium amide. Over a period of several days at room temperature, a single new molybdenum product was formed. Spectroscopic data were consistent with the formulation $(CpMo)_2(S_2CH_2)(S_2C{=}CH_2)$ (eq 11). The nature of the



(11)

product indicated that the amide reagent served as a deprotonating agent rather than a nucleophile, and this appeared to promote cleavage of the C–Mo bond. The same product was synthesized by the reaction of the cationic dithioacetate derivative with an alternate strong base such as sodium ethoxide. A second attempt to form an analogue of 8 involved the reaction of lithium amide with a cation having the η^3-dithiobenzoate ligand; in this case the deprotonation possibility has been eliminated. However, no reaction at all was observed in this system.

Reactions of Dications 4 and 5 with Hydrogen. We mentioned above that the isonitrile cleavage reaction did not take place in the presence of excess acid. Accordingly, when the 1,1-isonitrile insertion product was protonated to form 4, we found that the course of the reaction with hydrogen proposed in eq 6 was altered. Although the NMR resonances for 4 disappeared under a hydrogen atmosphere, no isonitrile cleavage product was observed. Instead, resonances for complex 1 and organic products, assumed to be imines or secondary amines, were observed in the final NMR spectra. The data suggested that, in the reaction of the dication 4 with hydrogen, cleavage of the C–S bond in the thiolate ligand was the favored pathway rather the intramolecular insertion of the iminium bond into the S–H ligand, as shown in Scheme I. Facile C–S bond cleavage under hydrogen has been observed in related cationic systems when the thiolate ligand contained electron-withdrawing groups.[24]

Because of the complex mixture of isonitrile and condensed and reduced isonitriles present in the acidified reaction mixtures, we did not identify the organic products resulting from the reaction of 4 with hydrogen. More detailed characterization was possible for the nitrile system. When eq 1, the nitrile cleavage reaction, was carried out in the presence of a small excess of triflic acid (0.3–0.5 equiv), the formation of the nitrile cleavage product was significantly inhibited. For example, in comparable NMR-scale reactions in CD_3CN, the formation of $[CpMo(S_2CH_2)(S_2\overline{CCD_3})MoCp]^+$ was complete within 1–2 h in the absence of excess acid and in 35–40 h in the presence of the acid. During the first 30–35 h of the latter reaction, resonances for 5 and for 1 were apparent in the NMR spectra and the yield of the nitrile cleavage product was less than 25%. After the resonances for 5 had disappeared, the formation of the nitrile cleavage product was rapidly completed. Resonances for $(CpMo(\mu\text{-}S))_2S_2CH_2$ were also observed in the final spectra.

Complex 1 was reacted with 1 equiv of triflic acid[41] and hydrogen in CH_3CN on a larger scale in order to identify the organic products. After 6 days the product solution was extracted with D_2O, and ethylammonium ion was identified in this fraction by NMR spectroscopy.[42] As described above, $[(CpMo)(S_2CH_2)(S_2\overline{CCH_3})(MoCp)]^+$ and $(CpMo(\mu\text{-}S))_2S_2CH_2$ were identified as the major molybdenum products. The formation of ethylammonium ion is consistent with cleavage of the C–S bond in an intermediate complex to form, initially, an iminium ion and 1 (Scheme II). Room-temperature hydrogenation of an iminium ion in the presence of $(CpMo(\mu\text{-}S))_2S_2CH_2$ has been observed independently by using the protonated form of benzylidenemethylamine. A similar hydrogenation accounts for the formation of the saturated product $EtNH_3^+$. The catalytic conversion of the nitrile to an iminium ion, as shown in Scheme II, is proposed to be the major pathway in the presence of excess acid. After the excess acid is thus consumed, 1 is available for further reaction with the nitrile solvent to form the nitrile cleavage product.

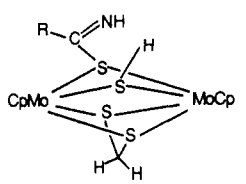
In summary, two competing reaction pathways of 1 with nitriles and isonitriles can be directed by control of the relative proton concentration in these systems. In the absence of excess acid, intermediate A (for the nitrile system) is proposed to undergo intramolecular S—H addition to the C=N bond. The process ultimately results in C—N bond cleavage. In the presence of excess acid, intermediate B is proposed to be present. The intramo-

(40) This result is consistent with our observation that only 1 and the product were observed when eq 1 was monitored by NMR spectroscopy.

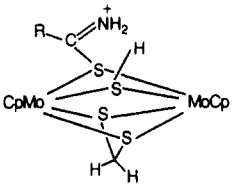
(41) When >1 equiv of excess acid was used, little decrease in the NMR resonances of 5 was observed over a period of several days. This observation is consistent with the expected inhibitory effect of excess acid on the proposed hydrogen activation process in which protons are produced.

(42) NH_4^+ was presumably also present in this fraction, but it was not identified by ^1H NMR spectroscopy. A similar reaction was carried out with benzonitrile, and the resulting product $C_6H_5CH_2NH_3^+$ was identified by GC, mass spectroscopy, and ^1H NMR spectroscopy.

(43) McKenna, M.; Wright, L. L.; Miller, D. J.; Tanner, L.; Haltiwanger, R. C.; Rakowski DuBois, M. *J. Am. Chem. Soc.* **1983**, *105*, 5329.



A



B

lecular S—H addition in B appears to be inhibited, and carbon–sulfur bond cleavage is the preferred path. Studies are underway in our laboratory to further define mechanistic features of carbon–sulfur bond reduction in related thiolate-bridged dimers. In the nitrile system, this process results in the formation of an iminium compound and, ultimately, in the formation of an alkylammonium ion.

