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Desulfurization of Organic Sulfur Compounds Mediated by a Molybdenum/Cobalt/Sulfur Cluster

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Abstract: The bimetallic cluster $Cp'_2Mo_2Co_2S_3(CO)_4$ (**1**) reacts with organic sulfur compounds, e.g. ^tBuSH, $Me_2CHCH_2CH_2SH$, PhSH, ^tBuNCS, *cis*-2,3-dimethylthiirane, and thiophene, to give the cubane cluster $Cp'_2Mo_2Co_2S_4(CO)_2$ (**2**) in high yield. With the thiols, the organic products are the parent hydrocarbons. The thiophene desulfurization products are saturated and unsaturated C_1–C_4 hydrocarbons, and the thiocyanates produce RNC that reacts with **1** and **2** to form the carbonyl substitution products $Cp'_2Mo_2Co_2S_3(CO)_3(RNC)$ and $Cp'_2Mo_2Co_2S_4(CO)(RNC)$, respectively. The *cis*-2,3-dimethylthiirane produces *cis*-2-butene stereospecifically. The mechanistic implications are discussed, and the desulfurization reactions are compared to the hydrodesulfurization (HDS) reactions catalyzed by an alumina-supported Mo/Co/S composition.

Introduction

The characterization of complex, multicomponent heterogeneous sulfide catalysts continues to challenge the ingenuity of chemists.[1] Often, many phases are present and more than one active site or reaction channel may be present, and it is not always clear which phase catalyzes a given channel. The presence of more than one phase certainly complicates spectroscopic studies and renders detailed interpretation of classical kinetic studies virtually impossible.

The chemistry of transition metal clusters has helped the study of heterogeneous catalysts and catalysis in several ways.[2,3] Modes of ligand binding to multi-metallic sites are often the same on metal surfaces and clusters. Ligand transformations on clusters may be used as guides to similar reaction pathways on the heterogeneous catalysts. Clusters may be adsorbed on surfaces and their surface reactions may then be followed by various spectroscopic techniques.[4] The surface structures formed in these reactions are often catalytically active and comparison of the activity of catalysts prepared from organometallic cluster precursors with that of conventionally prepared catalysts can give useful information on active site structures and reaction mechanisms.[5]

A good example of a complex catalyst is the Co/Mo/S compositions (and the related Ni/W/S systems) used to catalyze the hydrodesulfurization (HDS) of fossil fuel feed stocks.[6] The catalyst is conventionally prepared by impregnating a high-surface-area alumina with ammonium molybdate and a cobalt salt in an aqueous medium. The impregnated alumina is then dried and calcined at ca. 500 °C. After calcining, the surface species consist of molybdenum oxide, cobalt oxide, and cobalt molybdate.[7] Some of the cobalt ions appear to occupy tetrahedral and octahedral holes in the alumina lattice.[7a,b] This pre-catalyst is then treated with hydrogen and a source of sulfur (H_2S, organic sulfur compounds, or the feedstock) at temperatures near 350 °C. This "sulfidation" step converts the molybdenum oxides into an "MoS_2-like" phase. Small crystallites of MoS_2 have been imaged with scanning electron microscopy (SEM), but some of the molybdenum present is not detected by SEM and is believed to be present as a two-dimensional sheet structure, similar to one "slab" of the MoS_2 layer structure, that lies flat on the support surface.[8] EXAFS data show that the average coordination environment of the molybdenum consists of a shell of six sulfur atoms at 2.4 Å and a second shell of about three molybdenum atoms at 3.2 Å.[9,10]

The role of the cobalt promoter is less well established. EXAFS spectra indicate the average cobalt coordination environment contains primarily sulfur atoms at a distance of 2.19 Å.[9b] Mössbauer emission spectroscopy shows at least three phases for the cobalt,[9c] one of which has been assigned to a "CoMoS" phase that was proposed to consist of cobalt atoms decorating the edges of the basal planes in the MoS_2-like structure. Although cobalt clearly prefers to bind to the edges of the basal planes in bulk MoS_2 crystals,[11] there is as yet no direct evidence for the proposed Co–Mo–S phase in the EXAFS spectra of the supported catalysts.

