with anisotropic displacement parameters for all non-hydrogen atoms gave the final R of 0.038 (R_w = 0.046). All hydrogen atoms were found in the difference Fourier maps and were included in the refinement as fixed contributors to the structure factors. The final difference map was essentially featureless, with the highest peak being 0.14 e Å^{-3}.

Acknowledgment. We thank the National Science Foundation (Grant No. CHE-8815742) for the generous support of this program, the Midwest Center for Mass Spectrometry (an NSF Regional Instrument Facility; Grant No. CHE-8211164) for obtaining several mass spectra, and both the NIH (Grant No. RR-01672) and the NSF (Grant No. CHE-8300958) for providing the Enraf-Nonius CAD4 single-crystal diffractometer. Additionally we thank Dr. M. A. Sturgess for the preparation of 12 (method 1).

Supplementary Material Available: Tables of positional and thermal parameters for **16a** and **17** (4 pages); listings of structure factors (41 pages). Ordering information is given on any current masthead page.

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[14] Sheldrick, G. M. "SHELXS-86: A Program for Crystal Structure Determination"; University of Göttingen, Göttingen, FRG, 1986.

Insertions of Unactivated Olefins into the Hydrosulfido Ligand of a Cationic Cyclopentadienylmolybdenum Complex

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The cationic complex $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SH)]SO_3CF_3$ ($[1]SO_3CF_3$) has been reacted with a series of terminal and internal olefins to form the cationic product in which the olefin has inserted into the S–H bond of the bridging ligand. The reaction has been found to be reversible for most olefins. The regiochemistry of the insertion reaction has been studied, and relative rates of insertion have been determined as olefin substituents were varied. For reactions involving internal olefins, the kinetic insertion products were found to rearrange to more stable products. A mechanism for the olefin insertion reaction has been proposed that involves attack of an electrophilic sulfido ligand in 1 on the more electron-rich carbon of the olefin. Secondary products have been isolated from many of the reaction solutions and characterized by spectroscopic data. The secondary products result from air oxidation of 1 and further reaction of this oxidized derivative with olefins.

Introduction

The cationic complex of the formula $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SH)]X$ ($[1]X$; X = SO_3CF_3, BF_4) has been found to undergo interesting reactions with organic oxygen-[1] and nitrogen-containing[2] substrates that result in the cleavage of the carbon–heteroatom bond. In some cases an intermediate reaction step has been proposed that involves S–H addition to an unsaturated substrate.[2] In previous work we have established that μ-SH ligands in cyclopentadienylmolybdenum dimers do undergo addition reactions with certain unsaturated molecules. For example, a neutral molybdenum(III) complex that contained a nucleophilic μ-SH ligand reacted with olefins activated by electron-withdrawing groups.[3] A few other examples of the insertion of activated olefins into an SH ligand in nucleophilic complexes have also been reported.[4,5] We expected the reactivity of the SH ligand in 1 to differ significantly from that of previously studied systems because this cationic molybdenum(IV) derivative should be both more acidic and more electrophilic in character than the previously reported SH complexes. In this paper, we describe the reactivity of the SH ligand in 1 with respect to addition to carbon–carbon double bonds. This system provides the first example of the addition of a coordinated SH ligand to a series of unactivated olefins. A unique feature of the olefin insertions into this metallothiol complex is the reversibility of the reactions.

Results

Regiochemistry of Olefin Insertion Products. $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SH)]SO_3CF_3$ reacted with alkenes to form cationic products with μ-alkanethiolate ligands. The list of alkenes that have been used in this study and the resulting alkanethiolate products are given in Table I. Products of the reactions have been isolated and characterized by NMR and mass spectroscopy and, in most cases, by elemental analyses; these data are summarized in Table II. In the reactions of the hydrocarbon-containing terminal olefins, Markovnikov addition products were isolated in every case. Regioselectivity was greater than 95%. The insertion reactions with these olefins were also monitored by NMR spectroscopy, and the data confirmed that the kinetic products showed the same regiochemistry as the isolated complexes indicated in Table I. The reactions with the terminal disubstituted olefins were carried out at low temperature in order to isolate the Markovnikov addition products with tertiary carbons in

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[1] Godziela, G.; Tonker, T.; Rakowski DuBois, M. *Organometallics* **1989**, *8*, 2220.

[2] (a) Coons, D. E.; Laurie, J. C. V.; Haltiwanger, R. C.; Rakowski DuBois, M. *J. Am. Chem. Soc.* **1987**, *109*, 283. (b) Bernatis, P.; Rakowski DuBois, M. Submitted for publication in *Organometallics*.

[3] Casewit, C. J.; Rakowski DuBois, M. *J. Am. Chem. Soc.* **1986**, *108*, 5482.

[4] Rauchfuss, T. B.; Ruffing, C. O. *Organometallics* **1985**, *4*, 524.

[5] (a) Seyferth, D.; Womack, G. B.; Henderson, R. S. *Organometallics* **1986**, *5*, 1568. (b) Seyferth, D.; Womack, G. B. *J. Am. Chem. Soc.* **1982**, *104*, 6839. (c) Seyferth, D.; Henderson, R. S. *J. Organomet. Chem.* **1981**, *218*, C34.

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Table I. Experimental Data for the Insertion Reactions of Olefins with Complex 1

olefin	reacn, conditions	μ-SR ligand in isolated product	yield, %
	Terminal Olefins		
C_2H_4	CH_3CN, 0 °C, 5 h, 10 equiv	SCH_2CH_3	93
	(a) Monosubstituted Olefins		
$H_2C{=}CH(CH_3)$	CH_3CN, room temp, 18 h, 3 equiv	$SCH(CH_3)_2$	61
$H_2C{=}CH(CH_2CH_3)$	CH_2Cl_2, room temp, 3 days, 5 equiv	$SCH(CH_3)(C_2H_5)$	79
$H_2C{=}CH(C_6H_5)$	$CHCl_3$, room temp, 12 h, 2 equiv	$SCH(CH_3)(C_6H_5)$	80
$H_2C{=}CH(CN)$	CH_2Cl_2, room temp, 1 day, 7 equiv	SCH_2CH_2CN	42
$H_2C{=}CH(SPh)$	CH_3CN, -40 °C, 3 days, 3 equiv	$SCH(CH_3)(SPh)$	72
$H_2C{=}CH(CO_2CH_3)$	CH_2Cl_2, room temp, 21 days, 5 equiv	$SCH_2CH_2CO_2CH_3$	51
	(b) Disubstituted Olefins		
$H_2C{=}C(CH_3)_2$	CH_3CN, -35 °C, 10 days, 18 equiv	$SC(CH_3)_3$	76
$H_2C{=}C(CH_3)(C_2H_5)$	CH_3CN, -38 °C, 7 days, 10 equiv	$SC(CH_3)_2(C_2H_5)$	72
	Internal Olefins		
$CH_3C(H){=}CH(CH_3)$	CH_3CN, room temp, 12 h, 2 equiv	$SCH(CH_3)(C_2H_5)$	80
$CH_3C(H){=}C(CH_3)_2$	$CHCl_3$, room temp, 2 days, 10 equiv	$SCH(CH_3)CH(CH_3)_2$	85
$(CH_3)_2C{=}C(CH_3)_2$	CH_2Cl_2, room temp, 14 days, 8 equiv	$SCH_2CH(CH_3)CH(CH_3)_2$	54

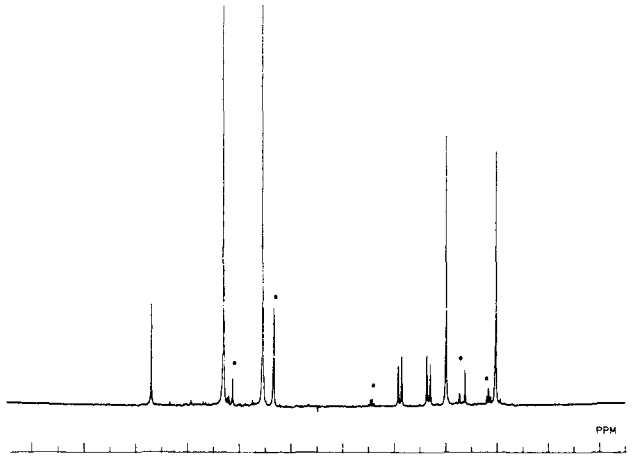
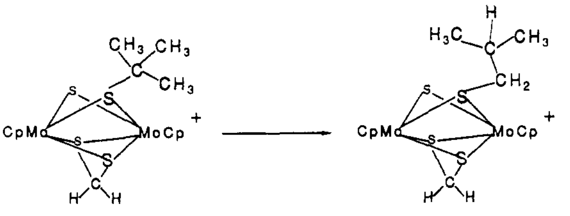
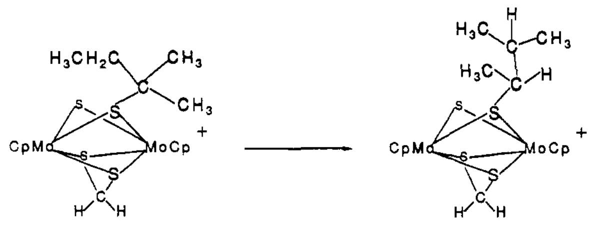