Concluding Remarks. The reductive cleavage of the carbon–nitrogen triple bond in nitriles and isonitriles, which is achieved by 1 in the presence of hydrogen, results in the formation of ammonia and primary amines, respectively. The characterization of products resulting from nitrile and isonitrile insertions into the S–H ligand of 1 in the absence of hydrogen lend support for the sulfur-based mechanism proposed for the reduction of the carbon–nitrogen bond order. The molybdenum ion is proposed to play a role in promoting cleavage of the carbon–nitrogen single bond and in stabilizing the resulting dithio acid ligand. Such multiple sites of interaction between a substrate and a metallosulfur complex could be an important feature in the mechanisms of the nitrogenase enzymes, which achieve the cleavage of C≡N and N≡N bonds at ambient temperatures. An apparent driving force for the reactions reported in this paper is the stability of the final molybdenum complex, $[CpMo(S_2CH_2)(S_2\overline{CR})\overline{MoCp}]^+$. The cation appears to be stable indefinitely in the presence of air or water and, unlike other sulfido-bridged cyclopentadienylmolybdenum cations, is unreactive toward most nucleophiles. Nevertheless, it would be intriguing to find conditions that permit further reduction of the coordinated hydrocarbon fragment in this complex to model the formation of methane and other alkanes in the enzyme reactions. Such a multielectron process may be possible in an electrochemical experiment, and future studies will investigate the electrochemical reactivity of these derivatives.

Experimental Section

Nitriles and isonitriles were purchased from Aldrich. Nitriles with R = CH_3, CH_3CH_2, C_6H_5, and $C_6H_5CH_2$ were distilled under nitrogen from P_2O_5, and $(CH_3)_2CHCN$ was distilled from CaH_2. Other nitriles and isonitriles were used without purification. Chloroform, propylene carbonate, and most deuterated solvents were dried over 4-Å molecular sieves and used without further purification. $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SH)]CF_3SO_3$ (1(CF_3SO_3))[27] and $(CpMo(\mu\text{-}S))_2S_2CH_2$[41] were prepared as previously described. It is important that reactions of 1 be carried out in dry solvents, since 1 is deprotonated by trace amounts of water.[27]

Physical Measurements. Proton NMR spectra were recorded on JEOL FX-90Q, Bruker WM250, or Chemagnetics A200 spectrometers. Carbon NMR spectra were recorded on a Bruker WM250 spectrometer. Chemical shifts (ppm) were referenced to $SiMe_4$ by using the solvent signal as a secondary reference. Infrared spectra were recorded on a IBM IR130 FTIR spectrometer. Elemental analyses were performed by Spang Microanalytical Laboratories. Both FAB and EI mass spectra were obtained on a VG Analytical 7070 EQ-HF spectrometer.

Reactions of 1 with Nitriles under Hydrogen: Isolation of Ammonia. After reactions with the nitriles were complete, solvent was removed at reduced pressure and the residue was extracted with H_2O for 1–2 days. The concentration of NH_4^+ in the extract was determined by the indophenol test.[23] For the HCN reaction a small fraction (10 μL) of propylene carbonate from the reaction mixture was shaken with H_2O and then the NH_4^+ concentration was determined by the indophenol test. Alkylamines do not interfere with this test.[23]

$[(CpMo)(S_2CH_2)(S_2\overline{CR})\overline{MoCp}]BF_4$ (R = CH_3, CH_3CH_2, C_6H_5). A red-purple solution of the BF_4 salt of 1 (0.050 g, 0.088 mmol) in 10 mL of the nitrile was degassed and placed under hydrogen (400 Torr at −196 °C) in a Schlenk flask. The reaction mixture was stirred at room temperature for 1 day, and then solvent was removed at reduced pressure. After extraction with water, as described above, the remaining solid was dissolved in a minimum amount of acetonitrile and the yellow-brown product was precipitated with diethyl ether.

R = CH_3: yield 0.018 g, 35%; yield of NH_4BF_4 32%. See Table I for NMR data. Mass spectrum (FAB): *m/e* 491 (P^+ of cation), 450 ($((CpMoS_2)_2^+$), 418 ($((Cp_2Mo_2S_3)^+$), 387 ($((CpMoS)_2^+$). Elemental analyses for the bromide salt have been published previously.[24]

R = CH_3CH_2: yield 0.021 g, 40%; yield of NH_4BF_4 47%. Mass spectrum (FAB): *m/e* 505 (P^+ of cation), 450 ($((CpMoS_2)_2^+$), 418 ($((Cp_2Mo_2S_3)^+$). Anal. Calcd for $C_{14}H_{17}Mo_2S_4BF_4$: C, 28.39; H, 2.87; S, 21.63. Found: C, 28.33; H, 2.75; S, 21.69.

R = C_6H_5: yield 0.017 g, 30%; yield of NH_4BF_4 39%. Mass spectrum (FAB): *m/e* 553 (P^+ of cation), 507 ($(P - SCH_2)^+$), 450 ($((CpMoS_2)_2^+$), 418 ($((Cp_2Mo_2S_3)^+$). Elemental analyses for the chloride salt have been published previously.[24]