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The above-described "CoMoS" model for the HDS catalyst is largely due to the extensive work of Topsøe and co-workers and is now widely accepted.[9a,10a] However, the mechanistic role of the cobalt promoter is still unresolved,[6c] as are mechanistic details of the hydrodesulfurization reaction itself.

Recently, the coordination chemistry of thiophene has received a great deal of interest,[12,13] partly because thiophenic compounds are more difficult to desulfurize than thiols or alkyl sulfides. As a result of these investigations, much has been learned about the coordination modes of thiophene to transition metal centers, and several interesting C–S bond cleavage reactions have been observed that may have some relevance to the C–S bond activation step in the catalyzed HDS of thiophenic compounds.[14-16]

Most of the recent investigations of reactions of organic sulfur compounds with transition metal complexes have involved mononuclear derivatives, but several reports of C–S bond activation at dinuclear and polynuclear centers have appeared. Rauchfuss et al. showed that a thiaferracyclohexadiene is an intermediate in the desulfurization of thiophene with $Fe_3(CO)_{12}$.[14e] Boorman et al. studied the cleavage of a C–S bond of sulfides coordinated to two metal centers,[17] and Rakowski DuBois recently reported that a dinuclear molybdenum complex can desulfurize thiirane.[18] Jones et al. have observed cleavage of the C–S bond of thiophene in dinuclear Co and Rh complexes.[15e-h] Adams and co-workers have reported an extensive study of the reactions of cyclic sulfides with triosmium clusters in which both C–H and C–S bond cleavages may occur.[19]

We have been studying the reactions of the Mo/Co/S cluster $Cp_2Mo_2Co_2S_3(CO)_4$ (**1**) in the belief that this cluster may most closely approximate the metal composition and environment of any known mono- or polynuclear metal complex.[20,21] In fact, under typical heterogeneous conditions, this cluster appears to form the same catalytically active phase as the conventionally prepared HDS catalyst (as judged by reactor studies),[20-22] but the environment of the cobalt is quite different in the two catalysts (as judged by Co-EXAFS spectra).[20,23] In this paper, we report some desulfurization reactions of organic sulfur compounds in homogenous solution mediated by the cluster **1**.

Table 1. Reaction of $Cp'_2Mo_2Co_2S_3(CO)_4$ with *cis*-2,3-Dimethylthiirane (Relative Concentrations *vs.* Time)

time (h)	$Cp'_2Mo_2Co_2S_3(CO)_4$[a]	$Cp'_2Mo_2Co_2S_4(CO)_2$[a]	C_4H_8S[a]	C_4H_8[a]
0.0	1.00		8.45	
0.5	0.58	0.18	7.77	0.64
1.0	0.21	0.13	6.24	1.66
2.0	0.06	0.04	5.19	2.52

[a] Relative to the initial amount of $Cp'_2Mo_2Co_2S_3(CO)_4$, using *p*-xylene-d_9 as the internal standard.

Experimental Section

General Considerations. All manipulations and reactions were carried out under a nitrogen atmosphere by use of standard Schlenk line techniques or by use of a glovebag. All high-pressure, high-temperature reactions were carried out in a stainless steel Parr high-pressure reactor. Reagent grade solvents were dried and distilled prior to use: toluene, diethyl ether, and tetrahydrofuran from Na/benzophenone; dichloromethane and hexane from CaH_2. $Cp'_2Mo_2Co_2S_3(CO)_4$,[24] $Cp'_2Mo_2Co_2S_4(CO)_2$,[25] and *cis*-2,3-dimethylthiirane[26] were prepared by published procedures. All other reagents were purchased from Aldrich Chemical Co. ^1H and ^{13}C NMR data were collected on a Bruker AM-300 or Bruker WM-360 spectrometer. ^{31}P NMR data were collected on a General Electric GN-500 NB spectrometer. IR spectra were obtained on a Nicolet 5-DXB spectrometer. Mass spectra were collected on a Finnegan 4021 quadrupole mass spectrometer. GC-MS spectra were obtained on a VG-70-250-S high-resolution mass spectrometer. Elemental analyses were done by Galbraith Laboratories Inc., Spang Microanalytical Laboratory, or the Microanalysis Laboratory, University of Michigan. Thiophenes were purchased from Aldrich and purified according to the procedure outlined by Angelici.[16d]