Figure 1. 200-MHz ^{1}H NMR spectrum of [CpMo(S$_2$CH)(SCH$_2$C(Me)$_2$S)MoCp]BF$_4$ in CD$_2$Cl$_2$. Assignments are given in the Experimental Section. Resonances marked with an asterisk are due to solvents or impurities.

the thiolate ligands. These products were found to undergo rearrangements in solution as shown in reactions 1 and 2. NMR spectroscopy was useful in identifying the



(1)



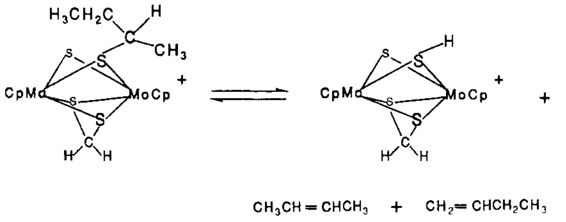
(2)

rearranged products. For example, the product of reaction 2 contains a chiral center at the α-position of the thiolate ligand, and in the NMR spectrum two Cp singlets and two terminal methyl doublets were observed (see Table II).

The reactions of 1 with the tri- and tetrasubstituted olefins were not carried out at low temperature because the rates were quite slow even at room temperature. Products with tertiary carbons in the thiolate substituents were detected by NMR spectroscopy as the kinetic products in these reactions, but only products resulting from anti-Markovnikov addition to the trisubstituted olefin and to an isomerized form of the tetrasubstituted olefin were isolated (see Table I).

The reactivities of three terminal olefins with heteroatom substituents were also examined. Phenyl vinyl sulfide reacted with the molybdenum complex similarly to the other terminal olefins to give the Markovnikov addition product, but the terminal olefins with the electron-withdrawing cyano and carboxylato substituents inserted into the μ-SH bond of the complex to form kinetic and isolated products with the opposite regiochemistry.

Reversibility of the Olefin Insertion Reaction. When the triflate salt of the 2-butanethiolate cation was heated to 70 °C under nitrogen in acetonitrile solution, the elimination of butene was observed and the protonated molybdenum complex was formed (eq 3). As the solution

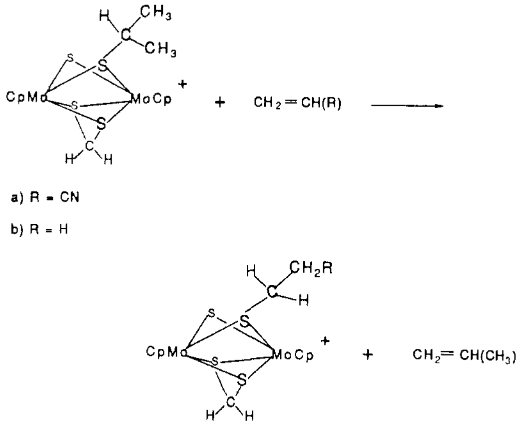


(3)

was cooled, the reverse insertion reaction was observed by ^{1}H NMR spectroscopy. NMR spectral analysis of the butenes formed and isolated at high temperatures indicated that the ratio of 1- and 2-butene isomers was ca. 1:8.

When an alkanethiolate cation was reacted with 1 equiv of a second olefin, a new alkanethiolate product was formed in some cases. For example, the 2-methyl-2-propanethiolate complex reacted with propene at room temperature to form the propanethiolate cation and 2-methylpropene. Propene was displaced from the propanethiolate ligand in reactions with ethene and acrylonitrile at 70 °C (eq 4). In contrast, the reverse reactions did not take place under the same conditions. Nor did products a and b in eq 4 react with ethene or acrylonitrile, respectively. The general trend was observed that the more substituted thiolate ligands eliminated olefins more readily.

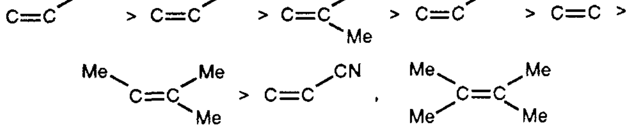
Relative Rates of Olefin Insertions. The insertions of terminal olefins were generally quite rapid at room temperature. For example, when the reactions of similar concentrations of the molybdenum complex with ethene, propene, styrene, or 2-methylpropene (3–5 equiv) were



(4)

monitored by NMR spectroscopy at ambient temperature, the insertions were complete by the time the first NMR spectrum was recorded (3–5 min). In these NMR experiments, apparent product inversion isomers were observed. For example, for the insertion of ethylene, the initial product observed in the spectrum displayed resonances (ppm) that were consistent with an ethanethiolate-bridged cation: 1.16 (t, Me), 2.20 (q, CH_2), 4.52 (s, S_2CH_2), and 6.9 (s, Cp). Over a period of 20–30 min, new resonances grew in at 1.0, 2.0, and 4.11 ppm, which corresponded to those of the final ethanethiolate complex isolated in large-scale reactions. Similar intermediate species were observed in the other olefin insertion reactions that were monitored by NMR spectroscopy. Reactions of 1 with internal olefins were slower than those with terminal olefins. For example, when the reaction with 2-methyl-2-butene (3 equiv) was monitored by NMR spectroscopy under conditions identical with those used for the terminal olefins, approximately 20% of 1 was observed in the spectrum after 8 min. The slowest insertion reactions were observed with acrylonitrile (a terminal olefin with an electron-withdrawing substituent) and with 2,3-dimethyl-2-butene (a tetrasubstituted olefin). For example, the latter reaction was ca. 80% complete after 6 days.

The relative rates of olefin insertions were further probed by competition reactions, and a rate enhancement by σ- or π-electron-donating substituents in monosubstituted olefins was observed in these experiments. When an approximately equimolar mixture of ethene and propene was reacted with the protonated cation, the formation of the product with the propanethiolate ligand was favored by a ratio of 2.5:1. In the competition of propene and 2-methylpropene for 1, the formation of the 2-methylpropene insertion product was favored in a ratio of 2:1. A similar competition between styrene and 2-methylpropene indicated that the rate of styrene insertion was faster. On the basis of these qualitative experiments, the relative ordering of reaction rates was observed for the following olefins:

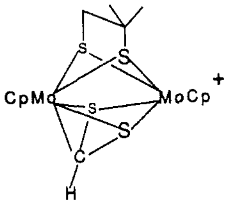


$$\mathrm{C{=}C{-}SPh > C{=}C{-}Ph > C{=}C(Me)_2 > C{=}C{-}Me > C{=}C > Me{-}C{=}C(Me)_2 > C{=}C{-}CN\,,\ (Me)_2C{=}C(Me)_2}$$

Reactions of the Insertion Products with Hydrogen. The reaction of $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SCH(Me)Ph)]X$ (X = Br, SO_3CF_3) with 1–2 atm of hydrogen at 50 °C in chloroform solution has been studied previously.[6] Hydrogenolysis of the C–S bond of the alkanethiolate ligand was observed, and ethylbenzene and the protonated cation 1 were identified as the products. However, the cations with other alkanethiolate ligands did not react with hydrogen under similar conditions to form hydrogenolysis products. For example, when the triflate salt of the 2-butanethiolate cation was heated under H_2 at 70 °C, only the elimination of butene (reaction 3) was observed. When the same cation was heated in the presence of a more nucleophilic counterion, e.g., bromide ion, the formation of 2-bromobutane and of $(CpMo\mu\text{-}S)_2S_2CH_2$ was observed.[7]

Despite our failure to observe hydrogenolysis reactions, when selected cations were heated under a deuterium atmosphere, evidence was observed for the incorporation of deuterium into the thiolate ligand. For example, when the 2-methyl-2-propanethiolate cation was reacted at 30–35 °C for 2 weeks under 2 atm of D_2 in a sealed NMR tube, the thiolate ligand in both the original cation and in its rearranged isomer showed significant levels of deuterium substitution (see Experimental Section). This conclusion was based on the integration of alkyl resonances relative to integrations of Cp and solvent peaks, which remained relatively constant in intensity. H–D coupling was observed in the alkyl resonances as well as in the product HD, which increased in concentration over the reaction period.

