Electrophilic Substitution of Nitrogen Heterocycles by Molybdenum Sulfide Complexes

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The electrophilic tetranuclear complex $[(Cp'Mo(\mu\text{-}S))_2(S_2CH_2)]_2(BF_4)_2$ (**1**: $Cp' = C_5H_5$ (**1a**), C_5H_4Me (**1b**)), in which two dinuclear complexes are joined by a sulfur−sulfur bond, reacts with the electron-rich nitrogen heterocycles pyrroles and indoles at room temperature. The reactions involve heterolytic scission of the disulfide bond by the nucleophiles followed by proton transfer, and the products are $[(Cp'Mo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SH)]BF_4$ (**2**) and $[(Cp'MoS)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}S\text{-pyrrolyl})]BF_4$ (**3**−**6**). The reactions have been characterized for pyrrole, 1-methylpyrrole, 1,2,5-trimethylpyrrole, and 1-methylindole. The regiochemistry of the reactions depends on pyrrole substituents. Complex **1** also reacts readily with the coordinated pyrrolyl ligand in $(PMe_2Ph)_3Cl_2Re(NC_4H_4)$. The electrophilic substitution occurs on the 3-position of the heterocycle to form $[(Cp'Mo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SC_4H_3N)ReCl_2(PMe_2Ph)_3]BF_4$ (**7**). Complex **7** undergoes a further reaction with **1** to give the hydrogen abstraction product $[(Cp'Mo)_2(S_2CH_2)(\mu\text{-}S_2C_4H_2N)ReCl_2(PMe_2Ph)_3]BF_4$ (**8**). An X-ray diffraction study of **8b** confirms that the 3- and 4-carbons of the pyrrolyl ligand are coordinated to the μ-sulfido ligands of the molybdenum dimer. The new products suggest that there are a number of ways in which electron-rich heterocycles might interact with a sulfided molybdenum catalyst in the hydrodenitrogenation reactions. Reactions of **1** with other nucleophiles have also been surveyed.

Introduction

Five-membered nitrogen heterocycles, such as pyrrole and indole, are common impurities in petroleum feedstocks that are removed by the catalytic hydrodenitrogenation process.[1,2] The heterogeneous catalyst most commonly used for this process is sulfided molybdenum adsorbed on alumina or other supports. Nitrogen heterocycles are known to adsorb strongly on sulfided catalysts, but very little is known about the mode of their adsorption.[2] Because the mechanistic features of the HDN reactions are not well-defined on a molecular level, studies of discrete metal−heterocyclic complexes have been carried out in order to investigate fundamental questions on how the heterocycle might interact with and be activated by a catalyst surface. Although several aspects of the reactivity of coordinated pyrrole,[3−9] indole,[10−13] and indoline[14−18] ligands have been investigated, no model studies are available to show how these heterocycles might interact with a *sulfided* metal surface.

The reactivity of the five-membered nitrogen rings is dominated by the π-electron-rich character of the molecules, and electrophilic substitution and addition reactions are well-known for these systems. For this reason we have investigated the reactivity of pyrrole derivatives with electrophilic molybdenum sulfide complexes. The molecular metal sulfide compounds studied here may provide fundamental information about possible interaction modes of heterocycles with the heterogeneous catalysts. The latter are known to also contain electrophilic centers, particularly S−H sites that display Brønsted acidity.[19] During the course of chemical transformations on the surface, hydrogen atom transfer from S−H sites could also lead to electrophilic disulfide linkages on the catalyst.

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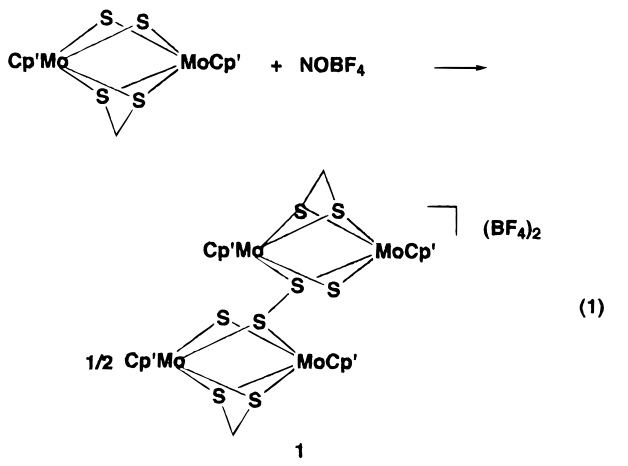
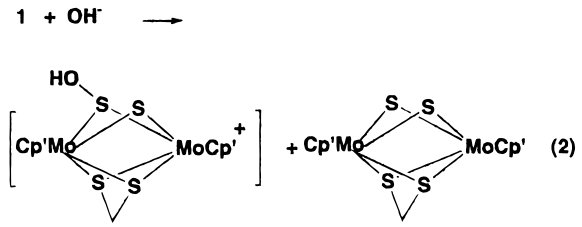
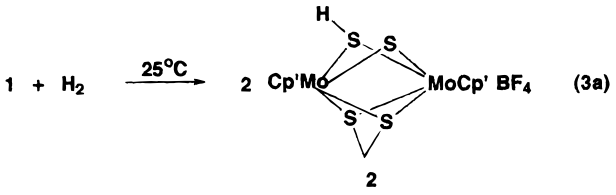
In previous work we have shown that the one-electron oxidation of $(Cp'MoS)_2S_2CH_2$ results in the formation of the diamagnetic tetranuclear dication **1**, which contains two dimers linked by a bond between bridging sulfido ligands (eq 1).[20] The sulfur−sulfur bond distance



in **1** is relatively long (2.14 Å), and this appears to be a reactive electrophilic site in the molecule. Complex **1** undergoes reactions similar to those of organic disulfides. For example, heterolytic scission of the S−S bond by nucleophiles has been observed for **1** (eq 2).[20]



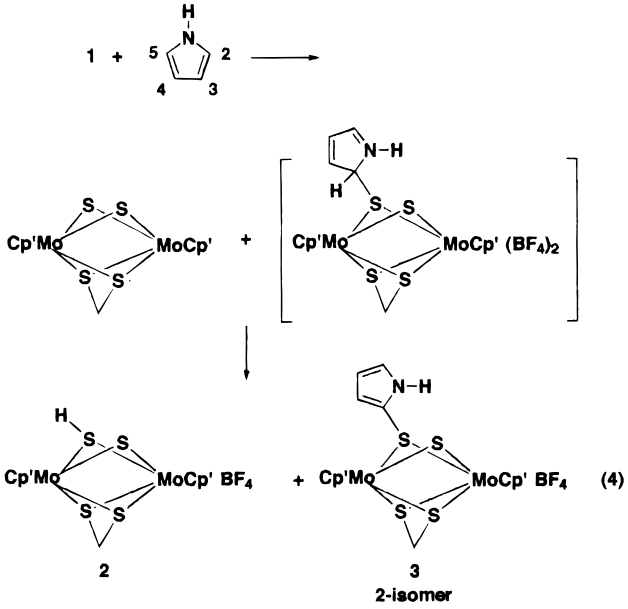
However, this metallo disulfide also undergoes reactions that are not characteristic of the organic analogues. For example, **1** reacts rapidly and quantitatively with molecular hydrogen at room temperature to form the cationic hydrosulfido complex **2** (eq 3a) and reacts with PhSH to abstract a hydrogen atom (eq 3b).[20]