$[(CpMo)(S_2CH_2)(S_2\overline{CCH_2C_6H_5})\overline{MoCp}]CF_3SO_3$. In a Schlenk tube was combined 1 (0.10 g, 0.16 mmol) and $C_6H_5CH_2CN$ (28 μL, 0.24 mmol) in 5 mL of chloroform. The reaction mixture was degassed in three freeze–pump–thaw cycles and sealed under 600 Torr of hydrogen at −196 °C. The purple suspension was stirred at room temperature for 3 days, during which time much precipitate disappeared and the solution became blue. The reaction mixture was frozen at −196 °C, CF_3SO_3H (15 μL, 0.17 mmol) was added, and the reaction mixture was recharged with 600 Torr of hydrogen. The purple suspension was stirred an additional 4 days, and the solution became brown with a brown-purple precipitate. Solvent was removed at reduced pressure, and the residue was chromatographed on acidic alumina with 80/20 (v/v) $CH_3CN/CHCl_3$. The first brown band was collected; evaporation of solvent at reduced pressure gave an oil, which was dissolved in CH_3CN and precipitated with diethyl ether. The light brown crystals were filtered and dried in vacuo: yield 0.080 g, 69%; yield of $NH_4SO_3CF_3$ 93%. FAB-MS: *m/e* 567 (P of cation), 521 ($P - SCH_2$), 464 ($P - CCH_2C_6H_5$). Anal. Calcd for $C_{20}H_{19}F_3Mo_2O_3S_5$: C, 33.53; H, 2.67; S, 22.37. Found: C, 33.44; H, 2.83; S, 22.19.

$[(CpMo)(S_2CH_2)(S_2\overline{CCO_2CH_2CH_3})\overline{MoCp}]CF_3SO_3$. Complex 1 (0.10 g, 0.16 mmol) and $CH_3CH_2O_2CCN$ (16 μL, 16 mmol) were combined in 5 mL of chloroform in a Schlenk tube, and a procedure similar to that described above was followed. The total reaction period was 4 days. The product was isolated as a purple crystalline material: yield 0.062 g, 57%; yield of $NH_4SO_3CF_3$ 88%. FAB-MS: *m/e* 549 (P of cation), 503 ($P - SCH_2$), 464 ($P - CCO_2CH_2CH_3$). Anal. Calcd for $C_{16}H_{17}F_3Mo_2O_5S_5$: C, 27.51; H, 2.45; S, 22.95. Found: C, 27.17; H, 2.58; S, 22.35.

$[(CpMo)(S_2CH_2)(S_2\overline{CCH(CH_3)_2})\overline{MoCp}]CF_3SO_3$. Complex 1 (0.10 g, 0.16 mmol) and $(CH_3)_2CHCN$ (29 μL, 0.32 mmol) were added to 10 mL of chloroform in a Schlenk tube, and a procedure similar to that described above was followed, except that the reaction temperature was 50 °C. The product was isolated by filtering the reaction solution and crystallizing the complex from the filtrate by the addition of diethyl ether. Further recrystallization from CH_3CN/Et_2O gave light brown crystals, which were dried in vacuo: yield 0.052 g, 48%. FAB-MS: *m/e* 519 (P of cation), 473 ($P - SCH_2$), 418 ($P - SCH_2CCH(CH_3)_2$). Anal. Calcd for $C_{16}H_{19}F_3Mo_2O_3S_5$: C, 28.75; H, 2.86; S, 23.98. Found: C, 28.74; H, 2.95; S, 23.94.

$[(CpMo)(S_2CH_2)(S_2\overline{CCH(C_6H_5)_2})\overline{MoCp}]CF_3SO_3$. Complex 1 (0.080 g, 0.13 mmol) and $(C_6H_5)_2CHCN$ (0.25 g, 1.3 mmol) were combined in 5 mL of chloroform in a Schlenk tube, and a procedure similar to that described above was followed. The total

reaction time was 3 days. The product was isolated as a brown crystalline material: yield 0.020 g, 19%; yield of $NH_4SO_3CF_3$ 37%. FAB-MS: *m/e* 643 (P^+ of cation), 597 (P - SCH_2), 464 (P - $CCHPh_2$).

$[(CpMo)_2(S_2CH_2)(S_2\overline{CH})MoCp]CF_3SO_3$. In a Schlenk tube was combined 1 (0.050 g, 0.081 mmol) and CF_3SO_3H (23 μL, 0.25 mmol) in 4 mL of propylene carbonate. The solution was frozen at −196 °C, and NaCN (0.004 g, 0.08 mmol) was added to the reaction mixture. The mixture was cautiously deoxygenated in three freeze–pump–thaw cycles and sealed under 400 Torr of hydrogen. The purple solution was heated to 50 °C and stirred. After 14 days the purplish brown solution was transferred to a short-path distillation apparatus and solvent was removed at ~1 Torr and 95 °C. A purple-brown solid remained, which was chromatographed on acidic alumina with 50/50 $CHCl_2/CH_3CN$. A brown band was collected, which gave an oily brown residue after solvent was removed at reduced pressure. The residue was dissolved in CH_3CN, and addition of diethyl ether precipitated light brown crystals that were filtered and dried in vacuo: yield 0.023 g, 46%; yield of $NH_4SO_3CF_3$ 58%. FAB-MS: *m/e* 477 (P of cation), 464 (P - CH), 432 (P - SCH), 418 (P - SCH_2 - CH). Anal. Calcd for $C_{13}H_{13}F_3Mo_2O_3S_5$: C, 24.93; H, 2.09; S, 25.59. Found: C, 25.06; H, 2.10; S, 25.40.

Reaction of 1 with Acrylonitrile and Hydrogen. Complex 1 (0.010 g, 0.16 mmol) and CH_2=CHCN (16 μL, 0.24 mmol) were combined in 5 mL of $CHCl_3$. The solution was degassed in three freeze–pump–thaw cycles and sealed under 600 Torr of H_2 at −196 °C. The reaction mixture was stirred for 5 days at 50 °C; then solvent was removed at reduced pressure to produce an oily brown solid. The following resonances in the ^1H NMR spectrum (CD_3CN) of the crude product were tentatively assigned to $[CpMo(S_2CH_2)(S_2\overline{CCH=CH_2})MoCp]^+$ (ppm): 6.61, 5.67 (2 s, Cp); 6.71, 5.15 (2 d, S_2CH_2). Additional Cp resonances were observed at 6.98, 6.91, and 5.86 ppm. Attempts to separate the product mixture by column chromatography on alumina resulted in decomposition; yield of $NH_4SO_3CF_3$ 29%.