Characterization of a Second Reaction Product. In many of the reactions indicated in Table I, a second molybdenum product was also observed by NMR spectroscopy in yields that ranged from <5% to ca. 20%. When the reactions of 1 with olefins were carried out in the presence of oxygen rather than nitrogen, the relative yields of the second product increased significantly. Water was also identified as a product in the reactions carried out under oxygen. The secondary products were structurally very different from the olefin insertion products. Each of these derivatives showed a distinctive NMR pattern that included two Cp resonances separated by ~1 ppm and a singlet at 7.5 ppm, which was integrated for one proton. For example, the ^1H NMR spectrum for product II isolated from the reaction with 2-methylpropene is shown in Figure 1. The ^1H and ^{13}C NMR data for the complexes led us to propose structure A for the 2-methylpropene product.



A

Supporting evidence for the structure was obtained by the isolation of A in ~90% yield from the hydride abstraction reaction shown in eq 5. The analgous hydride abstraction reaction was also characterized for the ethene, propene, and acrylonitrile adducts. Characterization data are included in the Experimental Section. In the last two systems, NMR data were complex because of the presence of two isomers in solution. The isomers result from the two inequivalent positions that are possible for the methyl or cyano group on the alkanedithiolate ligand in the structures. Reaction 5 could be reversed when a hydride donor was reacted with the product cation. For example, when the ethene analogue of structure A was reacted with $NaBH_4$ supported on alumina, a near-quantitative yield

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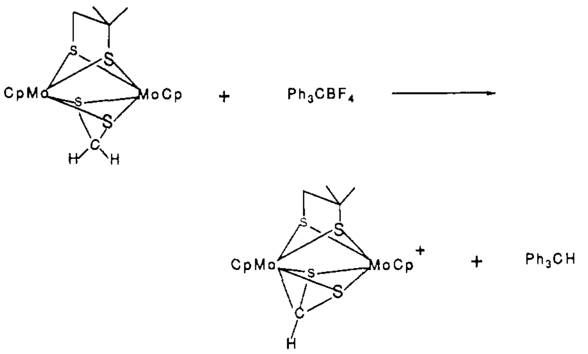
[6] Weberg, R. T.; Haltiwanger, R. C.; Laurie, J. C. V.; Rakowski DuBois, M. *J. Am. Chem. Soc.* **1986**, *108*, 6242.

[7] Weberg, R. T. Ph.D. Thesis, University of Colorado, Boulder, CO, 1986.



(5)

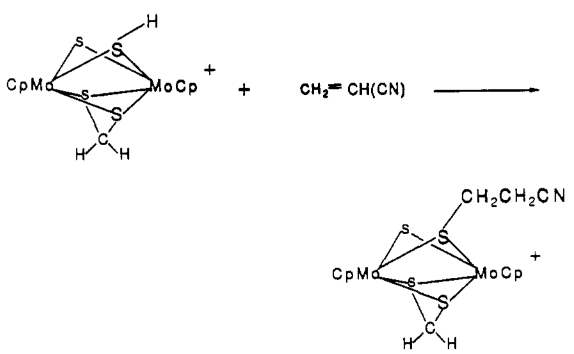
of $(CpMo)_2(S_2CH_2)(SC_2H_4S)$ was observed by NMR spectroscopy.

Discussion

Mechanism of the Olefin Insertion Reaction. The facile insertion of olefins into the SH ligand of the molybdenum complex can be compared to the additions of organic thiols to olefins. The latter reactions are generally catalyzed by strong acid and are found to result in Markovnikov addition products.[8] The mechanism involves protonation of the olefin to form a carbonium ion followed by nucleophilic attack by the thiol. In the metallosulfur systems studied here, the products also result from Markovnikov addition in most cases, but it seems unlikely that a similar mechanism is operative. The pK_a of the protonated molybdenum complex in dry acetonitrile is 8.3;[9] the olefin insertion reactions carried out in this solvent are therefore unlikely to involve free carbonium ion formation. An alternate mechanism can be proposed on the basis of our observations that the μ-sulfido ligands in the related cations $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SR)]^+$ show electrophilic character. For example, carbon nucleophiles react with the μ-S ligand in these cations to form bis(alkanethiolate) derivatives.[6,10] The interaction of the electrophilic sulfido ligand in 1 with the more electron-rich carbon of the olefin, followed or accompanied by hydrogen transfer from μ-SH to the other olefinic carbon, is a mechanism consistent with the observed kinetic products. The anti-Markovnikov addition products observed in the reactions of 1 with terminal olefins containing electron-withdrawing groups, e.g. acrylonitrile and methyl acrylate, are also consistent with an initial interaction between the sulfido ligand and the more electron-rich olefinic carbon.

The relative rates of the insertion reactions of the olefins as a function of substituent were generally consistent with the proposed electrophilic nature of the reactant molybdenum complex, but the data suggested that the reactions were also quite sensitive to steric bulk on the olefin. For example, the rates of insertion of terminal olefins substituted with electron-donating groups were greater than that of ethene, but increased substitution around the double bond led to significantly slower insertion rates.

The insertions of activated alkenes and alkynes into the SH bond of a μ-hydrosulfido ligand in a related neutral molybdenum(III) dimer have been characterized previously.[3] Stepwise nucleophilic attack on unsaturated molecules by a μ-sulfido ligand in an anionic Mo(III) dimer followed by protonation of the resulting product has also been studied.[3] For example, the structurally related molybdenum dimers have been found to react regioselectively with acrylonitrile as shown in reactions 6–8. The ionic molybdenum complexes react to form products with the same regiochemistry, but the reactions occur by different pathways. Nucleophilic attack of the sulfido ligand in the anionic molybdenum complex occurs at the β-carbon of acrylonitrile because of the potential stabilization of negative charge at the α-C atom in the resulting intermediate. In contrast, the regiochemistry of addition of the electrophilic complex 1 appears to be determined not by the maximum stabilization of a charged intermediate, but by the initial interaction between the electrophilic sulfur and nucleophilic carbon sites. It is interesting that the reaction of the neutral Mo(III) derivative with acrylonitrile results in an addition product of regiochemistry opposite to that of the ionic complexes. Although the mechanism of the Mo(III) reaction is not known, the difference in product orientation may provide a useful probe of the nature of the reactive intermediate in SH addition reactions in other systems that are carried out under a hydrogen atmosphere.



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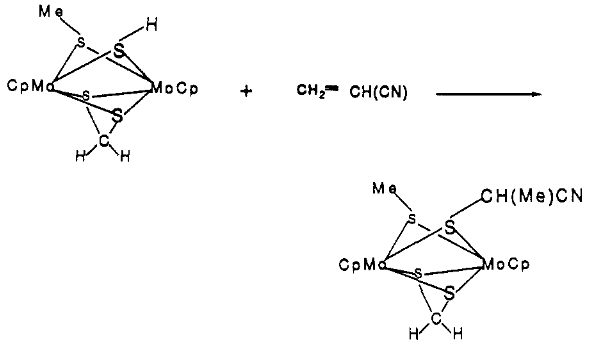

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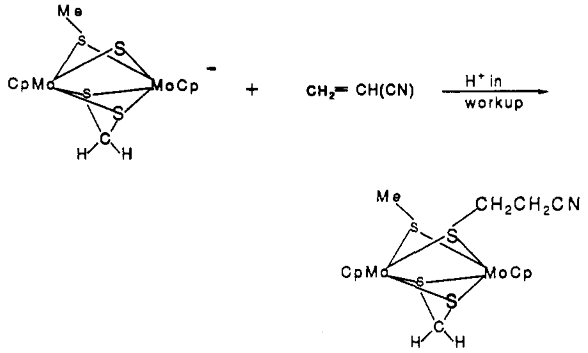

