J. Am. Chem. Soc. **1981**, *103*, 3429-3436 3429

and Schuell, type BA-85). The filters were then washed with 4 mL of 0.3 M NaCl and 0.03 M sodium citrate and dried, and the radioactivity was determined by liquid scintillation counting. The average number of DNA strand breaks was calculated by assuming a Poisson distribution of target sites.[16]

Acknowledgments are made to Dow Chemical USA and the National Science Foundation for partial support of this research.

Supplementary Material Available: Tables of coordinates and anisotropic thermal parameters for complex **15** and a listing of observed and calculated structure factors for complex **15** (11 pages). Ordering information is given on any current masthead page.

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Kinetic Studies and a Molecular Orbital Interpretation of Reactions at Bridging Sulfur Ligands in Dimeric Molybdenum Complexes

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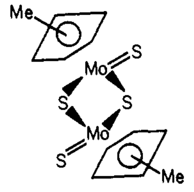
Abstract: Kinetic studies of previously reported exchange reactions at the bridging sulfur atoms in cyclopentadienylmolybdenum dimers have been carried out. The kinetics of the reaction of $[CH_3C_5H_4Mo^{IV}(S)SH]_2$ (I) with benzyl isocyanide which results in the formation of H_2 and $[CH_3C_5H_4MoS_2CNCH_2C_6H_5]_2$ (II) have been studied by the method of initial rates. The reaction shows a first-order dependence on the molybdenum dimer I and a first-order dependence on isocyanide with $k = (7.8 \pm 1.0) \times 10^{-4}$ L mol^{-1} s^{-1} at 31.5 °C. Activation parameters have been derived from rate studies of the reaction over a temperature range of 0–55 °C. The $\Delta H^{\ddagger}$ for the reaction is 7.9 kcal/mol and $\Delta S^{\ddagger} = -38$ cal K^{-1} mol^{-1}. The reaction of $[CH_3C_5H_4Mo^{III}SC_2H_4S]_2$ (III) with benzyl isocyanide results in the formation of the same dithiocarbonimidate complex, II, and ethylene. Studies of the initial rates of the latter reaction reveal a first-order dependence on the molybdenum complex III, but a zero-order dependence on isocyanide with $k = (1.0 \pm 0.1) \times 10^{-4}$ s^{-1} at 31.5 °C. Studies over the temperature range 20–55 °C established the following activation parameters: $\Delta H^{\ddagger} = 24.3$ kcal/mol and $\Delta S^{\ddagger} = 11$ cal K^{-1} mol^{-1}. The work suggests that the Mo(IV) dimer reacts by an associative mechanism, while the reaction of the Mo(III) derivative proceeds by a dissociative pathway. Extended Hückel calculations for a series of molybdenum dimers with bridging sulfur ligands have been completed. The different mechanisms of reaction for the Mo(IV) and -(III) dimers are discussed in terms of the molecular orbitals involved. An analogy is made between the molecular orbitals of the sulfur ligands in these dimers and those of 16- and 18-electron metal centers in organometallic complexes. The observed structure of the Mo_2S_4 core changes as the metal oxidation state varies from V to IV or III, and this structural difference is interpreted in terms of the relative energies of the frontier molecular orbitals.

The presence of sulfur ligands coordinated to molybdenum in enzyme systems[1-4] and in heterogeneous desulfurization catalysts[5,6] has led to the investigation of a large range of molybdenum sulfur complexes.[7-9] Of particular interest to us are the dimeric complexes of the general formula $[Me_nCpMoS_2R_i]_2$, where R is a hydrogen atom or alkyl or aryl group and i = 0, 1, and 2, n = 0, 1, and 5. Many of these complexes have interesting structural and reactivity patterns. The structures of complexes **1**–**5**[10-13] and a related π-toluyl derivative, **6**,[14] have been determined by X-ray diffraction techniques. It is interesting that **1** assumes the structure with two bridging and two terminal sulfur atoms while **2**–**6** all



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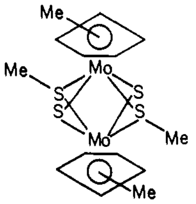

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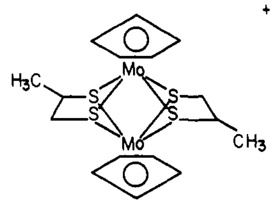

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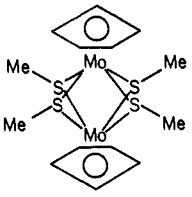

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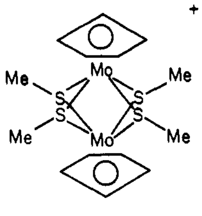

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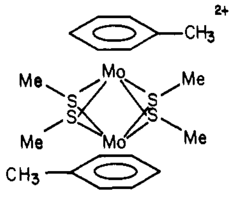

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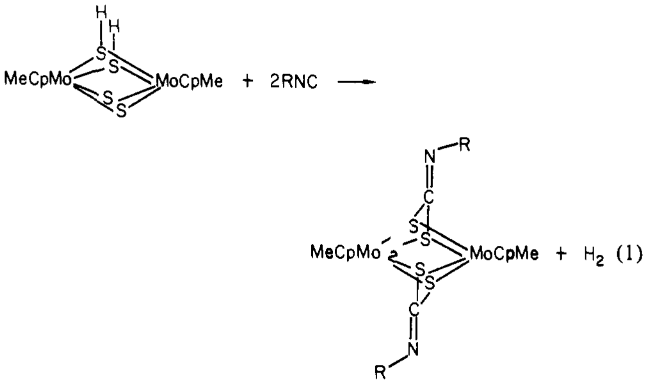
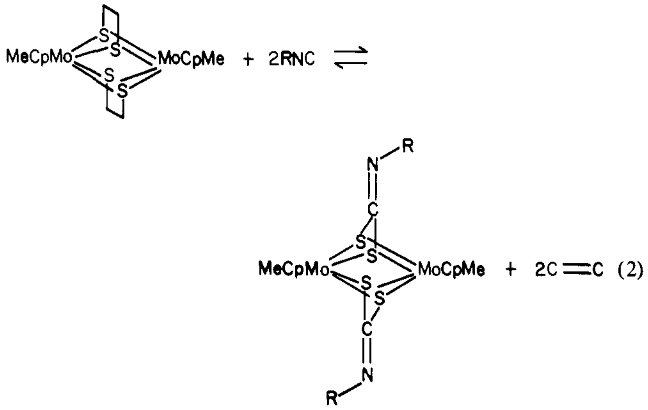
have quadruply bridged structures. A molecular orbital rationale for this structural difference will be presented in the second part of this paper.