Attempted Reaction of 1 with Hydrogen and Trimethylacetonitrile. Complex 1 (0.02 g, 0.03 mmol) and $(CH_3)_3CCN$ (3.7 μL, 0.033 mmol) were added to 0.6 mL of $CDCl_3$ in an NMR tube. The reaction mixture was degassed in three freeze–pump–thaw cycles and sealed under ~550 Torr of hydrogen at −196 °C. The purple slurry stood for 3 days at room temperature and was heated at 50 °C for 6 days. The NMR spectra showed no evidence for the formation of $[(CpMo)(S_2CH_2)(S_2\overline{CC(CH_3)_3})MoCp]SO_3CF_3$.

Attempted Reaction of 1 with Hydrogen and Dibromoacetonitrile. Complex 1 (0.010 g, 0.016 mmol) and Br_2HCCN (3 μL, 0.035 mmol) were combined in 0.7 mL of $CDCl_3$ in an NMR tube. The reaction mixture was degassed in three freeze–pump–thaw cycles and sealed under 500 Torr of hydrogen. The purple suspension was warmed to room temperature and stood for 9 days. The NMR spectra showed that no reaction had occurred.

Competition Reactions of 1 and Hydrogen with Nitriles. Complex 1 (0.020 g, 0.033 mmol) and 2 equiv each of two different nitriles were combined in chloroform in a Schlenk tube. The mixtures were degassed in three freeze–pump–thaw cycles and sealed under 550 Torr of hydrogen. The resulting purple suspensions were stirred at room temperature until the solution became deep blue and the purple precipitate had largely disappeared. Solvent and volatile reagents were removed at reduced pressure from the reaction mixtures, and a small fraction of the nonvolatile products from each reaction was completely dissolved in CD_3CN in an NMR tube. Relative product yields were found by integration of cyclopentadienyl resonances. On the basis of these data the relative rates of reaction of the two nitriles in each of the three competition reactions are as follows: CH_3CN:$(C_6H_5)_2CHCN$ ≈ 1:1; CH_3CN:$(CH_3)_2CHCN$ ≈ 1:1; CH_2CN:EtO_2CCN < 0.04:1.

$(CpMo)_2(S_2CH_2)(S_2CCH_2)$. (a) In a 50-mL round-bottom flask with a side arm was dissolved $[(CpMo)_2(S_2CH_2)(S_2\overline{CCH_3})]SO_3CF_3$ (0.050 g, 0.078 mmol) in 10 mL of absolute ethanol. A freshly prepared solution of NaOEt (0.0054 g of Na in 3 mL of absolute ethanol) was added, and the mixture was stirred at room temperature. Almost immediately, golden crystals began to precipitate from the solution. After 4 h, the crystals were filtered, washed with MeOH, and dried in vacuo. The product was further purified by dissolving the crystals in THF and filtering the solution. Removal of solvent from the filtrate at reduced pressure gave brown crystals of the product; yield 0.022 g, 57%. ^1H NMR ($CDCl_3$): δ 6.20 (s, S_2CH_2), 5.74 (s, C_5H_5), 3.66 (s, S_2CCH_2). ^{13}C NMR (off-resonance decoupled, $CDCl_3$): δ 179.43 (s, S_2CCH_2), 97.16 (t, *J* = 56.5 Hz, S_2CCH_2 or S_2CH_2), 94.70 (t, *J* = 69.1 Hz, S_2CCH_2 or S_2CH_2), 92.4 (d, *J* = 78.2 Hz, C_5H_5). EI-MS: *m/e* 490 (P^+), 444 (P^+ - SCH_2), 418 (P^+ - SCH_2 - CCH_2), 386 (P^+ - S_2CH_2 - CCH_2). Exact mass determination by EI-MS: Calcd (based on ^{98}Mo), 493.8086; found, 493.8082.

(b) $[(CpMo)_2(S_2CH_2)(S_2\overline{CCH_3})]Cl$[24] (0.020 g, 0.037 mmol) and $NaNH_2$ (0.003 g, 0.08 mmol) were partially dissolved in ~0.8 mL of CD_2Cl_2 in an NMR tube. The mixture was degassed in three freeze–pump–thaw cycles and sealed under vacuum at −196 °C. The reddish brown slurry was warmed to room temperature, and after 18 h no reaction was apparent by NMR spectroscopy. The mixture was heated to 50 °C, and over 25 days the solution became reddish orange. A trace of an uncharacterized black precipitate formed. NMR resonances of the soluble material were consistent with the presence of ~10% starting complex and 90% product.

Attempted Reaction of $[(CpMo)(S_2CH_2)(S_2\overline{CPh})MoCp]SO_3CF_3$ with Sodium Amide. In an NMR tube was combined the dithiobenzoate cation (0.020 g, 0.028 mmol) and $NaNH_2$ (0.002 g, 0.05 mmol) in 0.7 mL of CD_2Cl_2 to give a purple slurry. The reaction mixture was degassed in three freeze–pump–thaw cycles and sealed under vacuum at −196 °C. The mixture was heated to 85 °C, and after 10 h resonances corresponding to starting material and $(CpMo)_2(S_2CH_2)_2$[41] were observed in the NMR spectrum of the reaction mixture. Over the next 27 days the NMR spectrum remained unchanged. The initial formation of $(CpMo)_2(S_2CH_2)_2$ may have been due to the reaction of $NaNH_2$ with impurities in the starting material.