(8)

Rearrangement Reactions. The Markovnikov products resulting from reactions with terminal disubstituted olefins were unstable in solution (eq 1 and 2). The observed isomerization process is proposed to involve a reversal of the olefin insertion. Hydrogen transfer from the methylene group in the thiolate ligand to the adjacent sulfido ligand, followed or accompanied by the elimination of an isomerized olefin, is shown in eq 9. The reaction of 1 with the internal olefin to ultimately produce a stable anti-Markovnikov addition product has been confirmed in a separate experiment. This regiochemistry may be

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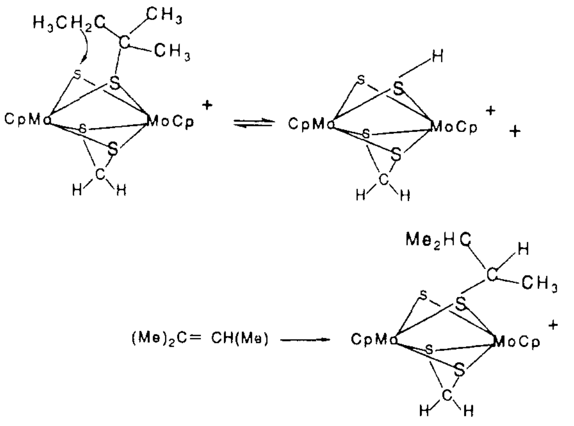
[8] Ohno, A.; Oae, S. In *Organic Chemistry of Sulfur*; Oae, S., Ed.; Plenum Press: New York, 1977; p 119.

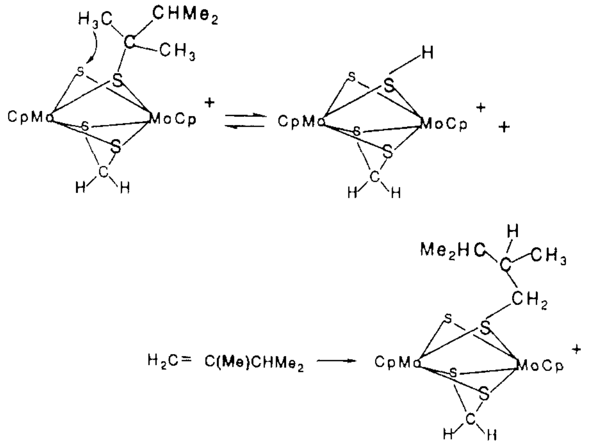
[9] Birnbaum, J.; Godziela, G.; Maciejewski, M.; Tonker, T.; Rakowski DuBois, M. *Organometallics*, in press.

[10] Casewit, C. J.; Haltiwanger, R. C.; Noordik, J.; Rakowski DuBois, M. *Organometallics* **1985**, *4*, 119.



(9)

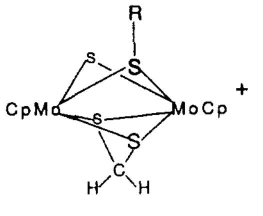
favored in the more stable addition product because the carbon coordinated to the $Cp_2Mo_2S_4$ core is less sterically hindered. A similar isomerization process (reaction 10) is proposed for the kinetic product from the reaction with the tetrasubstituted olefin.



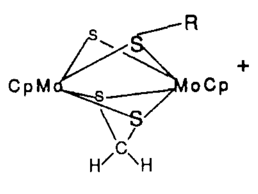
(10)

The reversible nature of the S–H addition process in many of these systems is an unusual feature of the metallosulfur complexes that is not observed in the additions of organic thiols to olefins. The reversibility has been confirmed by studying the temperature dependence of reaction 3. Significant levels of butenes were observed by NMR spectroscopy after heating the reaction solution at 70 °C for 2–3 days. The ratio of butene isomers observed in the olefin deinsertion reaction is consistent with the expected thermodynamic ratio that would be produced in an equilibrium process.[11]

The deinsertion process provides a facile means of C–S bond cleavage, which appears to be possible because of the geometric position and the electrophilic nature of the μ-sulfido ligand in the cations. The proposed mechanism implies that the thiolate substituent should be in an axial position[12] to permit hydrogen transfer to the adjacent bridging ligand:



axial

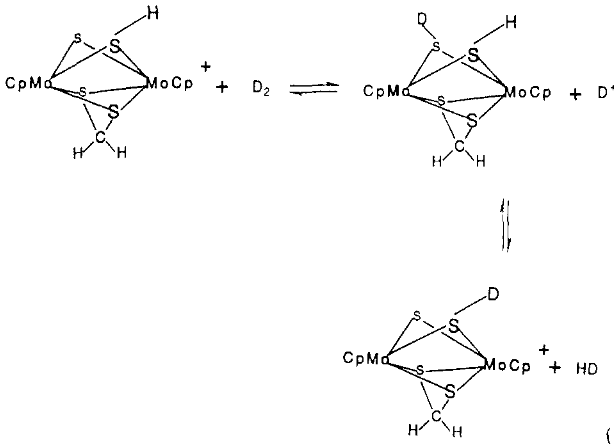


equatorial

Similarly, in the insertion reaction, the axial isomer should be the initial product. Several X-ray diffraction studies of related cations, where R = Me, thiophene, CH=CHPh, and C(Ph)=CH_2, have been carried out.[6,10,13,14] In every case the equatorial isomer was identified in the structural characterization. Evidence has been presented previously that the interconversion of axial and equatorial configurations is a rapid and facile process for the cationic derivative with R = C(Ph)=CH_2.[13] For the isolated cations resulting from the olefin insertion reactions, only one isomer has been observed in the NMR spectrum at room temperature. However, when the ethene and propene insertions were monitored by NMR spectroscopy, an intermediate species was observed that had spectral characteristics consistent with an inversion isomer of the final product. This kinetic product is tentatively assigned as the axial isomer.

Reactivity of Alkanethiolate Complexes with Hydrogen. In previous studies we have found several examples of alkanethiolate complexes with electron-withdrawing substituents that underwent sulfur–carbon bond cleavage under hydrogen.[6,15] However, the alkanethiolate cations reported here did not undergo hydrogenolysis under similar conditions. The electronic influence on the hydrogenolysis process is not yet completely understood, and studies are in progress to obtain more information on the mechanism of these reactions.

The incorporation of deuterium into the alkanethiolate ligands was observed when certain of the cationic complexes were heated under a deuterium atmosphere under conditions in which the olefin insertion reactions were reversible. The result suggests that deuterium is activated by and incorporated into 1, perhaps by reaction 11. A similar set of reactions has been observed for the methanethiolate cation.[13] If such equilibria occur for 1, deuterium incorporation into the thiolate ligand could take place through S–D addition to the olefin as well as through D^+-catalyzed rearrangements of the free olefin. Additional examples of deuterium substitution reactions involving 1 have been characterized and will be described in a separate paper.



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Formation of Secondary Reaction Products. In almost every insertion reaction studied, a second molybdenum-containing product was observed by NMR spectroscopy. These secondary products were dinuclear cations

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(11) Thermodynamic data for butenes was obtained from: Dean, J. A. *Handbook of Organic Chemistry*; McGraw-Hill: New York, 1987.

(12) Shaver, A.; Fitzpatrick, P. J.; Steliou, K.; Butler, I. S. *J. Am. Chem. Soc.* **1979**, *101*, 1313.

(13) Laurie, J. C. V.; Duncan, L.; Haltiwanger, R. C.; Weberg, R. T.; Rakowski DuBois, M. *J. Am. Chem. Soc.* **1986**, *108*, 6234.