The reactions of organic disulfides with the electron-rich nitrogen heterocycles appear to be quite limited, since other available reagents are more effective for the introduction of thiolate substituents on the rings.[21] Examples of nucleophilic attack of pyrrolyl and indolyl anions on disulfides have been reported,[22] and the reaction of methyl disulfide with indole in the presence of CuI was found to produce the 3-thiolate indole derivative.[23] In contrast, **1** reacts readily with neutral pyrrole derivatives, leading to electrophilic substitution of the nitrogen rings with the formation of new molybdenum-sulfido-substituted pyrrole complexes. The characterizations and reactivities of these products are reported here.

Results and Discussion

Reactions of 1 with Pyrroles. Compound **1** was found to react with several different pyrroles at room temperature over a period of 1−2 days to form new cationic products containing pyrrolyl thiolate ligands. Complex **2** or its conjugate base is also formed in this reaction, and isolated yields suggest that the products are formed in a 1:1 ratio. The reaction is illustrated in eq 4 using unsubstituted pyrrole as the reagent. The



net reaction involves the homolytic cleavage of a C−H bond of the pyrrole ring, but the reaction pathway is likely to proceed by heterolytic scission of the S−S bond by the nucleophilic ring, followed by loss of a proton from the heterocycle,[24] as shown in eq 4. The two molybdenum products can usually be separated by recrystallizations that take advantage of solubility differences. For example, **2** is readily deprotonated by undried solvents and the resulting neutral complex $(Cp'Mo(\mu\text{-}S))_2(S_2CH_2)$ can be extracted into nonpolar solvents. After recrystallization, the derivatives of the pyrrolyl thiolate cations have been characterized by spectroscopic techniques. Their formulation is confirmed by FAB mass

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Table 1. NMR Data for Pyrrolyl Thiolate Complexes of Molybdenum[a]

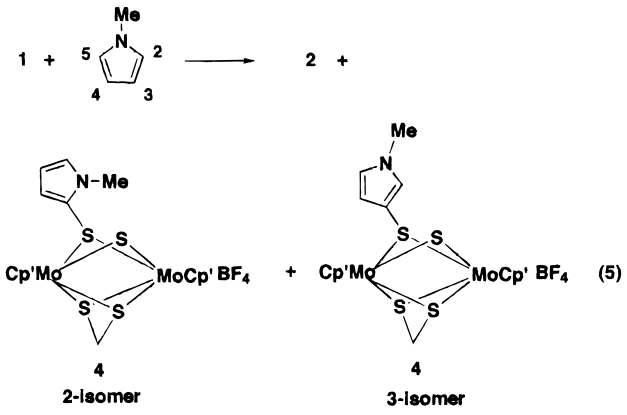
	pyrrole		other	
complex	^{1}H	^{13}C	^{1}H	^{13}C
3a, 2-isomer	5.70 (H3)[b]	118.47 (C3)[c]	7.04 (s, Cp)	105.23 (Cp)
	5.89 (H4)	109.84 (C4)	4.03 (s, S_2CH_2)	48.26 (S_2CH_2)
	6.65 (H5)	122.95 (C5)	9.0 (br s, NH)	
4a, 2-isomer	5.53 (H3), $J_{34} = 3.77$		7.03 (s, Cp)	
	5.83 (H4), $J_{45} = 2.78$		4.08 (s, S_2CH_2)	
	6.71 (H5), $J_{35} = 1.79$		3.50 (s, NMe)	
4a, 3-isomer	5.75 (H4), $J_{24} = 1.89$		7.00 (s, Cp)	
	6.25 (H2), $J_{25} = 2.08$		3.98 (s, S_2CH_2)	
	6.42 (H5), $J_{45} = 3.08$		3.49 (s, NMe)	
4b, 2-isomer	5.53 (H3), $J_{34} = 3.77$	119.23 (C3)	6.98, 6.92, 6.87 (3 m, Cp)	105.68, 105.45, 103.96, 103.69 (Cp)
	5.83 (H4), $J_{45} = 2.88$	108.72 (C4)	4.06 (s, S_2CH_2)	48.46 (S_2CH_2)
	6.72 (H5), $J_{35} = 1.79$	128.07 (C5)	3.50 (s, NMe)	35.00 (NMe)
			2.46 (s, CpMe)	16.88 (CpMe)
4b, 3-isomer	5.75 (H4), $J_{24} = 1.89$	114.25 (C4)	6.8−7.0 (3 m, Cp)	103.81, 103.91, 104.94, 105.05
	6.27 (H2), $J_{25} = 2.28$	127.19 (C2)	3.97 (s, S_2CH_2)	47.58 (S_2CH_2)
	6.43 (H5), $J_{45} = 2.68$	123.49 (C5)	3.48 (s, NMe)	36.58 (NMe)
			2.47 (s, CpMe)	16.88 (CpMe)
5a, 3-isomer	5.19 (H4)	111.95 (C4)	6.99 (s, Cp)	104.71 (Cp)
			4.01 (s, S_2CH_2)	48.65 (S_2CH_2)
			3.24 (s, NMe)	31.19 (NMe)
			2.03, 2.14 (2 s, Me)	11.83, 11.06 (Me)
5b, 3-isomer	5.10 (H4)		6.79 (m, Cp)	
			4.13 (s, S_2CH_2)	
			3.26 (s, NMe)	
			2.48 (s, CpMe)	
			2.14, 2.05 (2 s, Me)	
6b, 3-isomer	6.52 (s, H2)	134.31 (C2)	6.86, 6.93, 7.03 (3 m, Cp)	103.32, 103.57, 105.36, 105.09 (Cp)
			7.18 (t, H6)	121.55 (C6)
			7.25 (t, H5)	123.70 (C5)
			7.34 (d, H4)	111.47 (C4)
			7.57 (d, H7)	118.95 (C7)
			4.01 (s, S_2CH_2)	47.88 (S_2CH_2)
			3.71 (s, NMe)	33.53 (NMe)
			2.45 (s, CpMe)	16.87 (CpMe)

[a] Recorded in CD_3CN, chemical shifts reported in ppm, *J* values reported in Hz. [b] Multiplets not well resolved. [c] Resonances of quaternary carbons were not observed in these experiments.

spectra, which show the expected mass for the parent cations, and by elemental analyses.