Attempted Reaction of $(CpMo(\mu\text{-}S))_2S_2CH_2$ with Hydrogen and Ethyl Cyanoformate. In an NMR tube was combined the deprotonated form of 1 (0.015 g, 0.032 mmol) and $CH_3CH_2O_2CCN$ (5 μL, 0.05 mmol) in ~0.5 mL of THF-d_8. The reaction mixture was degassed in three freeze–pump–thaw cycles and sealed under 600 Torr of hydrogen at −196 °C. The mixture was warmed to room temperature, and after 27 days only resonances of starting materials were observed in the NMR spectrum.

Reaction of 1 with Acetonitrile and Triethylsilane. Complex 1 (0.050 g, 0.081 mmol) and Et_3SiH (16 μL, 0.10 mmol) were combined in 7 mL of CH_3CN in a Schlenk tube. The reaction mixture was degassed in three freeze–pump–thaw cycles and sealed under vacuum at −196 °C. The purple solution was warmed to room temperature and turned blue after 2 h of stirring. No further change occurred after an additional 14 h. Solvent was removed at reduced pressure, leaving a mixture of reddish brown and blue solids. The ^1H NMR spectrum in $CD_3CN/CDCl_3$ (11) showed that $(CpMo(\mu\text{-}S))_2S_2CH_2$ and $[CpMo(S_2CH_2)(S_2\overline{CCH_3})MoCp]^+$ were the major products formed in the reaction.

Reaction of 1 with Hydrogen and Isonitriles. Complex 1 (0.050 g, 0.081 mmol) and an isonitrile (8.5–10 μL, 0.080–0.082 mmol) were combined in 8–10 mL of dichloromethane in a 125-mL Schlenk tube. The reaction mixtures were degassed in three freeze–pump–thaw cycles and sealed under 375–400 Torr of H_2. The reaction mixtures were stirred and warmed to the following temperatures over the given time periods: reaction a with benzyl isocyanide, 70 °C, 3 days; reaction b with *n*-butyl isocyanide, ambient temperature, 6 days; reaction c with *tert*-butyl isocyanide, ambient temperature, 3 days. Over the course of the reactions, the reaction mixtures changed from a yellow solution with purple precipitate to a green- or yellow-brown solution. In reaction a, yellow-brown crystals formed. Solvent was removed at reduced pressure upon completion of the reactions, and the brown solid that remained was extracted with toluene and filtered to give a yellow or brown solution. The portion of the solid that did not extract into toluene was shaken vigorously in ~25 mL of diethyl ether containing ~2.5 g of Na_2CO_3 and filtered. This was repeated three to five times, and the filtrates were combined and shaken

with ~20 mL of 10% aqueous HCl. Removal of the diethyl ether and H_2O at reduced pressure and 50 °C gave slightly impure RNH_2·HCl (R = $C_6H_5CH_2$, $CH_3(CH_2)_3$, $(CH_3)_3C$), which was verified by comparison of ^1H NMR and mass spectral data with those of authentic samples. Yields: reaction a, 68%; reaction b, 38%; reaction c, 33%. The toluene and diethyl ether insoluble product was extracted with acetonitrile and filtered to give a yellow filtrate. Addition of diethyl ether to the filtrate gave light brown crystals of $[CpMo(S_2CH_2)(S_2\overline{CH})\overline{MoCp}]SO_3CF_3$, which were filtered and dried in vacuo. Yields: reaction a, 59%; reaction b, 36%; reaction c, 40%. Products that were not isolated but were determined to be present in the reaction mixture by ^1H NMR spectroscopy included the following: reaction a, $(CpMo)_2(S_2CH_2)_2$;[41] reaction b, $(CpMo(\mu\text{-}S))_2(S_2CH_2)$ and $[(CpMo)_2(S_2CH_2)(S_2CNH(CH_2)_3CH_3)]CF_3SO_3$ (see below for characterization data); reaction c, $(CpMo(\mu\text{-}S))_2(S_2CH_2)$ and $[(CpMo)_2(S_2CH_2)(S_2CNHC(Me)_3)]CF_3SO_3$. ^1H NMR (CD_2Cl_2): δ 6.16 (s, S_2CH_2), 5.87 (s, Cp), 1.37 (s, Me).

$(CpMo)_2(S_2CH_2)(S_2CNCH_2C_6H_5)$. In a 100-mL round-bottom flask with a side arm $(CpMo(\mu\text{-}S))_2S_2CH_2$ (0.050 g, 0.11 mmol) and $C_6H_5CH_2NC$ (13 μL, 0.11 mmol) were combined in 5 mL of dichloromethane. The mixture was stirred for 1 h at room temperature and turned from blue to orange-brown. Solvent was removed at reduced pressure to give a brown microcrystalline solid. The solid was washed with petroleum ether (bp 35–65 °C) and diethyl ether, in which the product is sparingly soluble. The light brown crystalline product was dried in vacuo; yield 0.045 g (70%). ^1H NMR ($CDCl_3$): δ 7.25 (br s, C_6H_5), 6.18 (s, S_2CH_2), 5.62 (s, Cp), 4.38 (s, N-CH_2). FAB-MS: *m/e* 582 ($P^+ + H^+$), 464 (P^+ - $CNCH_2C_6H_5$), 419 (P^+ - $CNCH_2C_6H_5$ - S_2CH). Anal. Calcd for $C_{19}H_{19}Mo_2NS_4$: C, 39.25; H, 3.29; S, 22.05. Found: C, 38.84; H, 3.13; S, 21.93.