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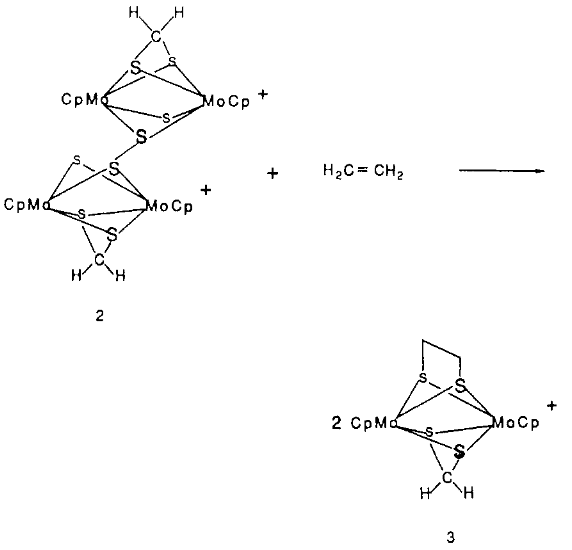
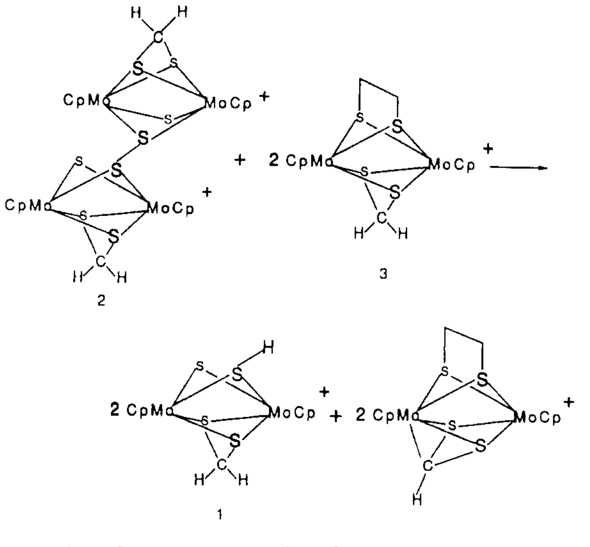
(15) Coons, D. E.; Haltiwanger, R. C.; Rakowski DuBois, M. *Organometallics* **1987**, *6*, 2417.

in which the olefin had interacted with sulfido ligands to form an alkanedithiolate bridge and in which the methanedithiolate ligand had been modified; see, for example, structure A. The formation of these products is attributed, at least in part, to the reactivity of a second cationic derivative, $[(CpMo(\mu\text{-}S))_2S_2CH_2]_2^{2+}$ (**2**), which is believed to be present in the reaction mixtures in low concentrations. The protonated cation **1** is oxidized to the tetranuclear dication **2** quite readily in the presence of air. An X-ray diffraction study has established that the structure of **2** involves the linking of two dinuclear units through a S–S bond between μ-sulfido ligands.[9] The air sensitivity of **1** was not recognized by us in our early studies of the complex because the physical properties and NMR characteristics of **2** are very similar to those of **1**.[9]

The competing reactions of **2** in the olefin reaction systems have been identified. The reaction of **2** with excess olefin resulted in cleavage of the sulfur–sulfur bond and formation of a cationic olefin adduct, **3** (eq 12).[9] The further reaction of the olefin adduct with **2** has been found to result in the formation of the observed secondary product in the olefin insertion reactions (eq 13). The reaction demonstrates the ability of **2** to function as a hydrogen atom acceptor. The reaction chemistry of this derivative is described in more detail in a separate paper.[9]

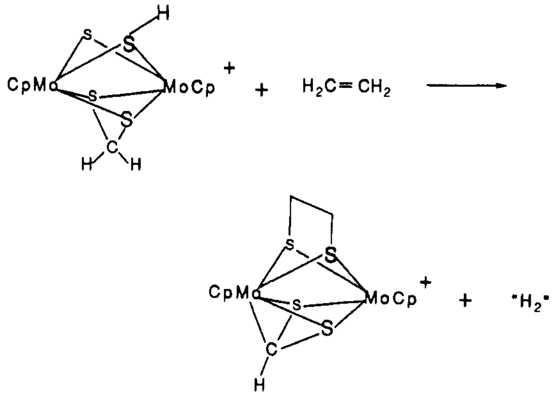


(12)



(13)

The conversion of reactants to the secondary product involves a net dehydrogenation as shown in eq 14. We have investigated whether other species in our reaction solution, in addition to **2**, might also serve as hydrogen acceptors. For example, when reactions were carried out under oxygen, yields of the secondary products were significantly increased and water was also observed as a product. As mentioned above, we know that oxygen is involved in the conversion of **1** to the dication **2**, and **2** reacts readily with an olefin as shown in eq 12. We have found that the cationic olefin adduct **3** reacts readily with oxygen, or with hydrogen peroxide, to form the observed secondary product as well.



(14)

We also investigated whether olefins could serve as the hydrogen acceptor in this system, perhaps through the stepwise transfer of proton and hydride ions. When **1** was reacted with acrylonitrile in the absence of oxygen, a low yield of the secondary product was formed, but no propionitrile was detected. *tert*-Butylethylene has been used as an effective hydrogen acceptor in other systems.[16] However, the reaction of $[(CpMo(\mu\text{-}S))_2(S_2CH_2)(SC_2H_4S)]$ with 1 equiv of triflic acid and this olefin failed to produce any *tert*-butylethane. We conclude that a contaminant of $[(CpMo(\mu\text{-}S))_2S_2CH_2]_2^{2+}$ in **1** is responsible for observed dehydrogenations in the absence of oxygen, as discussed above.

Although we have carried out many reactivity studies with molybdenum derivatives containing the methanedithiolate ligand,[1-3,6,9,10,13,15,17] the secondary products described here provide the first evidence for reactivity involving this ligand. In addition to the hydrogen atom abstractions from cation **3**, described above, the methanedithiolate ligand was also found to be subject to hydride abstraction in neutral molybdenum(III) derivatives (see reaction 5). The hydridic nature of the ligand is rather surprising since the deprotonation of mercaptans by strong base is well-known.[18] Unsuccessful attempts to deprotonate the methanedithiolate ligand in Mo(III) dimers of this type have been reported earlier.[17] The hydridic nature of the ligand demonstrates the unusual electronic distributions that are possible in the $Mo_2S_4R_x$ unit in these systems.

Summary and Conclusions

The cationic dinuclear complex with the μ-SH ligand undergoes regioselective S–H addition reactions with unactivated olefins. The regioselectivity is attributed to the electrophilicity of the sulfido ligand in the cation, which controls the orientation of the approaching olefin. The insertion reactions are reversible; olefin deinsertion appears to be favored for thiolate ligands that are highly substi-

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Table II. Characterization Data for $[(\mathrm{CpMo})_2(\mathrm{S_2CH_2})(\mu\text{-S})(\mu\text{-SR})]\mathrm{SO_3CF_3}$