In the ^{1}H NMR spectrum of the crystallized product **3a** (**a**, Cp′ = C_5H_5; **b,** Cp′ = MeC_5H_4) only one isomer was apparent. A broadened resonance for the NH proton of **3a** was observed at 9.0 ppm, and three multiplets were observed for the hydrogens of the pyrrole at 5.70, 5.89, and 6.65 ppm. In an HSQC experiment, these pyrrole hydrogen signals correlated with carbon resonances at 118.5, 109.8, and 122.9 ppm, respectively. The product is assigned as the 2-pyrrolyl thiolate derivative on the basis of comparisons with related, more fully characterized isomers discussed below. The most downfield proton and carbon resonances are assigned to the hydrogen and carbon atoms α to the nitrogen based on the relative shifts of α- and *β*-positions in the free pyrrole ring. ^{1}H NMR data for the new complexes are given in Table 1, and ^{13}C NMR data are presented for either the Cp or MeCp derivative of each product.

When the reaction of **1** was carried out with 1-methylpyrrole, two isomeric products of **4** were observed in the NMR spectrum. For example, in the reaction using the MeCp derivative, isomers usually occur in an approximate 2:1 ratio. Several thiolate-bridged cations of the type $[(Cp'Mo)_2(S_2CH_2)(\mu\text{-}SR)(\mu\text{-}S)]^+$ have been identified in previous work,[25] but in all previous studies of these cations, only one isomer has been observed, and this has been identified by X-ray studies as the derivative with an equatorial conformation of the thiolate substituent. Since there is no reason to expect both axial and equatorial isomers for this particular thiolate substituent, the isomers are attributed to different positions of attack by the sulfido electrophile, as shown in eq 5. Although electrophilic attack at the 2- (or α-)



position of pyrrole is usually favored, both steric and electronic effects can promote attack on the 3- (or *β*-) carbon in some cases.[26]

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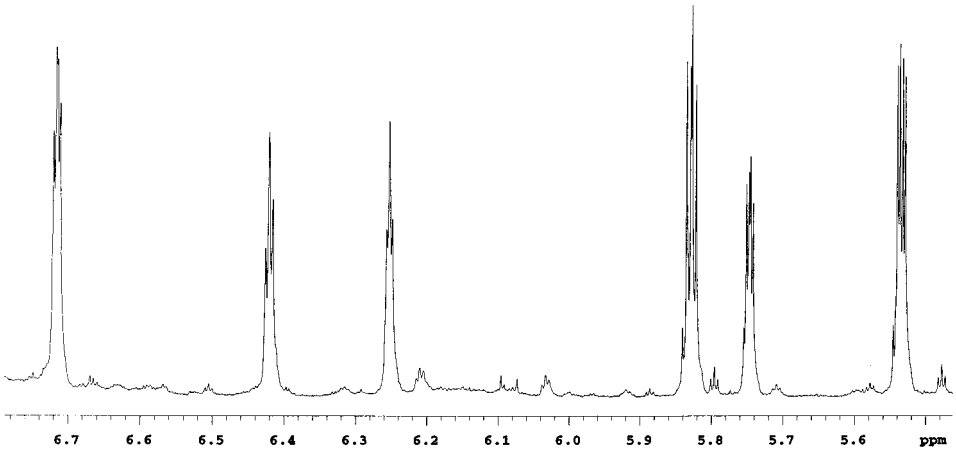
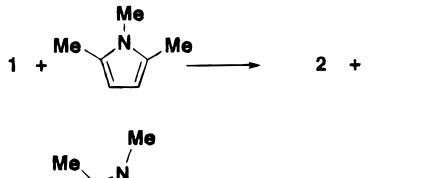


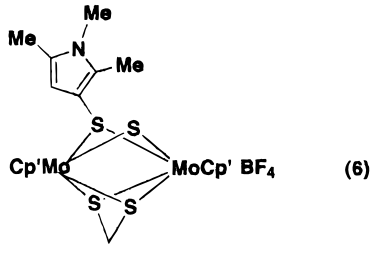
Figure 1. Resonances for pyrrole hydrogens in the 500 MHz ^{1}H NMR spectrum of two isomers of **4b**. The major product is assigned to the 2-isomer, and the minor product is the 3-isomer. See Table 1 for assignments and coupling constants.

In the ^{1}H NMR spectrum of **4b**, three well-resolved multiplets characteristic of an ABX spectrum are observed for the hydrogens of the pyrrole ring in each isomer (Figure 1). These have been analyzed to obtain coupling constants for the pyrrole hydrogens. The values for coupling constants in substituted pyrroles are well-established and are diagnostic of the position of substitution on the ring.[27] The *J* values obtained for the major isomer (see Table 1) are consistent with the assignment of a 2-substituted pyrrole ring, while the coupling constants for the minor isomer are indicative of a 3-substituted ring.

The ^{13}C NMR spectra for the isomers of **4b** are consistent with the above isomer assignments. In the HSQC spectrum of the 2-isomer, multiplets at 5.53 (H3), 5.83 (H4), and 6.71 (H5) ppm correlate with carbon resonances at 119.2 (C3), 108.7 (C4), and 128.1 (C5) ppm. For the isomer assigned to the 3-substituted pyrrole ligand, carbon resonances occur at 123.5 and 127.2 ppm for the α-carbons (C2 and C5) and at 114.2 ppm for the *β*-position (C4). No evidence for interconversion of the isomers in solution was observed over a period of several days.

Related derivatives have been synthesized using similar reaction conditions. In the reaction of **1** with 1,2,5-trimethylpyrrole only a single substitutional isomer is possible, and only one isomer of the thiolate cation **5** was observed (eq 6). The chemical shifts for the





(6)

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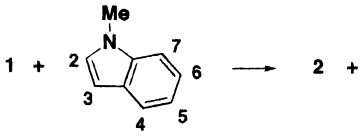
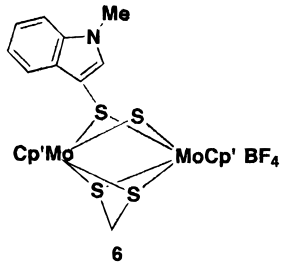
H4 and C4 resonances of the pyrrolyl thiolate ligand of **5a** were 5.19 and 111.9 ppm, respectively, similar to the values assigned above to the *β*-positions of the pyrrole rings in the isomers of **4**.

The reaction of **1b** with 1-methylindole also proceeded to form a single isomer (>96%) of the electrophilic substitution product **6b** (eq 7). Electrophiles generally





(7)

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react with indoles to give the 3-substituted derivatives,[28] and NMR data for **6b** suggest that the substitution of the molybdenum sulfide electrophile shows similar selectivity. In the ^{1}H NMR spectrum the multiplets of the six-membered carbocyclic ring show chemical shifts that are quite similar to those of free indole[29] (see Table 1). A singlet at 6.52 ppm was assigned to H2 of the indolyl ring. This signal correlates with a ^{13}C resonance at 134 ppm, which is consistent with the downfield chemical shifts observed for α-carbons in the other pyrrolyl thiolate derivatives.