The complex $[MeCpMo(S)SH]_2$, which is structurally analogous to **2**, reacts with various unsaturated molecules (e.g., ethylene, acetylene, isocyanides) to yield dimers with bridging dithiolate or dithiocarbonimidate ligands, e.g., reaction 1.[11] These reactions



are similar to the exchange reactions which occur at the sulfur ligands in $[Me_nCpMoSC_2H_4S]_2$ e.g., reaction 2.[15] The facile



cleavage of S–H and S–C bonds results in the elimination of H_2 and ethylene, respectively. These reactions bear similarities to ligand substitutions commonly observed for metal hydride and metal–olefin complexes.[16,17] In order to obtain some mechanistic information on the reactions of these sulfur-bridged dimers, we have studied the initial rates of reactions 1 and 2 with R = benzyl. The results of these studies are reported below. In the second part of this paper these kinetic results are interpreted in terms of the frontier molecular orbitals participating in the reactions.

Results and Discussion

Kinetic Studies of the Reaction of $[MeCpMo(S)SH]_2$ with Benzyl Isocyanide. Reaction 1 proceeds quantitatively and can be conveniently followed by proton NMR. The kinetic studies were normally carried out under pseudo-first-order conditions (excess benzyl isocyanide). Under these conditions removal of the sample from the NMR probe during a given run was not required. Figure 1 shows the plot of ln $[[MeCpMo(S)SH]_2]/[[MeCpMo(S)SH]_2]_i$ vs. time for various ligand and dimer concentrations in $CDCl_3$. The reaction is first order in dimer for initial dimer concentrations ranging from 5.50×10^{-3} to 3.20×10^{-2} M. The linear dependence of k_{obsd} on the concentration of benzyl isocyanide, which ranged from 1.23×10^{-1} to 1.85 M, indicates a first-order dependence of the reaction rate on the concentration of benzyl isocyanide as well. From this data the second-order rate constant of $(7.8 \pm 1.0) \times 10^{-4}$ L mol^{-1} s^{-1} was obtained at 31.5 °C. These results suggest an associative mechanism with the rate-limiting step being the coordination of benzyl isocyanide by $[MeCpMo(S)SH]_2$. Variable-temperature studies have established the activation parameters for this reaction listed in Table I. We have reported previously that the reaction of $[MeCpMo(S)SH]_2$ with a mixture of H_2 and D_2 results in the formation of HD.[11] This result is also consistent with the SH complex reacting by an associative mechanism.

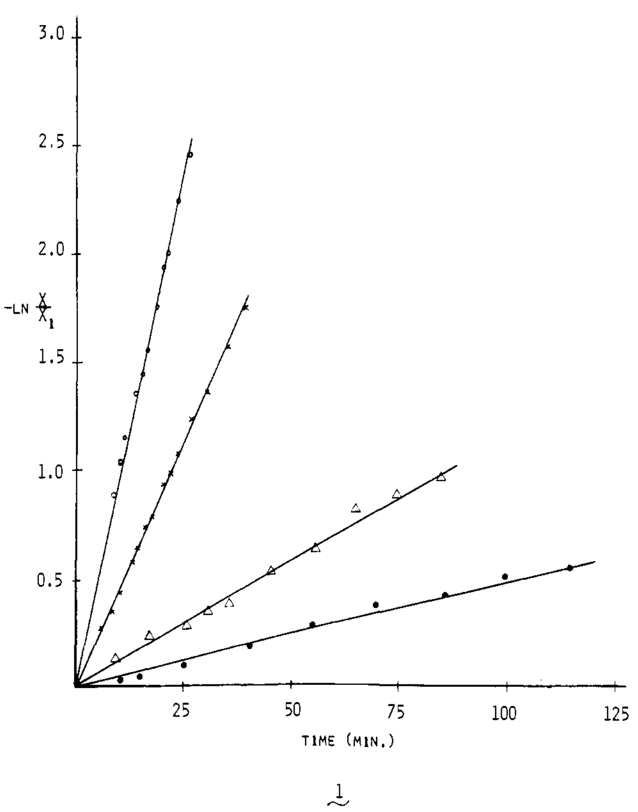


Figure 1. First-order plots of $-\ln [[MeCpMo(S)SH]_2]_t/[[MeCpMo(S)SH]_2]_i$ at various dimer and benzyl isocyanide concentrations in chloroform solution at 31.5 °C: ○, $[dimer]_i = 0.0143$ M, [RNC] = 1.85 M; ×, $[dimer]_i = 0.0143$ M, [RNC] = 0.925 M; △, $[dimer]_i = 0.0055$ M, [RNC] = 0.247 M; ●, $[dimer]_i = 0.0088$ M, [RNC] = 0.123 M.

Because the Mo(III) complexes $[CpMo(SMe)_2]_2$ and $[CpMoSCH_2CH_2S]_2$ are isolable, it might be anticipated that the intermediate of reaction 1, $(MeCp)_2Mo_2(SH)_2(S_2CNR)$, might also be stable and observable by NMR during the course of the reaction. However, the elimination of hydrogen from such an intermediate is apparently rapid. The only two species observed in the NMR spectra were the starting SH complex and the final product.

There are at least two isomers of $[MeCpMo(S)SH]_2$ as evidenced by two SH resonances at 1.53 and 1.60 ppm upfield from Me_4Si (relative intensity 2:3 in $CDCl_3$).[11] The two isomer resonances maintain the same relative intensities throughout the course of reaction 1. No evidence for exchange of these ligands has been observed in variable-temperature NMR studies up to 110 °C. Two explanations for the observed behavior with isocyanide are that (1) both isomers react at the same rate or (2) a preequilibrium exists between the two isomers that is slow on the NMR time scale but fast relative to the reaction rate. We note that the structurally analogous complex $[CpMo(S)SCH_3]_2$[11] can be separated into two distinct isomers by chromatography[18] and no evidence for isomer interconversion is observed for this complex.

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Table I. Rate Constants as a Function of Temperature and Activation Parameters for Reactions of Molybdenum Dimers with Benzyl Isocyanide

complex	temp, °C	k, L mol^{-1} s^{-1}	$H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal K^{-1} mol^{-1}
$[MeCpMo(S)SH]_2$	0.5	2.6×10^{-4}	7.9	−38
	7.0	4.0×10^{-4}		
	21.5	5.4×10^{-4}		
	39.5	1.1×10^{-3}		
	50.0	3.8×10^{-3}		
		k, s^{-1}		
$[MeCpMoSC_2H_4S]_2$	20.5	2.2×10^{-5}	24.3	+11
	32.0	1.1×10^{-4}		
	34.5	1.5×10^{-4}		
	47.0	6.8×10^{-4}		
	50.0	1.2×10^{-3}		
	52.5	1.4×10^{-3}		