Reactions of *n*- and *tert*-Butyl Isocyanide with $(CpMo(\mu\text{-}S))_2(S_2CH_2)$. (a) $(CpMo(\mu\text{-}S))_2(S_2CH_2)$ (0.010 g, 0.022 mmol) was dissolved in ~0.7 mL of $CDCl_3$ in an NMR tube. The solution was degassed in three freeze–pump–thaw cycles, and $CH_3(CH_2)_3NC$ (2.3 μL, 0.022 mmol) was added to the reaction mixture at room temperature. The reaction mixture immediately turned brown and was frozen at −196 °C and sealed under vacuum. The brown mixture was warmed to room temperature and monitored by ^1H NMR spectroscopy. An equilibrium mixture containing starting materials and $(CpMo)_2(S_2CH_2)(S_2CN(CH_2)_3CH_3)$ was established over 1–6 h. At equilibrium greater than 90% of starting materials had been consumed. ^1H NMR for $(CpMo)_2(S_2CH_2)(S_2CN(CH_2)_3CH_3)$ ($CDCl_3$): δ 6.18 (s, S_2CH_2), 5.66 (s, Cp), 3.17 (t, J = 6.7 Hz, S_2CNCH_2) 1.41–1.15 (m, $S_2CNCH_2(CH_2)_2$), 0.86 (t, J = 7 Hz, $S_2CN(CH_2)_3CH_3$).

(b) $(CpMo(\mu\text{-}S))_2(S_2CH_2)$ (0.010 g, 0.022 mmol) and $(CH_3)_3CNC$ (2.4 μL, 0.022 mmol) were combined in 1.0 mL of degassed CD_2Cl_2. no color change occurred, and 0.7 mL of the blue solution was transferred to a NMR tube. The solution was frozen and sealed under vacuum at −196 °C. The mixture was warmed to room temperature and monitored by ^1H NMR spectroscopy. The spectra suggested that an equilibrium mixture of starting materials and $(CpMo)_2(S_2CH_2)(S_2CNC(CH_3))$ was established after 1 h. Similar spectra were obtained after 1 day, and by integration of resonances in the ^1H NMR spectra an equilibrium constant of 2.1×10^2 M^{-1} was calculated for the forward reaction. ^1H NMR for $(CpMo)_2(S_2CH_2)(S_2CNC(CH_3)_3)$: δ 6.19 (s, S_2CH_2), 5.63 (s, Cp), 1.17 (s, $C(CH_3)_3$).

$[(CpMo)_2(S_2CH_2)(S_2\overline{CNH(CH_2)_3CH_3})]CF_3SO_3$ (2). Complex 1 (0.10 g, 0.16 mmol) and $CH_3(CH_2)_3NC$ (17 μL, 0.16 mmol) were combined in a Schlenk tube in 10 mL of dichloromethane. The mixture was degassed in three freeze–pump–thaw cycles, sealed under vacuum, and then warmed to 50 °C and stirred. Over the course of the reaction, the reaction mixture was orange with a purple precipitate that appeared to decrease in quantity. After 2 days the reaction mixture was filtered and ~100 mL of diethyl ether was rapidly added to the orange filtrate. Orange-brown crystals formed after 2 days. The solution was decanted, and the crystals were dried in vacuo; yield 0.031 g, 28%. ^1H NMR (CD_2Cl_2): δ 8.79 (br s, NH), 6.12 (s, S_2CH_2), 5.88 (s, Cp), 3.19 (q, J_{av} = 6.4 Hz, NH(CH_2)), 1.56–1.26 (m, $S_2CNH(CH_2)_2$), 0.91 (t, J = 7.3 Hz, $S_2CNH(CH_2)_3CH_3$). FAB-MS: *m/e* 548 (P^+), 465 (P^+ - $CN(CH_2)_3CH_3$), 419 (P^+ - SCH_2 - $CN(CH_2)_3CH_3$), 386 (P^+ - S_2CH_2 - $CNH(CH_2)_3CH_3$). IR (Fluorolube mull): 1537 cm^{-1} (m, $\nu_{C=N}$).

Reaction of 2 with Protic Acid. Complex 2 (0.010 g, 0.014 mmol) was dissolved in 0.7 mL of degassed CD_2Cl_2 in an NMR tube to give an orange solution. CF_3SO_3H (4.0 μL, 0.044 mmol) was added to the reaction mixture, and the tube was sealed under vacuum. No color change was observed, but ^1H NMR spectra, recorded over 1 h to 13 days, showed the reaction was complete in <1 h. Broad resonances were observed that are tentatively assigned to $[(CpMo)(S_2CH_2)(S_2\overline{CNH_2(CH_2)_3CH_3})\overline{MoCp}]^{2+}$ (3). ^1H NMR spectra obtained at −45 °C showed the resonances for protons associated with C_5H_5 and S_2CH_2 had sharpened. ^1H NMR (CD_2Cl_2, −45 °C): δ 8.70 (br s, NH_2), 6.79 and 5.84 (2 s, Cp's), 6.46 and 5.00 (2 d, J = 9.2 Hz, S_2CH_2), 3.69 (br s, N-CH_2), 1.72 (br m, N-CH_2CH_2), 1.36 (br m, $N(CH_2)_2CH_2$), 0.91 (t, J = 7.1 Hz, N-$(CH_2)_2CH_3$).

Attempted Reaction of 2 with Hydrogen. Complex 2 (0.005 g, 0.007 mmol) was dissolved in 0.7 mL of CD_2Cl_2 to give an orange solution that was degassed in three freeze–pump–thaw cycles and sealed under 400 Torr of H_2 at −196 °C. The reaction mixture was warmed to room temperature and monitored by ^1H NMR spectroscopy over 17 days. No reaction was observed.