			^{1}H NMR,[a,b] ppm			elem anal., found (calcd)		
no.	reactant olefin	R	Cp	S_2CH_2	R	% C	% H	% S
1	ethene	CH_2CH_3	6.93 (s)	4.18 (s)	1.98 (q, CH_2, J = 7 Hz) 1.06 (t, CH_3, J = 7 Hz)	25.95 (26.17)	2.72 (2.67)	25.00 (24.95)
2	propene	$CH(CH_3)_2$	6.94 (s)	4.23 (s)	2.09 (sept, CH, J = 7 Hz) 1.10 (d, CH_3, J = 7 Hz)	27.33 (27.44)	2.93 (2.92)	24.56 (24.42)
3	1-butene	$CH(CH_3)(CH_2CH_3)$	6.93 (s) 6.91 (s)	4.30 (s)	1.9 (m, CH) 1.35 (m, CH_2) 1.03 (d, CH_3, J = 7 Hz)	28.41 (28.67)	3.14 (3.16)	23.69 (23.87)
4	2-methylpropene (kinetic prod.)	$C(CH_3)_3$	6.95 (s)	4.17 (s)	1.21 (s, CH_3)	28.60 (28.66)	3.28 (3.16)	23.82 (23.91)
5	2-methylpropene (rearranged prod.)	$CH_2CH(CH_3)_2$	6.92 (s)	4.20 (s)	1.81 (d, CH_2, J = 7 Hz) 1.52 (m, CH) 0.86 (d, CH_3, J = 7 Hz)			
6	2-methyl-1-butene or 2-methyl-2-butene (rearranged prod.)	$CH(CH_3)CH(CH_3)_2$	6.92 (s) 6.89 (s)	4.29, 4.27 (AB, J = 2.5 Hz)	1.96 (m, CH_α) 1.50 (m, CH_β) 0.91 (d, CH_3, J = 7 Hz) 0.79 (2 d, $(CH_3)_2$, J = 7 Hz)	29.66 (29.82)	3.41 (3.39)	23.18 (23.42)
7	2-methyl-1-butene or 2-methyl-2-butene (kinetic prod.)	$C(CH_3)_2CH_2CH_3$	6.92 (s)	4.23 (s)	1.46 (q, CH_2, J = 7 Hz) 1.06 (s, CH_3) 0.81 (t, CH_3, J = 7 Hz)	29.94 (29.82)	3.36 (3.39)	23.21 (23.42)
8	2,3-dimethyl-2-butene (rearranged prod.)	$CH_2CH(CH_3)CH(CH_3)_2$	6.91 (s)	4.29 (s)	1.80 (m, CH_2) 1.50 (m, CH_α) 0.95 (m, CH_β) 0.78, 0.76, 0.69 (3 d, CH_3, J = 7 Hz)			
9	2,3-dimethyl-2-butene (kinetic prod.)	$C(CH_3)_2CH(CH_3)_2$	6.94 (s)	4.06 (s)	1.03 (br s, 2 Me) 0.85 (d, 2 Me, J = 6.5 Hz)			
10	styrene	$CH(CH_3)(C_6H_5)$	6.99 (s) 6.32 (s)	4.25, 4.21 (AB, J = 4 Hz)	7.43, 7.06 (m, Ph) 2.98 (q, CH, J = 7 Hz) 1.52 (d, CH_3, J = 7 Hz)	35.18 (35.14)	3.37 (3.26)	19.84[c] (19.75)
11	phenyl vinyl sulfide	$CH(CH_3)SC_6H_5$	6.92 (s) 6.85 (s)	4.42, 4.32 (AB, J = 8 Hz)	7.34 (s, Ph) 3.26 (q, CH, J = 7 Hz) 1.29 (d, CH_3, J = 7 Hz)	32.12 (32.00)	2.91 (2.82)	25.56 (25.63)
12	acrylonitrile	CH_2CH_2CN	7.00 (s)	4.17 (s)	2.52 (t, CH_2, J = 7 Hz) 2.11 (t, CH_2, J = 7 Hz)	27.02 (26.99)	2.41 (2.42)	24.21 (24.02)
13	cyclohexene	C_6H_{11}	6.91 (s)	4.36 (s)	1.85 (m, CH_2) 1.57 (m, CH_2) 1.15 (m, $(CH_2)_4$)			
14	methyl acrylate	$CH_2CH_2CO_2CH_3$	6.96 (s)	4.28 (s)	3.65 (s, CH_3) 2.44 (t, CH_2, J = 6 Hz) 2.15 (t, CH_2, J = 6 Hz)			

[a] Entries 1, 2, 4, and 5 were recorded in CD_2Cl_2; entry 12 was recorded in CD_3CN; all other samples were recorded in $CDCl_3$. [b] Entries 4, 5, 7, and 11 were recorded at 90 MHz; entries 1, 2, and 6 were recorded at 250 MHz; all other entries were recorded at 200 MHz. [c] Bromide salt.

tuted at the α-carbon atom. The reversibility of the reactions accounts for observed isomerizations of several of the thiolate cations. The insertion reactions constitute a first step in a reduction of olefins that occurs at sulfide ligand sites. In this sense, complex 1 provides an interesting acidic analogy to the many hydridic hydrometalation reagents that are known to insert olefins. Future studies will include an investigation of the reactivity of the thiolate cations with nucleophiles to determine whether a free reduced hydrocarbon or thiol might be produced in a further analogy to the hydrometalation reagents.

Experimental Section

Materials. $[(\mathrm{CpMo})_2(\mu\text{-S_2CH_2})(\mu\text{-S})(\mu\text{-SH})]\mathrm{CF_3SO_3}$ ([1]CF_3SO_3),[2a,9] $(\mathrm{CpMoS})_2(\mu\text{-S_2CH_2})$, and $(\mathrm{CpMo})_2(\mathrm{S_2CH_2})(\mathrm{SCH_2CH_2S})$[18] were synthesized as reported previously. Hydrogen, oxygen, ethylene, and propylene were purchased from Matheson. Other reagent-grade alkenes, $NaBH_4$ (ca. 10% supported on alumina), $NOBF_4$, and $(C_6H_5)_3CBF_4$ were purchased from Aldrich. Deuterated solvents were stored over 4A molecular sieves before use. CH_3CN and CH_2Cl_2 were distilled from CaH_2 or P_2O_5 and stored over 4A molecular sieves.

Instrumentation. ^{1}H NMR spectra were measured at 90 MHz on a JEOL FX-90Q spectrometer, at 200 MHz on a Chemmagnetics A-200 instrument, at 250 MHz on a Bruker WM-250 spectrometer, or at 500 MHz on a Varian VXR-500S instrument. ^{13}C NMR spectra were measured at 62.9 MHz on a Bruker WM-250 spectrometer. Chemical shifts were referenced to the solvent. Mass spectra were obtained on a VG Analytical 7070 EQ-HF tandem mass spectrometer. Elemental analyses were performed by Spang Micro Analytical Laboratories of Eagle Harbor, MI.

Syntheses. Reactions were carried out under vacuum or a nitrogen atmosphere with standard Schlenkware, unless otherwise noted.

Olefin Insertion Products. In a typical procedure, a solution of $[(\mathrm{CpMo})_2(\mu\text{-S_2CH_2})(\mu\text{-S})(\mu\text{-SH})]\mathrm{CF_3SO_3}$ ([1]CF_3SO_3; 0.10 g, 0.16 mmol) and styrene (19 μL, 0.16 mmol) in $CHCl_3$ (ca. 10 mL) was degassed by two freeze–pump–thaw cycles and stirred at room temperature under vacuum for 12 h. The resultant red solution was filtered and the volume of $CHCl_3$ reduced to about 1–2 mL. Diethyl ether (ca. 6 mL) was added, and the resulting red precipitate was washed with ether (3 × 4 mL) and dried in vacuo. In most reactions the insertion products were contaminated with the secondary product (see Discussion). Separation of the two products was achieved in some cases by recrystallization from CH_3CN or CH_2Cl_2 by addition of hexanes. In some cases insertion products were purified by column chromatography on acidic alumina (pH = 6). The purple insertion product was eluted with CH_2Cl_2 or CH_3CN. The variation of reaction solvents (CH_3CN, CH_2Cl_2, $CHCl_3$, or CH_3NO_2) did not significantly alter the nature or ratio of the products. Reaction conditions for each olefin and corresponding yields of isolated insertion products are listed in Table I. Characterization data for each insertion product are listed in Table II. In cases where elemental analyses are not shown, complete separation of the insertion product from the secondary product was not achieved. FAB mass spectra were also obtained for each insertion product. Spectra consistently showed envelopes that corresponded to the parent cation (P^+) and to the fragments $P^+ - R$ (m/e 450) and $Cp_2Mo_2S_3^+$ (m/e 418).

Syntheses of the Secondary Products $[\mathrm{CpMo(S_2CH)(SCR_2CR_2S)MoCp}]^+$. Secondary products in the olefin insertion reactions were formed in low yields and were difficult to purify. The following alternate procedure was therefore used for the synthesis of these complexes. $(CpMo(\mu\text{-}S))_2S_2CH_2$ (150 mg, 0.32 mmol) was dissolved in 10 mL of CH_2Cl_2. An olefin (ethene, propene, 2-methylpropene, or acrylonitrile; 5–10 equiv) was transferred to the reaction flask at −196 °C. The flask was warmed to 20 °C and the mixture stirred until the deep blue solution turned the orange-brown color characteristic of the olefin adduct (1–10 min).[18] The flask was then recooled to −196 °C and $(C_6H_5)_3CBF_4$ (120 mg, 1.1 equiv) was added. The flask was warmed to 20 °C and the solution stirred at this temperature for 1 day. A light brown precipitate formed and was filtered from the solution. The product was recrystallized from CH_3CN; 50–90% yields were obtained.