The cyclic voltammetry of representative examples of the pyrrolyl thiolate derivatives was studied with a glassy-carbon electrode in acetonitrile. For example, for the mixture of isomers of the 1-methylpyrrole derivative **4b**, distinct waves for the two isomers were not resolved. Two quasi-reversible one-electron-reduction waves were observed at −0.71 and −1.63 V vs ferrocene. Two

(27) Jones, R. A.; Bean, G. P. *The Chemistry of Pyrroles*; Academic Press: New York, 1977; pp 472−476.
(28) Gilchrist, T. L. *Heterocyclic Chemistry*, 2nd ed.; Wiley: New York, 1992; Chapter 6.5.
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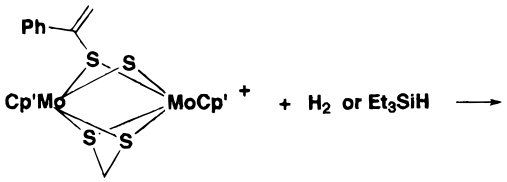
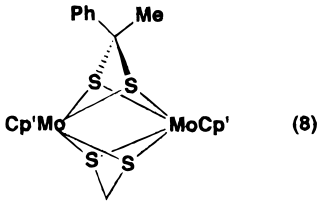
reduction waves at similar potentials have been observed for other thiolate cations of this type, and these reductions were found to be primarily metal-based.[26d] The cyclic voltammogram of **5a** showed only one reversible reduction at a potential of −0.73 V vs ferrocene.

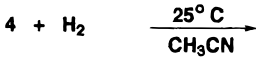
Reactions of Pyrrolyl Thiolate Complexes. In previous work cationic molydenum derivatives with unsaturated thiolate substituents were found to undergo reactions with hydrogen or other reducing agents to reduce the substituent on the sulfur ligand: e.g., eq 8.[26b]

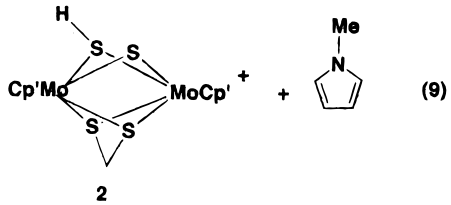




(8)

Similar conditions were examined for the pyrrolyl thiolate derivatives to determine whether an intramolecular S−H addition might be extended to an aromatic substituent under mild conditions. Complex **4a** was found to react with hydrogen at room temperature in acetonitrile solution. However, the reaction led to the formation of free methylpyrrole and **2a**,[30] and no reduced heterocyclic products were detected (eq 9).



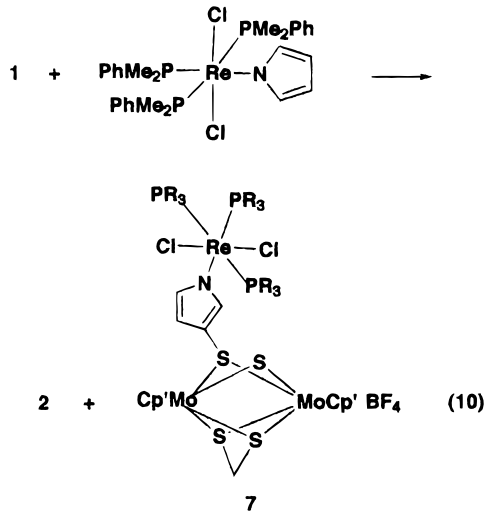


(9)

2

Similar results were observed when **4a** was reacted with the reducing agent Et_3SiH at room temperature. No evidence for reduction of a coordinated heterocycle was observed, and the only molybdenum product identified was $(Cp'Mo(\mu\text{-}S))_2S_2CH_2$.

Synthesis of Mixed-Metal Pyrrolyl Complexes. To obtain models for the study of how multiple metal coordination might activate the pyrrole ring, the reaction of an N-metalated pyrrole ligand with **1** has also been carried out. The addition of the *N*-pyrrolyl complex $(PMe_2Ph)_3Cl_2Re(NC_4H_4)$[9] to a dichloromethane solution of **1** at room temperature also resulted in electrophilic substitution of a sulfido ligand on the pyrrolyl ligand, similar to the substitutions described above for uncomplexed pyrroles. The product isolated from this reaction was formulated as $[(Cp'Mo)_2(S_2CH_2)(\mu\text{-}S)(\mu-SC_4H_3N)ReCl_2(PMe_2Ph)_3]BF_4$ (**7**), as shown in eq 10. In the elec-



(10)

7

trospray mass spectra for **7a** and **7b**, a parent ion for each cation was observed at *m*/*z* values of 1201 and 1229, respectively.

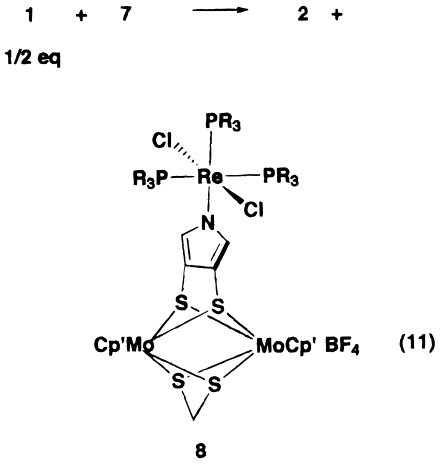
The ^1H NMR spectra of **7a** and **7b** are each consistent with the presence of a diamagnetic thiolate-bridged cation of molybdenum containing a paramagnetic rhenium pyrrolyl complex as the thiolate substituent. For example, for **7b** four Cp multiplets are observed in the region between 6.0 and 6.6 ppm, while singlets at 2.1 (6 H) and 4.6 ppm (2 H) are assigned to equivalent methyl groups of the Cp rings and the methanedithiolate protons, respectively. The resonances of the pyrrolyl ring show paramagnetic shifts because of coordination to the octahedral Re(III) ion. In previous studies of electrophilic substitution reactions on the pyrrole ring in $(PMe_2Ph)_3Cl_2Re(NC_4H_4)$, ^1H NMR spectroscopy was found to be a very useful technique for establishing the regiochemistry of the reactions because of the characteristic chemical shifts of the ring hydrogens.[9] The resonances of the α-hydrogens of the Re(III)-coordinated ring were found to occur upfield in the region of 0 to −3 ppm, while those of the β-hydrogens occurred downfield near +10 ppm. The ^1H spectrum of **7b** provides clear evidence for the electrophilic substitution of the sulfido ligand at a β- (or 3-) position of the pyrrolyl ligand. Two inequivalent resonances for α-hydrogens are observed in the spectrum at −0.96 and −2.77 ppm, while a single β-hydrogen singlet is observed at 10.46 ppm. Similar shifts are observed in the spectrum of **7a**. This selectivity for substitution at the β-position is probably due to the steric bulk of the pyrrole N substituent.