Attempted Reaction of $(CpMo)_2(S_2CH_2)(S_2CNCH_2Ph)$ with Hydrogen in the Presence of $(CpMo(\mu\text{-}S))_2S_2CH_2$. The isonitrile adduct (0.010 g, 0.017 mmol) and $(CpMo(\mu\text{-}S))_2S_2CH_2$ (0.003 g, 0.006 mmol) were combined in 0.7 mL of THF-d_8 in an NMR tube. The resulting green reaction mixture was degassed in three freeze–pump–thaw cycles and sealed under 500 Torr of H_2 at −196 °C. The reaction mixture was warmed to room temperature, and after 2 days only starting materials were observed by ^1H NMR spectroscopy. The reaction mixture was heated to 50 °C for 7 days and to 70 °C for 7 days. The NMR spectrum remained largely unchanged, and no evidence for a hydrogenation reaction was observed.

Reaction of 1 with *n*-Butyl Isocyanide in Acetonitrile. $CH_3(CH_2)_3NC$ (1.7 μL, 0.016 mmol) was added to an NMR tube containing 1 (0.010 g, 0.016 mmol) dissolved in 0.7 mL of degassed CD_3CN. The reaction mixture was sealed under vacuum at −196 °C and warmed to room temperature. After 9 min the solution had changed from purple to yellow-brown. Resonances were observed in the ^1H NMR spectrum for $CH_3(CH_2)_3NC$ and $(CpMo)_2(S_2CH_2)(S_2CN(CH_2)_3CH_3)$ in equilibrium with its protonated form. Resonances for a second molybdenum, product were tentatively assigned to the 1,1-insertion product $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SCH{=}N(CH_2)_3CH_3)]^+$: δ 7.15 (s, Cp), 4.29 (s, S_2CH_2), 3.87 (t, NCH_2, J = 7.6 Hz), 1.6–1.2 (m, $(CH_2)_2$), 0.91–0.84 (m, CH_3). The last resonances disappeared in 30 min, and only resonances for $[(CpMo)_2(S_2CH_2)(S_2CNH(CH_2)_3CH_3)]^+$ and $(CpMo(\mu\text{-}S))_2(S_2CH_2)$ were observed in the NMR spectrum for an extended period.

$[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SCH{=}N(H)Bu)]^{2+}$ (4). 1 (0.010 g, 0.016 mmol) and CF_3SO_3H (0.4 μL, 0.004 mmol) were combined in 0.7 mL of degassed CD_2Cl_2 in an NMR tube, giving a purple slurry. $CH_3(CH_2)_3NC$ (1.7 μL, 0.016 mmol) was added, and the reaction mixture was sealed under vacuum at −196 °C and warmed to room temperature. The solution remained purple, and additional purple precipitate formed. After 6 min resonances were observed in the ^1H NMR spectrum for two major molybdenum products: 4 (ca. 60%) and an unidentified cation (40–70%). ^1H NMR for 4: δ 13.2 (b, weak, NH), 8.69 (d, SCH, J = 15.2 Hz), 7.19 (s, Cp), 4.45 (s, S_2CH_2), 3.76 (q, NCH_2, J = 6.4 Hz). ^1H NMR for unidentified product: δ 6.97 (s), 4.23 (s). Other resonances for these products between 1.68 and 0.93 ppm were observed but not resolved (see Figure 1). Minor resonances for other Mo-containing species were also observed.

An attempt was made to isolate and purify 4. The contents of the NMR tube were centrifuged, the purple liquid layer was decanted, and the solvent was removed at reduced pressure, giving a purple solid. The ^1H NMR (CD_2Cl_2) spectrum of the solid was similar to that reported above. However, attempts to purify the solid by crystallization from CH_2Cl_2/Et_2O resulted in decomposition.

Reaction of 4 with Hydrogen. The above reaction was repeated, and the crude product was dissolved in 0.7 mL of CD_2Cl_2. The solution was degassed, and 0.6 atm of H_2 was added at −196

°C. The purple reaction mixture was warmed to room temperature and monitored by NMR spectroscopy. Within 2 h resonances for 4 had disappeared. No evidence was seen for the formation of $[(CpMo)(S_2CH_2)(S_2\overline{CH})MoCp]CF_3SO_3$.

Reaction of 1 with *n*-Butyl Isocyanide and Hydrogen in the Presence of Protic Acid. $CH_3(CH_2)_3NC$ (1.7 μL, 0.016 mmol) was added to a purple slurry of 1 (0.010 g, 0.016 mmol) and CF_3SO_3H (0.4 μL, 0.005 mmol) in 0.7 mL of degassed CD_2Cl_2 in an NMR tube. The reaction mixture was sealed under 450 Torr of hydrogen at −196 °C and warmed to room temperature. The reaction mixture was brown-purple after 10 min with much purple precipitate. A ^1H NMR spectrum showed resonances for 1 (35%), 4 (40%), and the unidentified complex also observed in the absence of hydrogen. Other broad resonances between 1.68 and 0.91 ppm were observed but were not resolved. Weak resonances for other molybdenum-containing products were also seen. After 3 h the resonances for 4 had nearly disappeared while the intensity of the Cp resonance for 1 increased somewhat relative to the methyl resonances of the isonitrile. Since 1 is only partially soluble in CD_2Cl_2, the relative intensity of its resonances does not accurately reflect its percentage in the two phase reaction mixture.