Reaction of $Cp'_2Mo_2Co_2S_3(CO)_4$ (1) with $(CH_3)_3CSH$. $Cp'_2Mo_2Co_2S_3(CO)_4$ (approximately 10 mg), $(CH_3)_3CSH$ (0.014 mL, 0.12 mmol), and 0.7 mL of *p*-xylene-d_{10} were sealed in a NMR tube and heated in an oil bath at 115 °C. The NMR spectrum was taken periodically to follow the reaction; the only products were **2** and Me_3CH (Table 1S). The initial ratio of $Cp'_2Mo_2Co_2S_3(CO)_4$ to $(CH_3)_3CSH$ was 1:4.5. No other products were observed. Presumably 12% of the $(CH_3)_3CH$ (identified by its NMR spectrum: δ 0.89, $J_{HH} = 6.6$ Hz, methyl protons; the decet for the tertiary proton was not observed) is in the vapor phase since the normal boiling point is −12 °C.

Reaction of 1 with $(CH_3)_2CHCH_2CH_2SH$. $Cp'_2Mo_2Co_2S_3(CO)_4$ (0.117 g, 0.17 mmol) and $(CH_3)_2CHCH_2CH_2SH$ (1.0 mL, 8.0 mmol) were dissolved in 25 mL of toluene and refluxed for 1 h. The volatiles were collected in a liquid nitrogen trap and analyzed by GC-MS. $(CH_3)_2CHCH_2CH_3$, identified by a library match, was found to be the only volatile organic product.

Reaction of 1 with *cis*-2,3-Dimethylthiirane. $Cp'_2Mo_2Co_2S_3(CO)_4$ (approximately 10 mg), *cis*-2,3-dimethylthiirane (0.012 mL, 0.13 mmol), and 0.7 mL of *p*-xylene-d_{10} were loaded into an NMR tube with a J-Young valve and heated in an oil bath at 120 °C; the NMR spectrum was taken periodically to follow the reaction (Table 1). The initial ratio of $Cp'_2Mo_2Co_2S_3(CO)_4$ to *cis*-2,3-dimethylthiirane was 1:8.45. A GC-MS of the final solution showed only one isomer of 2-butene; the NMR spectrum confirmed it to be the *cis* isomer: δ 5.45 (qq, 2H, tertiary protons), 1.53 (dd, 6H, methyl protons), $^3J_{HH} = 4.7$ Hz, $^4J_{HH} = 0.9$ Hz.

Reaction of 1 with Cyclohexene Sulfide. $Cp'_2Mo_2Co_2S_3(CO)_4$ (0.168 g, 0.25 mmol), cyclohexene sulfide (0.20 mL of an approximately 85% solution, ~1.5 mmol), and 20 mL of toluene were refluxed overnight under a slow stream of nitrogen. A black insoluble powder was obtained (0.17 g). IR (KBr): 2923 (m), 2852 (mw), 1443 (m), 1261 (m), 1097 (m), 1027 (ms), 812 (s) cm^{-1}. Anal. Found: C, 30.35; H, 3.40; S, 22.68. The composition, $Cp'_2Mo_2Co_2S_4(C_6H_{10}S)$ ($C_{18}H_{24}Co_2Mo_2S_5$), requires C, 30.43; H, 3.40; S, 22.57.

Reaction of 1 with Thiophene. In a typical experiment, 100–200 mg of **1** were placed in the Parr reactor and 30 mL of thiophene added. The reactor was heated to the temperature desired and the contents stirred.