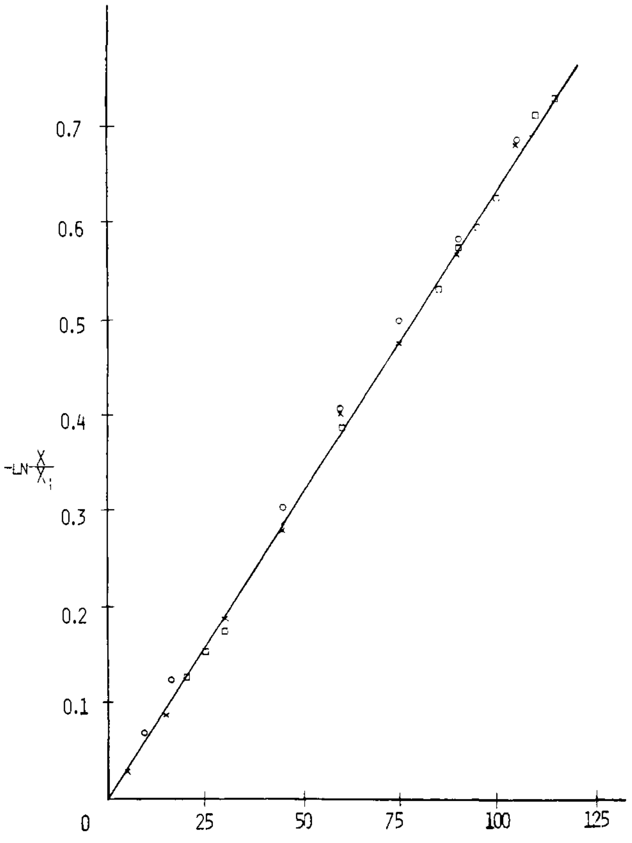
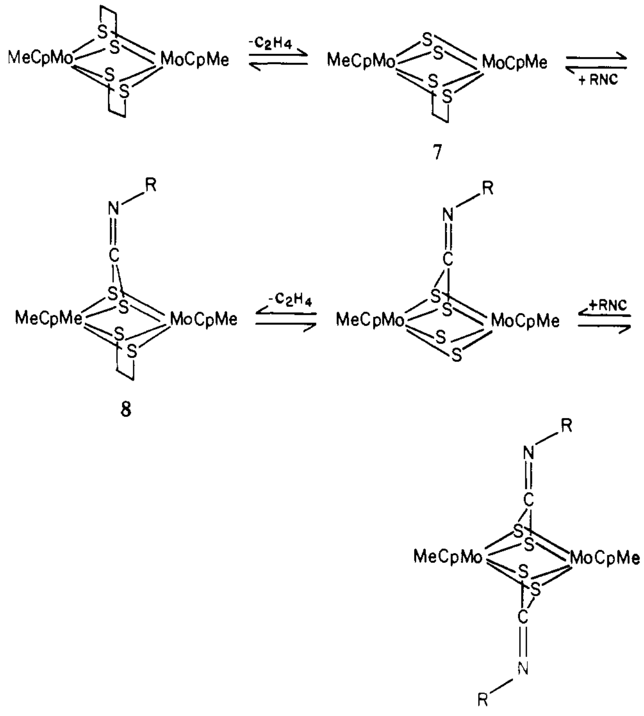


Figure 2. First-order plots of $-\ln$ $[[MeCpMoSC_2H_4S]_2]_t/[[MeCpMoSC_2H_4S]_2]_i$ in the reaction with benzyl isocyanide in chloroform solution at 31.5 °C: o, $[dimer]_i = 0.0405$ M, [RNC] = 1.73 M; ×, $[dimer]_i = 0.0142$ M, [RNC] = 0.247 M; □, $[dimer]_i = 0.0250$ M, [RNC] = 4.11 M.

Kinetic Studies of the Reaction of $[MeCpMoSC_2H_4S]_2$ with Benzyl Isocyanide and of $[CpMoSCH_2CH(CH_3)S]_2$ with Ethylene. The reaction of $[MeCpMoSCH_2CH_2S]_2$ with benzyl isocyanide in $CDCl_3$ (reaction 2) was carried out under pseudo-first-order reaction conditions similar to those described for reaction 1 and followed by proton NMR spectroscopy. The concentrations of $[MeCpMo(SCH_2CH_2S)]_2$ ranged from 2.80×10^{-3} M to 4.70×10^{-2} M and of benzyl isocyanide from 0.247 to 4.11 M with the ratio of benzyl isocyanide to $[MeCpMoSCH_2CH_2S]_2$ ranging from 17.4 to 164. Figure 2 shows typical plots of ln $[[MeCpMoSCH_2CH_2S]_2]/[[MeCpMoSCH_2CH_2S]_2]_i$ vs. time for various ligand and dimer concentrations. It can be seen from the linearity of the plots that the reaction is first order in molybdenum complex and that the observed rate constant of $(1.0 \pm 0.1) \times 10^{-4}$ s^{-1} shows no dependence on the concentration of benzyl isocyanide.

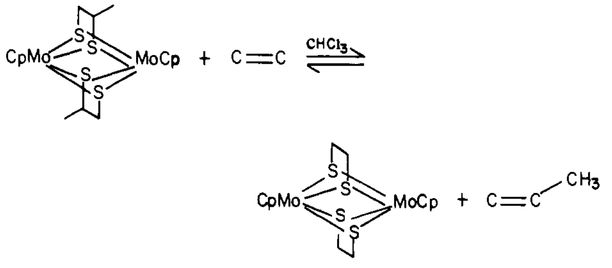
Scheme I



No inhibition of the rate was observed when the reaction was carried out in the presence of the radical inhibitor hydroquinone. Neither did a change of solvent from deuteriochloroform to carbon disulfide significantly affect the observed rate. The results are consistent with a dissociative mechanism with the rate-determining step being the loss of ethylene from the dithiolate bridge as shown in Scheme I. The activation parameters for this reaction (Table I) are significantly more positive than those derived for the reaction of $[MeCpMo(S)SH]_2$ with benzyl isocyanide, and this is also consistent with the proposed dissociative pathway.

In contrast to the reaction of $[MeCpMo(S)SH]_2$ with benzyl isocyanide where no intermediates were detected, the mixed-bridge dimer **8** in Scheme I is observed readily by NMR. We have not been able, however, to observe or isolate an intermediate such as **7**. Variable-temperature NMR studies of $[MeCpMoSC_2H_4S]_2$ up to 110 °C in the absence of any reactant showed a slight reversible broadening of resonances, but no new signals were observed.

We have also studied the reaction of $[CpMoSCH_2CH(CH_3)S]_2$ with ethylene (reaction 3).[12] The initial rates of this reaction were followed by monitoring by gas chromatography the production of propylene under pseudo-first-order concentrations of ethylene. The rate of this reaction is first order in $[CpMo(SCH_2CH(CH_3)S)]_2$ and shows no dependence on the pressure of ethylene at high ethylene/dimer ratios. The rate constant at 38 °C is $(1.0 \pm 0.2) \times 10^{-4}$ s^{-1}, comparable to that for reaction 2.