In the cyclic voltammogram of **7a** (obtained in acetonitrile at a glassy-carbon electrode), three reversible waves were observed: an oxidation at 0.167 V vs Fc and two reductions at −0.706 and −1.365 V. Comparison of the data to those of the mononuclear Re complex, which showed an oxidation at +0.016 V and a reduction at −1.42 V vs Fc,[9] suggests that the oxidation and more negative reduction of **7a** may be assigned to redox changes at the rhenium(III) center. The anodic shifts relative to those of the mononuclear complex reflect the electron-withdrawing character of the cationic substitu-

(30) Complex **2** was not isolated because it underwent further reaction under hydrogen in acetonitrile solution, as reported previously: Bernatis, P.; Laurie, J. C. V.; DuBois, M. R. *Organometallics* **1990**, *9*, 1607−1617.

ent on the pyrrolyl ligand in the complex. The reduction wave of **7a** at −0.706 V occurs at a potential very similar to those of the other molybdenum derivatives with pyrrolyl thiolate substitutents, and this wave is therefore assigned to a reduction of the molybdenum dimer in the heteronuclear complex.

We have begun to compare the reactivity of the pyrrolyl thiolate derivatives, e.g., **3**−**6**, with that of the heterotrinuclear complex **7.** For example, no further substitution reaction was observed on the pyrrolyl ring in **4** upon the addition of the electrophilic reagent **1**. However **7** does undergo a further reaction with **1** at room temperature to form a new product, **8**, resulting from hydrogen atom abstraction from the heterocycle. In the ^{1}H NMR spectrum of **8b**, for example, MeCp resonances were slightly broadened, suggesting a paramagnetic molybenum product, but the reasonably sharp resonances could still be readily assigned. In particular, the spectrum showed only a single resonance in the region of the pyrrole α-hydrogens at −1.27 ppm, while no downfield resonances assignable to pyrrole β-hydrogens were observed. The conversion of **7** to **8** is proposed to involve a second hydrogen atom abstraction to form a β,β-disubstituted pyrrolyl ligand as shown in eq 11.



Single crystals of **8b** were obtained by recrystallization from an acetonitrile/diethyl ether solution, and the proposed structure was confirmed by an X-ray diffraction study. A perspective drawing of the cation is shown in Figure 2, and selected bond distances and angles are given in Table 2. The structure confirms that each of the β-carbons of the pyrrolyl ring are coordinated to a bridging sulfide ligand of the molybdenum dimer. The bond distances and angles within the Mo_2S_4 core are close to those reported previously for other 1,2-alkenedithiolate derivatives of the dimers,[31] and bond distances and angles within the rhenium coordination sphere are very similar to those observed for the mononuclear pyrrolyl rhenium complex.[9] Similarly, the bond distances within the pyrrolyl ligand are similar to those found in the starting rhenium pyrrolyl complex,[9] and these data suggest that the aromatic character of the nitrogen heterocycle in **8b** remains intact. Further studies of **8** are planned in order to determine whether

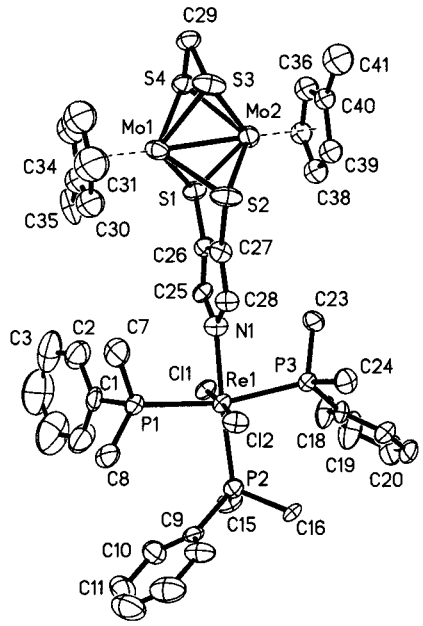


Figure 2. ORTEP diagram and numbering scheme for the cation of $[(MeCpMo)_2(S_2CH_2)(\mu\text{-}S_2C_4H_2N)Re(PMe_2Ph)_3Cl_2]BF_4 \cdot CH_3CN$ (**8b**).

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $[(MeCpMo)_2(S_2CH_2)(S\text{-}3c,S\text{-}4c\text{-}C_4H_2N)ReCl_2(PMe_2Ph)_3]BF_4$ (8b)

Bond Lengths			
Re(1)−N(1)	2.161(8)	Re(1)−Cl(1)	2.341(3)
Re(1)−Cl(2)	2.334(3)	Re(1)−P(2)	2.434(3)
Re(1)−P(1)	2.457(3)	Re(1)−P(3)	2.474(3)
N(1)−C(25)	1.375(13)	N(1)−C(28)	1.384(13)
C(25)−C(26)	1.386(15)	C(26)−C(27)	1.387(15)
C(27)−C(28)	1.371(156)	S(1)−C(26)	1.745(11)
S(2)−C(27)	1.762(11)	Mo(1)−S(1)	2.449(3)
Mo(1)−S(2)	2.445(4)	Mo(2)−S(1)	2.455(3)
Mo(2)−S(2)	2.433(3)	Mo−Mo	2.5815(15)
Bond Angles			
N(1)−Re(1)−Cl(1)	90.4(2)	N(1)−Re(1)−Cl(2)	92.1(2)
Cl(2)−Re(1)−Cl(1)	176.31(10)	P(2)−Re(1)−N(1)	176.3(2)
P(1)−Re(1)−P(3)	165.81(10)	N(1)−Re(1)−P(3)	82.1(3)
N(1)−Re(1)−P(1)	84.2(3)	Mo(1)−S(1)−Mo(2)	63.52(8)
Mo(1)−S(2)−Mo(2)	63.89(8)	S(1)−C(26)−C(27)	120.2(9)
S(2)−C(27)−C(26)	118.6(8)		

such multiple complexation to the heterocycle activates it to further reactions.

The results of this work suggest that there are several ways in which a reactive metal sulfide surface may interact with the electron-rich nitrogen heterocycles. In addition to the possibilities of η^5-coordination of the heterocycles to the metal site and η^1(N)-coordination of anionic pyrrolyl and indolyl ligands to the metal, it is also possible that these rings could interact with reactive sulfur sites on the catalyst surface, in either η^1- or η^2-bonding modes.