$[(Cp\overline{Mo)(\mu\text{-}S_2C}H)(\mu\text{-}SCH_2C(CH_3)_2S)MoCp]^+$. ^1H NMR (CD_2Cl_2, 200 MHz): δ 7.81 (s, 1, S_2CH), 6.32 (s, 5, Cp), 5.53 (s, 5, Cp), 2.87, 2.31 (AB, 2, SCH_2, J = 13 Hz), 1.98 (s, 3, CH_3), 1.01 (s, 3, CH_3). ^{13}C NMR (CD_3CN, gated decoupling experiment): δ 121.8 (d, S_2CH, J = 204 Hz), 98.9 (d, Cp, J = 182 Hz), 94.9 (d, Cp, J = 181 Hz), 56.9 (S, $SCMe_2$), 47.6 (t, SCH_2, J = 144 Hz), 33.9 (q, CH_3, J = 128 Hz), 31.0 (q, CH_3, J = 127 Hz). FAB MS: *m/e* 519 (P), 463 (P − $CH_2C(CH_3)_2$), 418 (P − $CH_2C(CH_3)_2$ − SCH). Anal. Calcd for $C_{15}H_{19}Mo_2S_4BF_4$: C, 28.75; H, 2.86; S, 23.98. Found: C, 29.06; H, 2.94; S, 23.50. ^{13}C DEPT and selected ^1H NMR decoupling experiments were also completed.

$[(Cp\overline{Mo)(\mu\text{-}S_2C}H)(\mu\text{-}SCH_2CH_2S)(MoCp)]BF_4$. ^1H NMR (300 MHz, CD_2Cl_2): δ 7.64 (s, 1, CH), 6.22 (s, 5, Cp), 5.44 (s, 5, Cp), 3.02, 3.00 (AA′BB′, 4 SCH_2CH_2S). FAB MS: *m/e* 491 (P), 463 (P − CH_2CH_2), 418 (P − CH_2CH_2 − SCH). Anal. Calcd for $C_{13}H_{15}Mo_2S_4BF_4$: C, 27.01; H, 2.62; S, 22.18. Found: C, 27.19; H, 2.71; S, 22.07.

$[(Cp\overline{Mo)(\mu\text{-}S_2C}H)(\mu\text{-}SCH_2CH(CH_3)S)(MoCp)]BF_4$. ^1H NMR (500 MHz, CD_3CN): major isomer, δ 7.52 (s, 1, S_2CH), 6.21 (s, 5, Cp), 5.52 (s, 5, Cp), 1.09 (d, 3, CH_3, J = 7 Hz); minor isomer, δ 7.58 (s, 1, S_2CH), 6.27 (s, 5, Cp), 5.46 (s, 5, Cp), 1.71 (d, 3, CH_3, J = 7 Hz); ratio of isomers 4:1. Additional multiplets for the propanedithiolate ligand were observed at 3.46, 3.32, 2.74, 2.48, 2.32, and 1.57 ppm but were not assigned to individual isomers. FAB MS: *m/e* 505 (P), 463 (P − CH_2CHCH_3), 418 (P − CH_2CHCH_3 − SCH).

$[(Cp\overline{Mo)(\mu\text{-}S_2C}H)(\mu\text{-}SCH_2CH(CN)S)(MoCp)]CF_3SO_3$. ^1H NMR (500 MHz, CD_3CN): major isomer, δ 7.64 (s, 1, S_2CH), 6.26 (s, 5, Cp), 5.65 (s, 5, Cp); minor isomer, δ 7.68 (s, 1, S_2CH), 6.38 (s, 5, Cp), 5.56 (s, 5, Cp). Additional multiplets for the 1,2-dithiolate ligand were observed at 4.28, 3.39, 3.21, 2.72, and 2.46 ppm but were not assigned to individual isomers. FAB MS: *m/e* 516 (P), 463 (P − CH_2CHCN), 418 (P − CH_2CHCN − SCH).

Thermal Decomposition of $[(CpMo)_2(\mu\text{-}S_2CH_2)(\mu\text{-}S)(\mu\text{-}SCH(CH_3)CH_2CH_3)]CF_3SO_3$. The 2-butanethiolate complex (30 mg, 0.045 mmol) was dissolved in 3 mL of $CHCl_3$ and heated under vacuum for 3 days at ~70 °C. While the reaction vessel was still at 70 °C, the volatiles were vacuum-transferred to an NMR tube, the tube was sealed, and products were analyzed at 20 °C by ^1H NMR spectroscopy. Integration indicated that an 8:1 mixture of 2-butene (cis and trans; 1.55 ppm, m, Me) and 1-butene (0.98 ppm, t, Me; 2.00 ppm, q, CH_2) were present.

Reactions of Alkanethiolate Cations with Olefins. An olefin insertion product (20 mg, 0.03 mmol) was dissolved in 0.8 mL of CD_3CN in a NMR tube. A second olefin (1–2 equiv) was transferred to the NMR tube, and the tube was sealed under vacuum at −196 °C. Reactions were carried out at temperatures ranging from 20 to 70 °C. Products, resulting from deinsertion of the original olefin and insertion of the second olefin, were identified by ^1H NMR spectroscopy. In some cases, olefin products were also identified by GC. Specific reactions are described in the Results.

Olefin Competition Reactions with 1. Complex 1 (19 mg, 0.033 mmol) was dissolved in 0.8 mL of CD_3CN in a NMR tube. Two olefins were added to the NMR tube either by syringe or by vacuum line transfer, so that an approximate equimolar ratio of the olefins was present in solution as indicated by NMR spectroscopy. The tube was sealed under vacuum at −196 °C. Reactions were monitored at 20 °C by ^1H NMR spectra within the first 5–30 min of reaction to determine the identity of the kinetically favored (alkanethiolato)molybdenum product. The following are examples of results observed in several determinations: propene/ethene (1.46 molar ratio) favored the propanethiolate product by a ratio of 2.4:1; styrene/phenyl vinyl sulfide (1.8:1) favored the phenyl vinyl sulfide insertion product by a ratio of 1.6:1; propene/2-methyl-1-propene (1:1) favored the 2-methyl-2-propenethiolate cation by a ratio of 2:1; styrene/2-methyl-1-propene (1.4:1) favored the styrene insertion product by a ratio of 2.8:1.

Qualitative Rates of Olefin Insertions. Complex 1 (15–25 mg, 0.03–0.04 mmol) was dissolved in 0.8 mL of CD_3CN in a NMR tube. An olefin (3–5.0 equiv) was transferred to the NMR tube, and the tube was sealed under vacuum at −196 °C. Reactions were monitored by ^1H NMR spectroscopy upon warming the tube to 20 °C. The following reaction times were observed: insertions of ethene, (6 equiv) propene, (5 equiv), styrene (5 equiv), and 2-methylpropene (3 equiv), complete by the time the first NMR spectrum was recorded (<5 min); 2-methyl-2-butene (3 equiv), 80% complete after 8.5 min; acrylonitrile (11 equiv), 80% complete after 21 h; 2,3-dimethyl-2-butene (3 equiv), 80% complete after 6 days.

Attempted Reactions of Alkanethiolate Cations with Hydrogen or Deuterium. Each (alkanethiolato)molybdenum cation (20 mg, 0.03 mmol) was dissolved in 0.8 mL of CD_2Cl_2 in a NMR tube. Hydrogen (600 Torr) was transferred to the NMR tube, and the tube was sealed at −196 °C. Reactions were carried out at 20 °C initially, and later the mixtures were heated to 50 °C and finally 70 °C for several days. Reactions were monitored by ^1H NMR spectroscopy. Except for the reaction of the phenylethanethiolate cation, discussed previously,[6] no evidence was observed for the hydrogenolysis of the S–C bond in the thiolate ligand to form free hydrocarbons. Deuterium was added to the solution of the 2-methyl-2-propanethiolate cation, and the solution was heated at 30–40 °C for 2 weeks and then at 45 °C for 1 week. After this time, the solution contained 28% $[(CpMo)_2(S_2CH_2)(SC(CH_3)_3)]^+$ with the methyl groups of the *t*-BuS ligand 85% deuterated, 57% $[(CpMo)_2(S_2CH_2)(SCH_2CHMe_2)]^+$ with the methyl groups 53% deuterated, and the methylene group ca. 60% deuterated. The third complex present in solution was 1 (~15%).

Reactions of 1 with Olefins in the Presence of Oxygen. Complex 1 (200–300 mg, 0.3–0.5 mmol) was dissolved in 10 mL of CH_3CN in a Schlenk tube. An olefin (2–5 equiv of ethene, propene, 2-methylpropene, or acrylonitrile) and 300 Torr of O_2 gas were transferred to the Schlenk tube. The reaction mixtures were stirred at 20 °C for 1–6 days. Products were precipitated from solution with diethyl ether and purified by column chromatography on alumina, first with CH_3CN eluent to obtain the alkanethiolate cation and then with CH_3OH to obtain the secondary product. The latter were isolated in yields of 40–70%. Characterization data are given above. In the reaction with acrylonitrile, volatiles were vacuum-transferred to an NMR tube after 16 h, and water was identified as a significant product in the ^1H NMR spectrum. Control experiments were carried out to establish that water was not an impurity in the solvent or in the oxygen reagent. The ^1H NMR spectrum of the nonvolatile material in the reaction flask showed that $[Cp\overline{Mo(S_2C}H)(SCH_2CH(CN)S)MoCp]SO_3CF_3$ was the major molybdenum product; yield 70%.