(3)

In summary, these kinetic studies indicate that the reactions of unsaturated molecules with the bridging sulfur ligands in molybdenum dimers may proceed by two different mechanisms. If two of the four bridging sulfur atoms are substituted, the reaction proceeds by an associative mechanism. In this case a vacant coordination site is present on the sulfur atoms; i.e., the

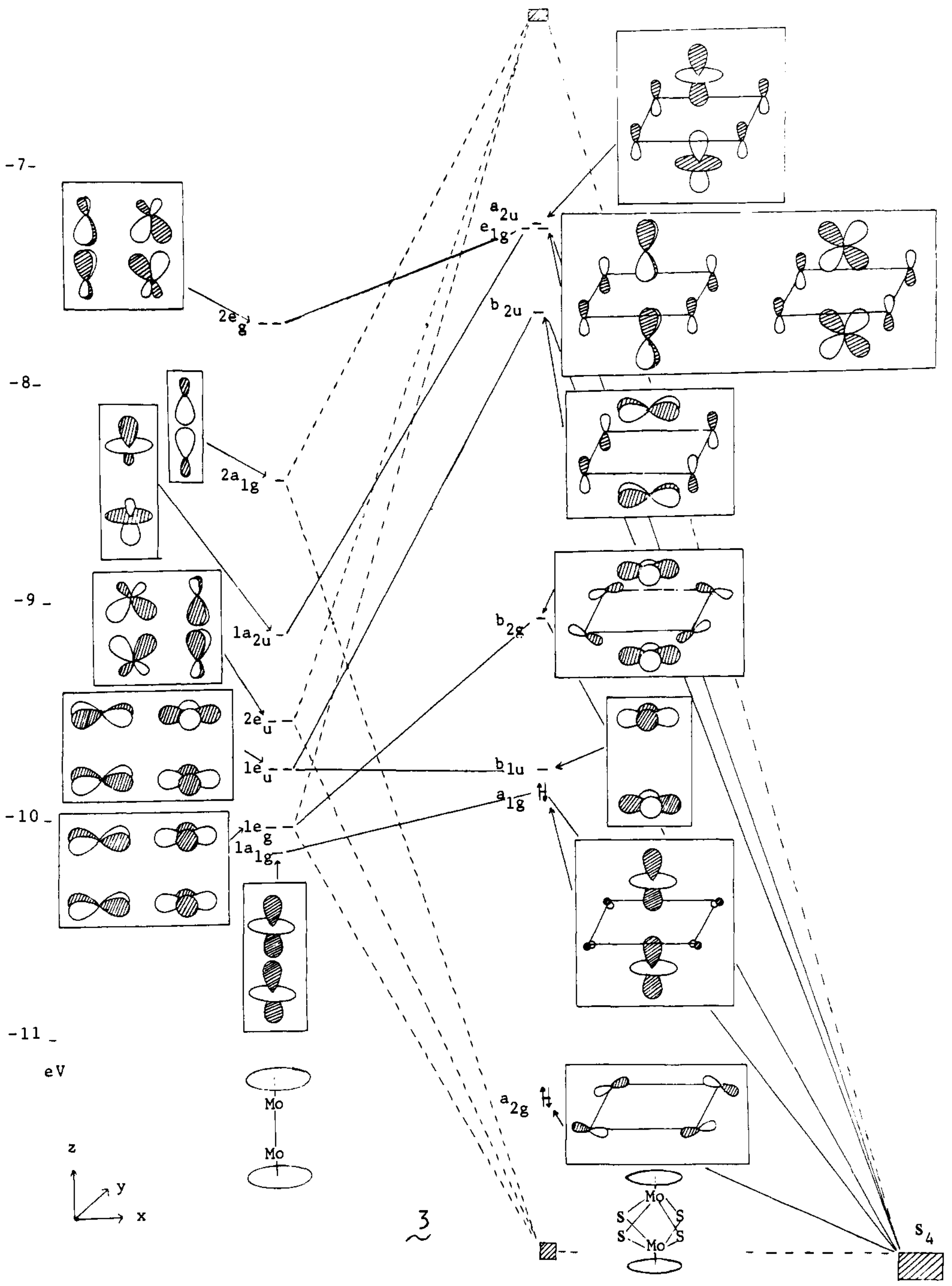


Figure 3. The frontier orbitals of the nonbridged dimer are shown on the left-hand side of the molecular orbital diagram, those for the quadruply bridged dimer are shown in the center, and the sulfur orbitals are represented on the right as a low-lying block of orbitals. Contributions from the Cp rings are not shown. Orbital occupancy is that of the hypothetical neutral quadruply bridged dimer.

dimer is coordinatively unsaturated. In contrast, if all four sulfur atoms are substituted, the dimer appears to be coordinatively saturated with respect to the sulfur ligands and the exchange reaction occurs by a dissociative mechanism. It is of interest to examine the structural and electronic features of $[MeCpMoSC_2H_4S]_2$ and $[MeCpMo(S)SH]_2$ which are important in determining their reaction pathways. In the second part of this paper we present the results of extended Hückel calculations on the molybdenum complexes. The studies will be used to provide a rationale for the different reaction mechanisms characterized here as well as for the different structural features observed for the Mo_2S_4 cores of known dimers.

Results of Extended Hückel Calculations. Our molecular orbital analysis will proceed along the series of complexes shown in Scheme II. The origin of the molecular orbitals of **9** from two metal–cyclopentadienyl fragments will be reviewed.[19] The interaction of four bridging sulfur atoms to produce the hypothetical dimer **10** forms the basis for understanding the structure and reactivity of the quadruply bridged complexes. The effect of the sequential addition of two pairs of hydrogen atoms to **10** to form **11** and **12** produces relatively minor perturbations of the frontier orbitals of **10**. However, the addition to the molecular orbital scheme of the pair of electrons associated with each pair of hydrogen atoms results in major changes in structure and reactivity.

The molecular orbitals of dimer **9** are shown on the left-hand side of Figure 3. These orbitals are simply the bonding and antibonding combinations of two CpM fragments. There is a set of $\pi(2e_u)$ and $\pi^*(2e_g)$ orbitals from the interaction of the fragment

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[19] Lauher, J. W.; Elian, M.; Summerville, R. H.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 3219. Elian, M.; Chen, M. M. L.; Mingos, D. M. P.; Hoffmann, R. *Inorg. Chem.* **1976**, *15*, 1148.