Reactions of 1 with Other Nucleophiles. The electrophilic substitution reactivity of **1** was found to be kinetically controlled and was limited to the most electron-rich heterocycles, pyrroles and indoles. No reaction was observed when **1b** was stirred with excess thiophene or 2,5-dimethylthiophene at room temperature, even though the C−H bond strengths in pyrrole and thiophene are estimated to be very similar (e.g., approximately 113 kcal/mol for the β-hydrogens).[32] Similarly at room temperature, no significant reaction

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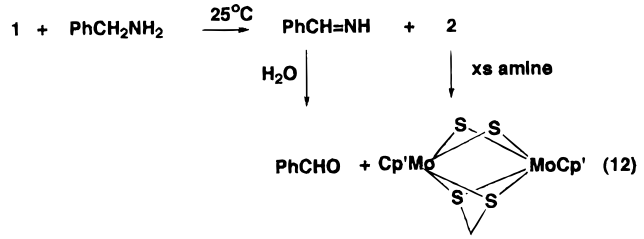
was observed between **1b** and dihydroanthracene with a C−H bond dissociation energy of 78 kcal/mol.[33]

In preliminary studies of the interactions of **1** with other potential nucleophiles, oxidation reactions have been identified. For example, the reaction of **1b** with a slight excess of benzylamine in acetonitrile under nitrogen was followed by ^{1}H NMR spectroscopy. An instantaneous color change was observed, and the formation of $(MeCpMo(\mu\text{-}S))_2S_2CH_2$ was observed in the spectrum along with new resonances which were tentatively assigned to PhCH=NH (see Experimental Section). Addition of 1 equiv of water to this solution caused the disappearance of these resonances and the formation of benzaldehyde (eq 12). A similar reaction of **1b**



(12)

(13)

with benzyl alcohol under nitrogen also resulted in the formation of benzaldehyde (eq 13), but this oxidation was much slower than that of the amine. In the unstirred reaction carried out in an NMR tube, the product appeared in low yield (ca. 40%) over a period of several days. Heating the solution to about 40 °C resulted in a higher yield of benzaldehyde, but significant decomposition of **1b** was also observed under these conditions. The oxidation of alcohols by metal−oxo complexes has been studied,[34−37] but to our knowledge, alcohol oxidations by metal−sulfido derivatives have not been reported previously. Further work is in progress to learn more about the scope and mechanisms of these oxidation reactions.

Experimental Section

General Procedures and Materials. Reactions were carried out under nitrogen using Schlenk-line and vacuum-line techniques, but products were isolated in air unless otherwise specified. Dichloromethane and acetonitrile were distilled from CaH_2 prior to use. Tetrahydrofuran, toluene, and diethyl ether were distilled from sodium/benzophenone. ^{1}H NMR spectra were recorded at 300 and 500 MHz on Varian VXR-300 and Varian Inova 500 MHz instruments, respectively. All chemical shifts are reported in ppm relative to tetramethylsilane. HSQC data were obtained on the Varian Inova 500 MHz spectrometer. Spectra for the pyrrole hydrogens in isomers of **4b** were simulated using the program gNMR, version 3.6. Mass spectra were obtained on a HB5989A mass spectrometer with ES ionization, on a VG Analytical 7070 EQ-HF mass spectrometer, or on a Finnigan MATR LCQ ion trap mass spectrometer. Cyclic voltammetry experiments were carried out under nitrogen on acetonitrile solutions containing 0.1−0.3 M Bu_4NBF_4 with a Cypress Systems electrolysis system. Ferrocene was used as an internal standard, and all potentials are referenced to the ferrocene/ferrocenium couple. Elemental analyses were performed by Desert Analytical Laboratory, Tucson, AZ. Pyrroles and indoles were purchased from Aldrich and used without purification. **[**$(Cp'Mo(\mu\text{-}S))_2S_2CH_2]_2(BF_4)_2$[20] (**1**), and *mer*-$(PMe_2Ph)_3Cl_2Re(NC_4H_4)$[9] were prepared as previously reported.

Synthesis of $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SC_4H_3NH)]BF_4$ (3a). $[(CpMo(\mu\text{-}S))_2(S_2CH_2)]_2(BF_4)_2$ (**1a**; 0.10 g, 0.091 mmol) was dissolved in a mixture of 10 mL of dichloromethane and 10 mL of acetonitrile, and pyrrole (43 μL, 0.62 mmol) was added via syringe. The solution was stirred for 2 days at room temperature, and then the solvent was reduced in vacuo to a volume of 2−3 mL. The solution was filtered to remove a blue or black precipitate. In many cases this was identified by NMR spectroscopy as $(CpMo(\mu\text{-}S))_2S_2CH_2$. Yield: 50−60% based on **1**. About 5 mL of Et_2O was added to the red filtrate, and this solution was cooled to 0 °C. The resulting red-brown precipitate was filtered and dried. Yield: 0.045 g, 82% based on moles of **1**. See Table 1 for ^{1}H and ^{13}C NMR data. MALDI MS: *m*/*z* 530 (P for cation). Anal. Calcd for $C_{15}H_{16}NMo_2S_4BF_4 + {}^1/_2CH_3CN$: C, 30.12; H, 2.77; N, 3.29. Found: C, 30.30; H, 3.09; N, 3.16.

Synthesis of $[(Cp'Mo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SC_4H_3NMe)]BF_4$ (4). Cp′ = MeCp (4b). $[(MeCpMo(\mu\text{-}S))_2(S_2CH_2)]_2(BF_4)_2$ (**1b**; 0.224 g, 0.194 mmol) and 1-methylpyrrole (0.120 mL, 1.35 mmol) were reacted according to the procedure described above. The product was recrystallized from CH_3CN/Et_2O. Yield: approximately 80%. See Table 1 for ^{1}H and ^{13}C NMR data. MS (FAB$^+$): *m*/*z* 572 (M^+); 493 ($M - C_4H_3NMe$)); 460 ($M^+ - SC_4H_3NMe$); 446 $(MeCpMo)_2S_3$). CV in CH_3CN/0.1 M Bu_4NBF_4 (V vs Fc): $E_{1/2} = -0.71$ V; $\Delta E = 138$ mV in cell where $\Delta E_{Fc} = 74$ mV; second $E_{1/2} = -1.63$ V, $\Delta E = 137$ mV. Anal. Calcd for $C_{18}H_{22}BF_4Mo_2NS_4$: C, 32.74; H, 3.51; N, 2.12. Found: C, 32.63; H, 3.41; N, 1.97.

Cp′ = C_5H_5 (4a). A similar procedure was followed using $[(CpMo(\mu\text{-}S))_2S_2CH_2)]_2(BF_4)_2$ and 1-methylpyrrole. Yield: 53%. See Table 1 for ^{1}H NMR data.