$[(CpMo)_2(\mu\text{-}S_2CH_2)(\mu\text{-}S)(\mu\text{-}SCCH_3{=}NH_2)](CF_3SO_3)_2$ (5). Triflic acid (15 μL, 0.16 mmol) was added to a purple solution of 1 (0.050 g, 0.081 mmol) in 10 mL of CH_3CN in a 100-mL Schlenk flask. No color change occurred as the solution was stirred at ambient temperature for 5 min. Addition of ~25 mL of diethyl ether gave a purple precipitate that was filtered, washed with ~10 mL of diethyl ether, and dried in vacuo; crude yield 0.035 g, 53%. ^1H NMR (CD_3CN): δ 7.19 (s, Cp), 4.38 (s, S_2CH_2), 2.45 (s, $CCH_3{=}NH_2$), 11.70 (br s, NH_2). FAB-MS: parent not observed, *m/e* 491 ($P^+ - NH_2$), 464 ($P^+ - CCH_3{=}NH_2$), 418 ($P^+ - SCH_2 - CCH_3{=}NH_2$). IR (KBr disk): 3105, 2926 (ν_{C-H} or ν_{N-H}), 1665 ($\nu_{C=N}$) cm^{-1}.

Reaction of Hydrogen with Benzylidenemethylamine in the Presence of 1. Complex 1 (0.010 g, 0.016 mmol) and $C_6H_5CH{=}NCH_3$ (2.0 μL, 0.016 mmol) were combined in 0.7 mL of CD_2Cl_2 in a NMR tube. The reaction mixture was sealed under 400 Torr of H_2 at −196 °C. The blue reaction mixture was warmed to ambient temperature and vigorously shaken. After 26 min, both $C_6H_5CH{=}NMe$ and $C_6H_5CH_2NHMe$ in equilibrium with their protonated forms were observed by proton NMR spectroscopy. After 1 day, greater than 95% conversion of $C_6H_5CH{=}NMe$ to $C_6H_5CH_2NHMe$ was observed.

Reaction of Hydrogen with Benzylidenemethylamine in the Presence of 1 and Protic Acid. Complex 1 (0.010 g, 0.016 mmol) and triflic acid (1.5 μL, 0.016 mmol) were combined in 0.7 mL of CD_2Cl_2 in a NMR tube. $C_6H_5CH{=}NMe$ (2 μL, 0.016 mmol) was added, and the purple reaction mixture was sealed under 400 Torr of H_2 at −196 °C. The reaction mixture was warmed to ambient temperature and vigorously shaken. The ^1H NMR spectrum after 2.5 h showed resonances consistent with $[C_6H_5CH{=}NHMe]^+$ and starting materials. On the basis of integration of C_6H_5 resonances, after 5 days ~67% of $[C_6H_5CH{=}NHMe]^+$ had been converted to $[C_6H_5CH_2NH_2Me]^+$. The concentration of 1 was unchanged throughout the reaction.

Reaction of 1 with Acetonitrile and Protic Acid in the Presence of Hydrogen. Complex 1 (0.05 g, 0.081 mmol) and triflic acid (7 μL, 0.077 mmol) were dissolved in 10 mL of acetonitrile and sealed under 400 Torr of H_2 at −196 °C. The purple-red reaction mixture was stirred 6 days at ambient temperature and turned light green after 4 days. Solvent was removed at reduced pressure, giving a green solid. ^1H NMR spectra of the crude solid in CD_3CN showed resonances for $(CpMo(\mu\text{-}S))_2S_2CH_2$ and $[(CpMo)(S_2CH_2)(S_2\overline{CCH_3})MoCp]^+$ in a 1:7.7 ratio based upon integration of Cp resonances. The solid was extracted with H_2O, and the H_2O was removed at reduced pressure, giving 0.015 g of a yellow solid. ^1H NMR spectra of the solid in D_2O showed resonances for acetamide and $[CH_3CH_2NH_3]CF_3SO_3$ in a 1.7:1 ratio based upon integration of methyl resonances. Acetamide appears to result from treatment of acetonitrile with aqueous acid.[5]

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Preparation, Molecular Structure, and Solution Properties of 1-[1,1′-Bis(diphenylphosphino)ferrocene]palladatetraborane

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1-[1,1′-Bis(diphenylphosphino)ferrocene]palladatetraborane, 1-{(dppf)Pd}B_3H_7 (1), has been prepared by the reaction of (dppf)$PdCl_2$ with octahydrotriborate(1−). The molecular structure of 1 has been determined: triclinic, $P\bar{1}$ (No. 2), a = 9.557 (1), b = 9.632 (1), c = 18.547 (2) Å, α = 75.39 (1), β = 80.72 (1), γ = 73.41 (1)°, Z = 2, V = 1575.9 (5) Å^3, R_F = 0.025. The triborane ligand is symmetrically disposed (within esd's) with respect to the Pd atom; the central Pd–B distance is only slightly shorter (2.154 (3) Å) than the remaining two (2.190 (3) and 2.182 (3) Å). Borane hydrogen atoms have been located directly. Variable-temperature ^1H NMR spectroscopic studies indicate that two fluxional processes involving the {(dppf)Pd} fragment are operational; at $T \geq 203$ K, facile mutual twisting of the cyclopentadienyl rings occurs, while at $T \geq 293$ K, inversion at each phosphorus atom is accessed. The borane ligand itself appears to be static on the 400-MHz time scale, although inversion at the phosphorus atoms effectively renders equivalent the two distinct terminal hydrogen atoms on each terminal boron atom. Complex 1 shows an irreversible redox process, contrasting with reversible processes observed for dppf and (dppf)$PdCl_2$.

Recently we have been interested in a series of pseudo-square-planar complexes involving the coordination of palladium(II) to two phosphine donors and to a triborane(7) ligand.[1-4] The latter is formally $[B_3H_7]^{2-}$ and considered, in mononuclear complexes at least,[5] to be an analogue of a π-allyl moiety (viz, the borane is termed a π-borallyl ligand). Although a series of palladium(II) and platinum(II) π-borallyl complexes has been previously prepared and reported,[1,2] the structural characterization[2]

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