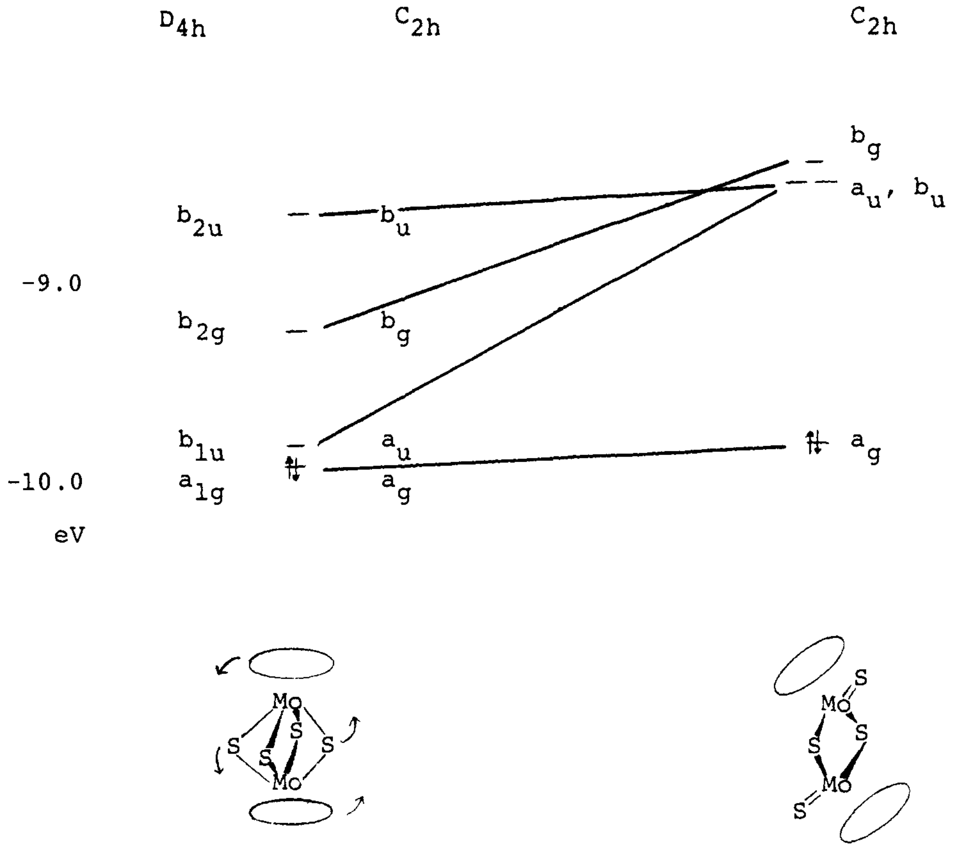

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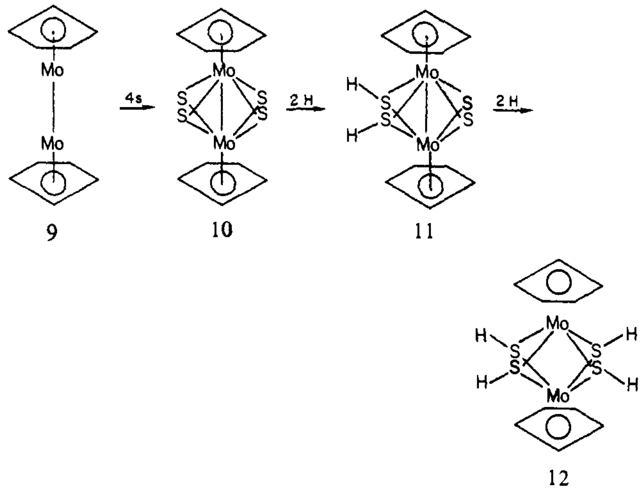
Figure 4. Correlation diagram for the opening of the quadruply bridged dimer to the doubly bridged dimer. See text for discussion.

Scheme II



xz and *yz* orbitals, a set of $\delta(1e_g)$ and $\delta^*(1e_u)$ orbitals which are bonding and antibonding combinations of the fragment *xy* and $x^2 - y^2$ orbitals, and a set of three σ orbitals ($1a_{1g}$, $1a_{2u}$, $2a_{1g}$) formed from the z^2 and sp-hybrid fragment orbitals. These three orbitals are the bonding and antibonding combinations of the z^2 orbitals and the bonding combination of the sp hybrid.

Adding four bridging sulfur atoms to **9** produces the interactions of **10** which are also shown in Figure 3. The major effect of the bridging sulfur atoms is to reduce the number and degeneracy of the frontier orbitals compared to the nonbridged dimer **9**. The $2a_{1g}$, both $2e_u$, and one of the $1e_g$ orbitals are removed from the set of frontier orbitals by strong interactions with the bridging sulfur ligands. (These interactions are shown as dotted lines in Figure 3.)

The symmetry of the orbitals is dominated by the local fourfold symmetry of the bridging sulfur atoms and the orbitals have been labeled (Figure 3) as if the molecule possessed D_{4h} symmetry. The $2e_g$ orbitals of the CpMoMoCp dimer are destabilized slightly by an antibonding interaction with the p_z orbitals of the four bridging sulfur atoms. The $1a_2$ orbital is significantly destabilized by the antibonding interaction of the torus of the z^2 atomic orbitals with the p_z orbitals of the four bridging ligands. In a similar manner the b_{2u} orbital arises from the antibonding combination of the *xy* orbital of the $1e_u$ set with p_z orbitals of the bridging ligands. The $x^2 - y^2$ orbital of the $1e_u$ set is not of proper symmetry to interact with any ligand orbitals, and therefore its energy is unperturbed by the sulfur atoms. It forms the b_{1u} orbital of the sulfur-bridged dimer. In contrast, the $x^2 - y^2$ orbital of the $1e_g$ set mixes in an antibonding fashion with the p_x and p_y orbitals of the sulfur atoms to form the destabilized b_{2g} orbital. This results in an interesting situation in which the b_{2g} orbital, a δ orbital, is higher in energy than the b_{1u} orbital, a δ^* orbital. We will return to examine the b_{2g} orbital as it is the site of interesting chemical activity. The σ set of frontier orbitals is complete with the a_{1g} orbital which is formed by a slightly destabilizing interaction of the z^2-bonding combination of the CpMMCp dimer with sulfur p_x and p_y orbitals. There is one other orbital of interest to us, and this is the a_{2g} orbital. This orbital is localized completely on the sulfur ligands and is sulfur–sulfur antibonding. This completes the analysis of the molecular orbitals for the hypothetical dimer **10**. We now turn to the question of why the "open" doubly bridged structure **1** seems to be preferred to the "closed" quadruply bridged structure for the Mo(V) dimer $[CpMoS_2]_2$.