Reaction of $[(Cp\overline{Mo)(\mu\text{-}S_2C}H)(\mu\text{-}SCH_2CH_2S)(MoCp)]BF_4$ with $NaBH_4$. The cationic complex (19 mg, 0.033 mmol) was dissolved in 0.8 mL of CD_3OD in an NMR tube. An excess of $NaBH_4/Al_2O_3$ was added to the tube, and the tube was sealed under vacuum at −196 °C. The tube was warmed to 20 °C. The reaction was complete in 20–30 min. ^1H NMR spectroscopy showed that the major product (~90% yield) was $(CpMo)_2(\mu\text{-}S_2CH_2)(\mu\text{-}SCH_2CH_2S)$.[18]

Reactions of $[(CpMo)_2(S_2CH_2)(SCH_2CH_2S)]BF_4$ (3).[9] (a) With $[(CpMo(\mu\text{-}S))_2(S_2CH_2)]_2(BF_4)_2$. The tetrameric dication (8 mg, 0.007 mmol) and **3** (8.2 mg, 0.014 mmol) were dissolved in 0.8 mL of CD_3CN in an NMR tube. The tube was sealed under vacuum at −196 °C. The tube was warmed to 20 °C and the reaction monitored by ^1H NMR spectroscopy. After 3 days at 20 °C the reaction was complete, and the ^1H NMR spectrum showed that an equal molar ratio of 1 and $[Cp\overline{Mo(S_2C}H)$-

$(SCH_2CH_2S)MoCp]^+$ was present.

(b) With O_2 or H_2O_2. Complex 3 (~15 mg, 0.020 mmol) was dissolved in CD_3CN, and an aqueous solution of H_2O_2 (~0.8 equiv) or gaseous O_2 (~1 equiv) was added. The NMR tubes were frozen at −196 °C, evacuated, and then sealed. Each of the reactions proceeded cleanly over a period of 2–4 days at 25 °C to form $[CpMo(S_2CH)(SCH_2CH_2S)MoCp]BF_4$, which was identified by NMR spectroscopy.

Reaction of $(CpMo)_2(S_2CH_2)(SCH_2CH_2S)$ with *tert*-Butylethene and Acid. $(CpMo)_2(S_2CH_2)(SCH_2CH_2S)$ (28 mg, 0.06 mmol) was dissolved in CD_3CN in an NMR tube, and triflic acid (1 equiv) and *tert*-butylethene (1.6 equiv) were added. The solution was degassed and sealed under vacuum. After 5 days, a small amount of $[(CpMo)_2(S_2CH)(SCH_2CH_2S)]^+$ (~20%) was observed by NMR spectroscopy but no *tert*-butylethane was detected.

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Reactions of $(C_5Me_5)Rh(PMe_3)(R)H$ with Electrophiles. Insertion of Unsaturated Molecules into Activated Carbon–Hydrogen Bonds

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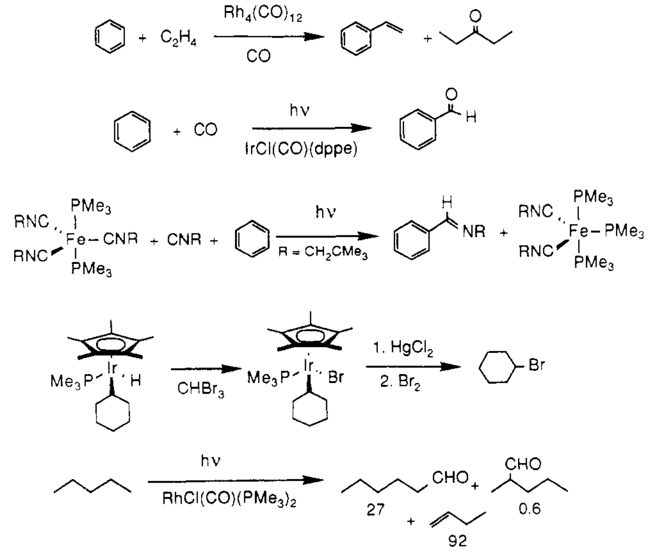
The complexes $(C_5Me_5)Rh(PMe_3)(aryl)H$ (aryl = C_6H_5, 2,6-$C_6H_3Me_2$) are found to react with several electrophiles. Treatment with CS_2 gives two products, the major species resulting from the elimination of benzene and formation of $(C_5Me_5)Rh(PMe_3)(CS_2)$. The minor product is formed by insertion into the Rh–H bond to give $(C_5Me_5)Rh(PMe_3)(Ph)(SCH{=}S)$. Reaction of the aryl hydride complex with PhNCS gives only the insertion product $(C_5Me_5)Rh(PMe_3)(Ph)(SCH{=}NPh)$. These two sulfur-bound derivatives react with either aniline or H_2S, respectively, to give $(C_5Me_5)Rh(PMe_3)(Ph)[SCH(SH)(NHPh)]$, which cleaves during isolation to give $(C_5Me_5)Rh(PMe_3)(Ph)(SH)$ and $PhNHCH{=}S$. Reaction of the aryl hydride complex with dimethyl acetylenedicarboxylate results in insertion of acetylene into the Rh–H bond, producing a mixture of the cis and trans vinyl complexes. HI cleaves the rhodium–aryl bond, and iodine induces both elimination of substituted styrene and iodination of the metal–xylyl bond in the cis complex. Treatment of the trans isomer with HI also cleaves the Rh–aryl bond, and iodine gives a mixture of products. The methyl complex $(C_5Me_5)Rh(PMe_3)(CH_3)H$ reacts with dimethyl acetylenedicarboxylate to give a mixture of cis and trans vinyl methyl complexes. Addition of iodine results in the formation of methyl iodide and $(C_5Me_5)Rh(PMe_3)[C(COOMe){=}CH(COOMe)]I$. *cis*-$(C_5Me_5)Rh(PMe_3)(2,6\text{-}C_6H_3Me_2)[C(COOMe){=}CH(COOMe)]$ crystallizes in the triclinic space group $P\bar{1}$ with $a = 8.928\ (5)$ Å, $b = 19.111\ (4)$ Å, $c = 8.590\ (2)$ Å, $\alpha = 94.21\ (2)°$, $\beta = 111.86\ (4)°$, $\gamma = 94.08\ (3)°$, $V = 1348.9\ (1.8)$ Å^3, and $Z = 2$. *trans*-$(C_5Me_5)Rh(PMe_3)[C(COOMe){=}CH(COOMe)](2,6\text{-}C_6H_3Me_2)$ crystallizes in the monoclinic space group $P2_1/n$ with $a = 15.090\ (2)$ Å, $b = 11.361\ (2)$ Å, $c = 16.886\ (4)$ Å, $\beta = 109.54\ (2)°$, $V = 2728.4\ (1.8)$ Å^3, and $Z = 4$.

Introduction

Many complexes have been discovered recently that form stable oxidative-addition adducts with carbon–hydrogen bonds of arenes and alkanes.[1] The next goal for the application of these reactions is the transformation of the M–C bond of the aryl and alkyl ligands to functionalized species prior to their elimination from the metal. Ultimately, the metal might be cycled back into the species that was found to activate the C–H bond, resulting in catalytic hydrocarbon functionalization.

The insertion of an adjacent unsaturated ligand into a metal–carbon bond has ample precedent in the organometallic literature and offers a pathway for transforming an activated hydrocarbon into a new organic group. Many molecules that activate C–H bonds have no such ligand in their coordination spheres, however. Furthermore, their coordinative saturation and lack of ligand lability prevents potentially reactive molecules in solution from coordinating to the metal. Consequently, only strong electrophiles have been found to be generally reactive with the oxidative-addition adducts of hydrocarbons with low-valent metals.[2]

Scheme I



Several notable exceptions have appeared in the literature recently,[3-5] including the insertion of CO, CNR, and olefins

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