Synthesis of $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SC_4H(Me)_2NMe)]BF_4$ (5). Compound 5a. Complex **1a** (0.10 g, 0.093 mmol) and 1,2,5-trimethylpyrrole (0.088 mL, 0.65 mmol) were reacted in a procedure similar to that described above. The purple-black product was recrystallized from $CHCl_3$/ether. Yield: 50−60%. See Table 1 for ^{1}H and ^{13}C NMR data. MALDI MS: *m*/*z* 572 (P of cation). CV in CH_3CN/0.3 M Bu_4NBF_4 (V vs Fc): $E_{1/2} = -0.73$ V, $\Delta E = 66$ mV; two irreversible oxidations were also observed with $E_{p,a} = 0.41$ and 0.66 V. Anal. Calcd for $C_{18}H_{22}NS_4Mo_2BF_4$: C, 32.79; H, 3.36; N, 2.12. Found: C, 32.51; H, 3.42; N, 2.38.

Compound 5b. A similar procedure was followed using $[(MeCpMo(\mu\text{-}S))_2S_2CH_2)]_2(BF_4)_2$ and 1,2,5-trimethylpyrrole. See Table 1 for ^{1}H NMR data.

Synthesis of $[(MeCpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SC_8H_5NMe)]BF_4$ (6b). Complex **1b** (0.070 g, 0.060 mmol) and *N*-methylindole (54 μL, 0.42 mmol) were reacted in a similar procedure. The purple-black product was recrystallized from $CHCl_3$/ether. Yield: 94%. See Table 1 for ^{1}H and ^{13}C NMR data. FAB MS: *m*/*z* 622 (P of cation). Anal. Calcd for $C_{22}H_{22}NMo_2S_4BF_4$: C, 37.35; H, 3.13; N, 1.98. Found: C, 37.07; H, 3.30; N, 1.75.

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(37) Shapley, P. A.; Zhang, N.; Allen, J. L.; Pool, D. H.; Liang, H. C. *J. Am. Chem. Soc.* **2000**, *122*, 1079−1091.

Reaction of 4a with Hydrogen. $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SC_4H_3NMe)]BF_4$ (**4a**; 0.030 g, 0.040 mmol) was dissolved in $CDCl_3$ (0.8 mL) and CD_3CN (0.4 mL) in a flask with a Teflon stopcock. The solution was freeze−pump−thaw degassed twice, and 60 mm of H_2 was added at −196 °C. The flask was sealed and the solution was warmed to room temperature and stirred for about 36 h. The solution was transferred to an NMR tube under nitrogen. The spectrum showed the presence of 50% $(CpMo(\mu\text{-}S))_2S_2CH_2$ and 50% $[(CpMo)_2(S_2CH_2)(S_2CCD_3)]BF_4$. The latter resulted from the reaction of **2a** with CD_3CN.[29] *N*-methylpyrrole was also identified in the spectrum. NMR: δ 5.90, 6.43 (2 m); 3.49 (s, NMe).

Reaction of $[CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SC_4H_3NMe)]OTf$ with Et_3SiH. The triflate salt of **4a** (prepared in a similar procedure starting with the triflate salt of **1a**) (0.040 g, 0.058 mmol) was dissolved in CH_3CN, and Et_3SiH (0.116 mmol, 36 μL) was added. The solution was stirred at room temperature for 4 days. The color of the solution changed from red to green-black. The solvent was removed in vacuo, and the remaining solid was washed with 1−2 mL of CH_3CN and filtered under nitrogen. The filtered solid was identified by NMR spectroscopy as $(CpMo(\mu\text{-}S))_2S_2CH_2$. The filtrate was evaporated, and the NMR spectrum showed primarily the same Mo complex and unidentified Et_3Si derivatives.

Synthesis of $[(Cp'Mo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SC_4H_3N)Re(PMe_2Ph)_3Cl_2]BF_4$ (7). Compound 7a. $[(CpMo(\mu\text{-}S))_2S_2CH_2]_2(BF_4)_2$ (**1a**; 0.088 g, 0.080 mmol) and $(PMe_2Ph)_3Cl_2Re(NC_4H_4)$ (0.11 g, 0.15 mmol) were dissolved in a mixture of 10 mL of CH_2Cl_2 and 10 mL of CH_3CN under a nitrogen atmosphere, and the solution was stirred at room temperature for about 24 h. The resulting brown-black solution was evaporated to dryness, and the solid was extracted with CH_3CN and filtered. The precipitate in the extraction was identified as $(CpMo(\mu\text{-}S))_2S_2CH_2$. Yield: 54%. The orange-brown acetonitrile filtrate was evaporated, and the solid was further purified by chromatography on an alumina column. The column was first eluted with CH_2Cl_2 to removed a rhenium impurity and then with CH_3CN to give an orange-brown band of the desired product. Yield: 0.032 g, 31%. (Another 20−30% could be isolated by further elution from the column, but this product still contained an unknown Re complex as an impurity.) ^{1}H NMR ($CDCl_3$): δ −3.18, 0.67, 0.82 (3 s, 6 H each, PMe); −2.81, −0.54 (2 s, 1 H each, α-H, pyrrole); 5.07 (s, 2 H, S_2CH_2); 6.48 (s, 10 H, Cp); 8.20 (t, 2 H, Ph); 8.77 (t, 4 H, Ph); 10.04 (t, 2 H, Ph); 10.37 (m, 3 H, Ph); 10.62 (s, 1 H, β-H, pyrrole); 13.18 (d, 4 H, Ph). MALDI MS: *m*/*z* 1201 (P of cation); 1064 (P − PMe_2Ph). CV in CH_3CN/0.3 M Bu_4NBF_4 (V vs Fc): $E_{1/2} = -0.17$ V, $\Delta E_p = 59$ mV; second $E_{1/2} = -0.71$ V, $\Delta E_p = 72$ mV; third $E_{1/2} = -1.36$ V, $\Delta E_p = 69$ mV. Anal. Calcd for $C_{39}H_{48}NCl_2S_4P_3Mo_2ReBF_4 + CH_3CN$: C, 37.06; H, 3.87; N, 2.11. Found: C, 36.78; H, 3.81; N, 1.68.

Compound 7b. The MeCp analogue was prepared by a similar procedure. ^{1}H NMR (CD_3CN): δ −3.20, 0.85, 0.97 (3 s, 6 H each, PMe); −2.77, −0.96 (s, 1H each, α-H, pyrrolyl); 2.07 (s, 6 H, MeCp); 4.63 (s, 2H, S_2CH_2); 6.12, 6.22, 6.34, 6.57 (m, 2H each, Cp); 8.36 (t, 2H, Ph); 8.88 (t, 4H, Ph); 9.81 (t, 2H, Ph); 10.34 (t, 1 H, Ph); 10.46 (s, 1 H, β-H, pyrrolyl); 10.94 (d, 2 H, Ph); 13.88 (d, 4 H, Ph). Electrospray MS: *m*/*z* 1230 (*P* of cation).