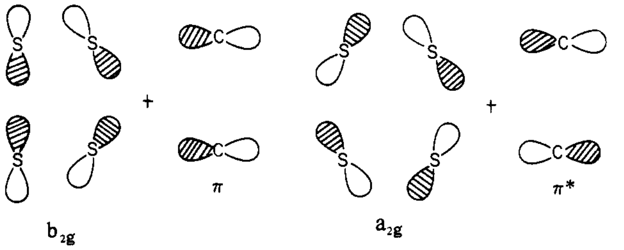
The molecular orbitals shown in Figure 3 are occupied through the a_{1g} orbital for a neutral Mo(V) dimer. The highest occupied

a_{1g} and the lowest unoccupied b_{1u} orbitals are nearly degenerate. The energy gap is only 0.1 eV (2.3 kcal) by our calculations. This near degeneracy can be removed by the symmetry-allowed process of the quadruply bridged dimer opening up.[20] A correlation diagram for this opening process is shown in Figure 4 with the frontier orbitals for the open doubly bridged dimer on the right. A 1.3-eV energy gap is calculated between the highest occupied and lowest unoccupied orbitals for the neutral open dimer.[21]

The effect of sequentially adding two pairs of substituents to the sulfur atoms of $[CpMoS_2]_2$ is now considered. In our calculations we have let the substituents be hydrogen atoms. The predominant effect is simply to add two electrons to the molecular orbital scheme for each pair of hydrogen atoms. It can be seen from Figure 4 that the addition of two electrons to the molecular orbital diagram favors a closed structure, and compounds of the type $CpMoS_4R_nMoCp$, where $n = 2$ and 4, are expected to have quadruple bridges. This is consistent with the X-ray diffraction studies of the Mo(IV) and Mo(III) dimers **2**, **3**, and **4**.

Reaction Mechanisms. The interactions of alkenes, alkynes, carbon monoxide, and isocyanides with transition-metal orbitals are well understood on the basis of the Dewar–Chatt bonding model.[22a] In this model a coordinatively unsaturated metal provides a vacant acceptor orbital of proper symmetry to interact with a σ-donor orbital of the ligand. In addition the metal also provides a filled donor of proper symmetry to interact with a vacant π^* orbital of the ligand. This model has helped a great deal in our understanding of the reactions of organometallic compounds and has contributed to the formulation of the 16–18-electron rule.[22b]

In contrast to our relatively good understanding of the bonding involved in the reactions between a transition-metal center and a ligand with σ-donor and π-acceptor orbitals, it is not obvious how these types of ligands interact with the bridging sulfur atoms of the dimers in reactions 1 and 2. If we examine the lowest unoccupied molecular orbital of $[CpMo(S)SH]_2$, we see that it has the correct symmetry to serve as an acceptor orbital for the σ orbital of an isocyanide or a π orbital of an alkene or alkyne.



In addition there is a reasonably high lying donor orbital (the a_{2g} orbital) of appropriate symmetry to interact with the π^* orbitals of isocyanides, olefins, and alkynes. Considering the good acceptor and donor properties of these orbitals, it is not surprising that the complex $[CpMo(S)SH]_2$ undergoes bimolecular substitution reactions. The dimers of the general formula $CpMoS_4R_2MoCp$ are thus analogous in bonding capabilities to a 16-electron metal center in an organometallic complex.

For the hypothetical complex $[CpMo(SH)_2]_2$ the b_{2g} orbital (Figure 5) is filled, and the interaction with the donor orbital of an incoming ligand is repulsive. This is the sulfur-bridged dimer analogue of the 18-electron metal center, and consequently the complex cannot react associatively. In addition, examination of the HOMO of $[CpMo(SH)_2]_2$ reveals that there is a positive overlap between cis-oriented hydrogen atoms. The energy of this orbital drops as the hydrogen atoms approach one another, and this also favors a dissociative elimination reaction. Such an orbital interaction offers an explanation of why Mo(III) dimers with cis SH ligands such as $[MeCpMo^{III}(SH)_2]_2$ and the intermediate of reaction 1, $(MeCp)_2Mo_2{}^{III}(SH)_2(S_2CNR)$, have not been detected spectrally or isolated. Similar positive overlap of the carbon p (π) orbitals in the ethanedithiolate-bridged ligands in $[CpMoSC_2H_4S]_2$ should promote the elimination of ethylene. The results of our kinetic studies of the reactions of $[MeCpMo^{III}SC_2H_4S]_2$ and $[MeCpMo^{III}SCH_2CH(CH_3)S]_2$ with isocyanide and ethylene, respectively, are consistent with the molecular orbital description presented here.

In summary, we propose that the four bridging sulfur atoms have acceptor and donor properties that are similar to those associated with a transition metal. In addition, the sulfur ligands of these Mo(IV) and Mo(III) dimers undergo addition and elimination reactions, respectively, which are analogous to those of 16- and 18-electron metal centers, respectively, in organometallic complexes. The catalytic applications of this sulfur ligand reactivity are being investigated.

Experimental Section

Materials. All molybdenum complexes were prepared as described previously. For these studies $[MeCpMoSC_2H_4S]_2$[12] was recrystallized from THF, and $[MeCpMo(S)SH]_2$[11] and $[CpMoSCH_2CHCH_3S]_2$[12] were recrystallized from $CHCl_3$. Benzyl isocyanide was purchased from Aldrich and used as obtained. Chloroform and deuteriochloroform used in kinetic experiments was passed through activated alumina prior to use. Carbon disulfide was distilled from P_2O_5. *p*-Phenylanisole was purchased from Eastman Organic Chemicals and recrystallized from chloroform/pentane. Ethylene was used as obtained from Matheson.

Spectra. NMR spectra were recorded on a Varian EM 390 spectrometer. The probe temperature was measured with MeOH or ethylene glycol standards before and after each kinetic run. The rate of disappearance of $[MeCpMo(S)SH]_2$ in reaction 1 was determined by measuring the methyl resonance at 2.31 ppm relative to the intensity of the methoxy resonance of the internal standard *p*-phenylanisole at 3.84 ppm. In a similar manner the rate of disappearance of $[MeCpMoSC_2H_4S]_2$ in reaction 2 was monitored by measuring the intensity of the Cp resonance at 4.98 ppm relative to the intensity of the methoxy resonance of the standard.

Gas Chromatographic Measurements. Chromatographs were recorded by using a Varian 920 gas chromatograph equipped with a thermal conductivity detector. Hydrocarbons were separated at room temperature by using a Parapak N column purchased from Varian. The rate of reaction 3 was monitored by measuring the area of the propene peak as a function of time relative to the area of an ethane peak included in the reaction flask at a known pressure as an internal standard. The relationship between pressures of ethane and propene and their respective GC peak areas was established by using known samples.

Kinetic Studies of Reactions with Benyl Isocyanide. A typical procedure for a single kinetics run is as follows. A 1.97 M solution (0.45 mL) of benzyl isocyanide in $CDCl_3$ was added to an NMR tube. The temperature of the probe was determined with the appropriate standard. Then 0.45 mL of a $CDCl_3$ solution of the appropriate molybdenum complex (0.026 M) and *p*-phenylanisole (0.051 M) was added to the NMR tube. The tube was shaken vigorously to mix reactants and inserted immediately into the probe. Spectra were recorded approximately every 10 min throughout the first half-life of the reaction. For the reaction with $[MeCpMoSC_2H_4S]_2$ at 31.5 °C the first-order rate constant was calculated from linear least-squares regression analysis of plots of the type shown in Figure 2. The average correlation coefficient was 0.99. The constant is the average of six runs and is reported $\pm 2\sigma$. For the reaction with $[MeCpMo(S)SH]_2$ at 31.5 °C the pseudo-first-order rate constant, k_{obsd}, was calculated from linear least-squares regression analysis of plots of the type shown in Figure 1, which had an average correlation coefficient of 0.99. The calculated second-order rate constant is the average of six runs and is reported $\pm 2\sigma$. To determine activation parameters for reactions 1 and 2, rates were measured by similar procedures at ~10 °C intervals over a temperature range 0–50 °C and 20–55 °C, respectively.

To determine whether the solvent significantly affected the rate of reaction 2, we carried out the above procedure with carbon disulfide as a solvent. The average rate constant of three runs with [RNC] varying from 0.41 to 2.83 M was $(1.0 \pm 0.1) \times 10^{-4}$ s^{-1}. To determine whether a radical inhibitor affected the rate of reaction 2, we carried out the above procedure with hydroquinone (19 mol % of dimer concentration). The

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(20) A similar argument has been used to explain the semibridging carbonyls in $[CpM(CO)_2]_2$ dimers (M = Cr, Mo). See: Jemmis, E. D.; Pinhas, A. R.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *102*, 2576.

(21) Although we have considered only the anti isomer, characterized by X-ray diffraction, syn isomers are also possible. Theoretical studies which compare the relative stabilities of syn and anti isomers of a series of $Mo_2{}^VS_4$ complexes have been reported: Chandler, T.; Lichtenberger, D. L.; Enemark, J. H. *Inorg. Chem.* **1981**, *20*, 75.

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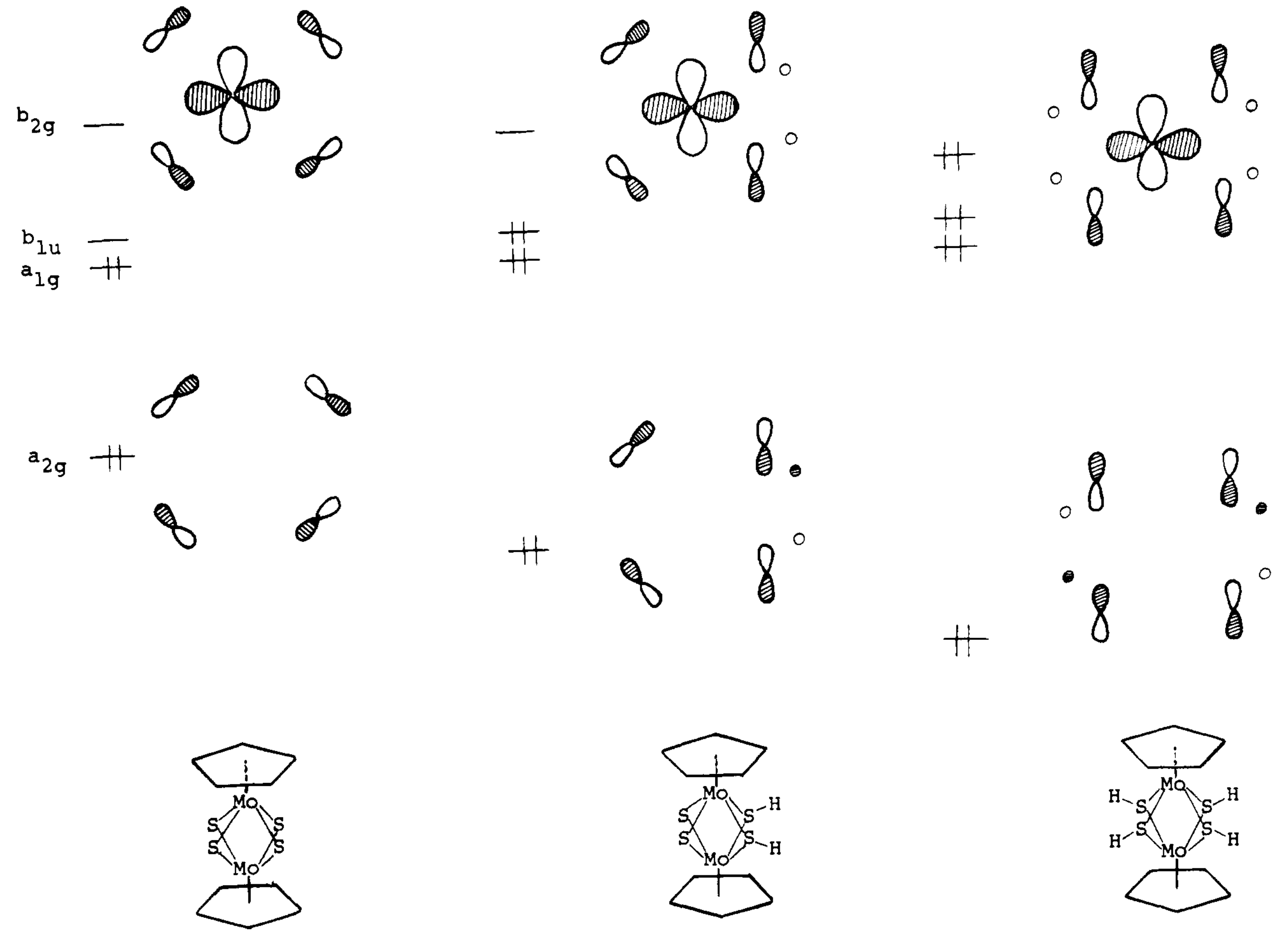

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Figure 5. Comparsion of orbital occupancy for $[CpMoS_2]_2$, $[CpMo(S)SH]_2$, and $[CpMo(SH)_2]_2$. Sketches of the molecular orbitals are viewed down the metal–metal vector.