Synthesis of $[(CpMo)_2(S_2CH_2)(\mu\text{-}S_2C_4H_2N)Re(PMe_2Ph)_3Cl_2]BF_4$ (8). Compound 8a. Complex **7a** (0.025 g, 0.019 mmol) and **1a** (0.011 g, 0.0095 mmol) were dissolved in 1 mL of CD_3CN, and the solution was stirred at room temperature for 2 days. The NMR spectrum of the solution confirmed that the reaction was complete to form **8a** and $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SH)]BF_4$ (**2a**). ^{1}H NMR (CD_3CN): δ −2.73 (s, 6H, PMe); −1.45 (s, 2H, α-H, pyrrole); 0.50 (s, 12 H, PMe); 3.88 (s, 2H, S_2CH_2); 6.11 (br s, 10 H, Cp) 8.44 (t, 2H, Ph); 8.85 (t, 4 H, Ph); 9.89 (t, 2H, Ph); 10.50 (t, 1 H, Ph); 11.28 (d, 2 H, Ph); 13.48 (d, 4 H, Ph). Elemental analyses were not obtained for **8a** or **8b** because of repeated difficulties in removing a small amount of **1** from the product.

Table 3. Crystal Data for $[(MeCpMo)_2(S_2CH_2)(S\text{-}3c,S\text{-}4c\text{-}C_4H_2N)ReCl_2(PMe_2Ph)_3]BF_4$ (8b)

formula	$C_{43}H_{55}BCl_2F_4Mo_2N_2P_3ReS_4$
fw	1356.83
cryst syst	monoclinic
unit cell dimens	
a (Å)	14.184(43)
b (Å)	11.211(2)
c (Å)	31.450(6)
α (deg)	90
β (deg)	93.466(11)
γ (deg)	90
vol, Å^3	4991.9(19)
space group	$P2_1/c$
Z	4
calcd density (Mg/m^{-3})	1.805
λ(Mo Kα) (Å)	0.710 73
temp (K)	177(2)
scan type	ω scans
θ range (deg)	$1.88 < \theta < 26.00$
no. of indep rflns	9826 (R(int) = 0.0628)
no. of rflns obsd	7526
abs coeff (mm^{-1})	3.333
R^a	0.0754
$R_w{}^b$	0.1421
GOF^c	1.236
largest, smallest peaks in final diff map (e/Å^3)	2.029, −1.869

^{a} R = R1 = $\sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$. ^{c} GOF = $S = [\sum[w(F_o^2 - F_c^2)^2]/(M - N)]^{1/2}$, where M is the number of reflections and N is the number of parameters refined.

Compound 8b. The MeCp analogue was prepared on a larger scale and isolated after chromatography on an alumina column. The product was eluted with CH_3CN as an orange-brown band. Yield: 19%. ^{1}H NMR (CD_3CN): δ −2.87 (s 6H, PMe); −1.27 (s, 2H, α-H, pyrrole); 0.59 (s, 12 H, PMe); 1.88 (s, 6 H, MeCp); 3.88 (s, 2H, S_2CH_2); 5.88, 5.90, 6.20, 6.32 (br s, 2 H each, Cp) 8.56 (t, 2H, Ph); 8.84 (t, 4 H, Ph); 9.81 (t, 2H, Ph); 10.42 (t, 1 H, Ph); 11.42 (d, 2 H, Ph); 13.84 (d, 4 H, Ph). ^{1}H NMR ($CDCl_3$): δ −3.99 (s 6H, PMe); −3.22 (s, 2H, α-H, pyrrole); 1.30 (s, 12 H, PMe); 3.98 (s, 6H, MeCp); 6.64 (s, 2H, S_2CH_2); 7.23, 7.61 (2m, 4H each, Cp); 8.02 (t, 2H, Ph); 8.90 (t, 4 H, Ph); 9.55 (d, 2H, Ph); 9.84 (m, 3H, Ph); 13.69 (d, 4 H, Ph).

X-ray Diffraction Study of $[(MeCpMo)_2(S_2CH_2)(S\text{-}3C,S\text{-}4C\text{-pyrrolyl})ReCl_2(PMe_2Ph)_3]BF_4$ (8b). Single crystals were grown by slow diffusion of diethyl ether into an acetonitrile solution. The sample was examined under a light hydrocarbon oil. The specimen crystal was mounted on a thin glass fiber atop a tapered copper mounting pin with a small amount of silicone grease. This assembly was then transferred to the goniometer of a Siemens SMART CCD diffractometer equipped with a Siemens LT-2A low-temperature apparatus operating at 177 K. After optical centering, cell parameters were determined using three sets of 20 0.3° ω scans. Each scan was exposed for 10 s using two correlated 5 s scans. Data collection covered a bit more than an arbitrary hemisphere of space to 0.68 Å, again using 0.3 ω scans, exposed here for 30 s each. All data were corrected for Lorentzian and polarization effects. An absorption correction was applied on the basis of intensities of redundant reflections. Final cell parameters were refined from 8049 reflections with $I > 3\sigma(I)$ harvested from the full data set.

Structure solution via direct methods in centrosymmetric space group $P2_1/c$ revealed much of the non-hydrogen structure. Additional atoms were located during subsequent cycles of least-squares refinement followed by difference Fourier map calculation. Hydrogens were placed at calculated positions and allowed to ride on the geometries, as well as the equivalent isotropic thermal parameters of the parent atoms. In addition to the cation/anion pair, a molecule of acetonitrile is present. One CH_3 group of a methylcyclopentadienyl ligand is disor-

dered, likely across three sites, though only two were modeled. Site occupancies for these methyl carbons, C(41) and C(41a), were set to 0.60 and 0.40. No hydrogens were modeled on these carbons. Except for these two sites, all non-hydrogen atoms were modeled with anisotropic parameters for thermal motion. Some large, ca. 2 e/Å^3, residual peaks remained near the heavy atoms; otherwise, the final difference map was essentially flat. Details for the data collection and solution are given in Table 3 and in the Supporting Information.

Reactions of 1b with Benzylamine and Benzyl Alcohol. In a glovebox **1b** (0.015 g, 0.013 mmol) was dissolved in CD_3CN in an NMR tube, and excess $PhCH_2NH_2$ (ca. 2 μL, 0.020 mmol) was added. The color immediately changed from red to blue-black. The NMR spectrum showed that **1b** had been quantitatively converted to $(MeCpMo(\mu\text{-}S))_2S_2CH_2$ and additional resonances at 4.76 (br s), 6.33, 7.34, 7.75 (m), and 8.46 (s) were tentatively assigned to PhCH═NH. Upon addition of H_2O (1 μL) to the tube, the above resonances disappeared and new resonances were observed; these were assigned to benzaldehyde by comparison to a standard spectrum. The reaction of **1b** with benzyl alcohol under nitrogen was monitored in a similar way. Resonances for benzaldehyde were observed to grow in over a period of several days at room temperature. Yield: 40% based on initial moles of **1**.

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Supporting Information Available: Tables giving crystal data, positional and thermal parameters, bond distances, and bond angles for **8b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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