Table II. Extended Hückel Parameters

atom	orbital	H_{ii}, eV	ζ_1	ζ_2
Mo	5s	−7.86	1.96	
	5p	−4.82	1.92	
	4d	−9.81	4.54 (0.5899)[a]	1.90 (0.5899)[a]
S	3s	−20.0	1.817	
	3p	−13.3	1.817	
C	2s	−21.4	1.625	
	2p	−11.4	1.625	
H	1s	−13.6	1.30	

[a] Coefficient used in double-ζ expansion of d orbitals.

rate of this reaction was not inhibited; $k = 1.2 \times 10^{-4}$ s^{-1}. With hydroquinone present in reaction 1 (13 mol % of dimer concentration), the rate was found to be slightly inhibited; $k = 6.5 \times 10^{-4}$ L mol^{-1} s^{-1}. Further studies are necessary to determine whether radicals play a significant role in this reaction.

Kinetic Studies of $[CpMoSCH_2CH(CH_3)S]_2 + C_2H_4$. The procedure for a typical run is described. In a 130-mL flask equipped with a Teflon high vacuum valve, an 8.0×10^{-3} M solution (25 mL) of the molybdenum complex in $CHCl_3$ was degassed in two freeze–pump–thaw cycles. Ethane (5.2 cmHg) and ethylene (49.7 cmHg) were added at ambient temperature. The flask was sealed, placed in a controlled temperature water bath at 38.0 ± 0.2 °C, and stirred with a magnetic stir bar. The vacuum valve was opened at regular intervals into a small evacuated area (~1 cm^3) adjacent to the flask equipped with a septum, and vapors were sampled. In a series of 11 runs, molar ratios of ethene to molybdenum complex were varied from 9 to 26. The decrease in concentration of $[CpMoSCH_2CH(CH_3)S]_2$ during the initial period of reaction was esimated by GC monitoring of the eliminated propene. The rate constant was calculated from linear least-squares regression analysis of the plots of ln $[CpMoSCH_2CH(CH_3)S]_2$ vs. time. The average correlation coefficient was 0.97, and the average rate constant is reported $\pm 1\sigma$.

Table III. Geometrical Parameters for Doubly and Quadruply Bridged Dimers

	bond dist, Å		bond angle, deg	
doubly bridged dimer	Mo–Mo	2.88	Mo–Mo-centroid[c]	125
	Mo–S_T[a]	2.10	MoMoS_T[a]	115
	Mo–S_B[b]	2.32		
	Mo–C	2.32		
quadruply bridged dimer	Mo–Mo	2.60	MoMo-centroid[c]	180
	Mo–S	2.42		
	Mo–C	2.32		
	C–H	1.10		
	S–H	1.30		

[a] S_T represents the terminal sulfur atom. [b] S_B represents the bridging sulfur atom. [c] MoMo-centroid represents the angle formed by the two Mo atoms of a given dimer and the centroid of the cyclopentadienyl ring.

Variable-Temperature Studies of SH Complexes. Proton NMR spectra of $[MeCpMo(S)SH]_2$ and of $[Me_5CpMo(S)SH]_2$ were recorded from 30 to 60 °C in $CDCl_3$ and from 30 to 90 °C in $CD_3C_6D_5$. No change in SH resonances was observed. Above 90 °C apparent decomposition occurred, and the SH resonances irreversibly disappeared. A solution of $[MeCpMo(S)SH]_2$ in $CD_3C_6D_5$ under 0.5 atm of H_2 was studied by NMR over the temperature range 30–100 °C. In this case no decomposition was observed, and no evidence for exchange of SH ligands was observed.

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Appendix

Extended Hückel calculations[23] were performed by using the weighted H_{ij} formula.[24] The atomic parameters used are listed in Table II with the molybdenum parameters taken from ref 25. A double-ζ expansion was used for the d orbitals. Geometrical parameters used to model the open doubly bridged and closed quadruply bridged dimers are given in Table III.

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The F_3NO^- Radical Anion. ESR Spectra, Structure, and Its Dissociation to F_2NO

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Abstract: The isotropic ESR spectrum of F_3NO^- in the SF_6 matrix has been obtained under conditions which minimize interference from signals due to other radicals and expose additional lines to those previously observed. These results confirm the higher order analysis of the spectrum in terms of hyperfine interaction with one nitrogen and three equivalent fluorines, exact matrix diagonalization calculations yielding the parameters $^{14}a(1) = 148.5 \pm 1.5$ G, $^{19}a(3) = 194.5 \pm 0.5$ G, and $g = 2.014 \pm 0.001$. The C_{3v} symmetry suggested by these results is supported by INDO calculations which indicate that this geometry is preferred to those of trigonal-bipyramidal (C_s) structures. In contrast, theoretical calculations of the g factor provide no clear-cut basis for discriminating between these various structures. Evidence was obtained for the dissociation of F_3NO^- to F_2NO on annealing the SF_6 matrix through the phase transition at 94 K, and this reaction is interpreted with reference to the characteristics of the semioccupied molecular orbital of F_3NO^-.

Some time ago, two of us reported the discovery of the hypervalent radical anion F_3NO^-,[6] a species of considerable interest in being the first example of a 33 valence electron radical composed only of first-row elements to compare with the well-established family of phosphoranyl radicals, including the formally analogous Cl_3PO^-[7] and F_3PO^-[8] radical anions. Subsequently, the related hypervalent species $c\text{-}C_nF_{2n}^-$ (n = 3-6)[9,10] and CF_3X^- (X = Cl, Br, I)[10,11] were generated by electron addition to halides of saturated carbon. However, attempts in our laboratory[1] to produce the congeneric radicals NF_4 and CF_4^- have met with failure although the methods used were exactly analogous to those which yield their second-row central atom counterparts PF_4[12] and SiF_4^-,[13] and, to the best of our knowledge, F_3NO^- remains the only known member of the potential class of 33 valence electron radicals drawn from first-row elements. Since F_3NO^- can also be regarded, in a formal sense, as having nine electrons accommodated around nitrogen, its uniqueness extends to an even larger class of electron-excess radicals based on first-row central atoms, including potentially important but hypothetical species such as CH_4^-, NH_4, H_3O, NH_3^-, and H_2O^-.

A thorough study of F_3NO^- therefore appeared to be warranted, and this paper extends the earlier communication[6] in three respects. First, we report the detection of two spectral components which were masked by hydrogen atom signals in the previously reported ESR spectrum.[6] These additional lines have allowed a more stringent test of the spectral analysis in terms of hyperfine interaction with one ^{14}N and three ^{19}F nuclei. Second, the structure of F_3NO^- has been probed by theoretical calculations, the aim being to see if the C_{3v} structure naturally suggested by the experimental results is preferred to the alternative model of a trigonal-bipyramidal (C_s) structure in which there is rapid exchange of the fluorine ligands between the axial and equatorial sites on the ESR time scale. The structure of F_3NO^- assumes particular importance in view of mounting evidence since 1975 that some phosphoranyl[14,15] and other hypervalent radicals of this type[10,11,16] assume local C_{3v} symmetry rather than the more common quasi-trigonal-bipyramidal structure[7,17-20] originally

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