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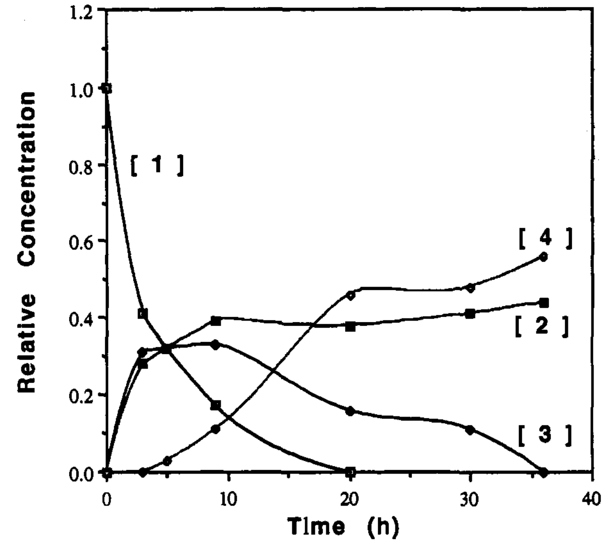


Figure 1. Relative concentrations of reactant and products during the desulfurization of ${}^tBuNCS$ by cluster **1**. The numbers refer to the compounds as numbered in the text.

Conversion to $Cp'_2Mo_2Co_2(CO)_2S_4$ (**2**) was observed at temperatures ranging from 110 to 150 °C. The lower the temperature, the longer the time needed for complete reaction. At 150 °C, a reaction time of 2 h ensured complete conversion of **1** to **2**. After allowing adequate time for the reaction to occur, the reactor was cooled to room temperature and transferred to a glovebag. The reactor was opened inside the glovebag and the reaction mixture transferred to a Schlenk flask. Some insoluble black residue remained in the reactor, and the color of the solution had changed from green-black to brown. The unreacted thiophene was evaporated under vacuum and the presence of **2** confirmed through its NMR and IR spectra. An analytically pure sample of **2** was obtained by column chromatography on alumina with dichloromethane as the eluant. Typically, isolated yields of 85–100% were obtained. For **2**: ^1H NMR (C_6D_6) 5.08 (m, 4H), 4.86 (m, 4H), 1.54 (s, 6H); IR (KBr) 1960, 1935 cm^{-1} (ν_{CO}); MS (EI) 652 (P^+), 624 ($P^+ - CO$), 596 ($P^+ - 2CO$). Anal. Calcd for $C_{14}H_{14}Mo_2Co_2O_2S_4$: C, 25.68; H, 1.93. Found: C, 25.78; H, 2.16. No reaction was observed when **1** was heated to 150 °C with an equimolar amount of thiophene in toluene solvent; cluster **1** was recovered unchanged. Apparently, the reaction rate is too slow with the lower concentrations of thiophene.

Thermolysis of 1. Toluene (40 mL) and 100 mg of **1** were placed in the reactor which was subsequently heated to 150 °C for 4 h. The reaction mixture was worked up as described above. The NMR of the product showed that no **2** had been produced and **1** was recovered unchanged.

Reaction of 1 with Thiophene and H_2. Thiophene (30 mL) and 100 mg of **1** were placed in the Parr reactor under a nitrogen atmosphere (glove bag) and then sealed. The reactor was subsequently charged with 15 atm of H_2 and heated to 150 °C for 2 h. An evacuated gas-collecting loop was connected to the cooled reactor, and a sample of the gases was collected in the loop placed in an isopentane/liquid N_2 slush bath. The excess H_2 was vented through an oil-bubbler and the condensed gases were analyzed by GC after being warmed to room temperature. Ethane, ethene, propane, propene, butane, and butene were observed. No butadiene was detected.

Reaction of 2 with CO. Toluene (40 mL) and 100 mg of **2** were placed in the reactor, which was subsequently charged with 69 atm of CO as above. The reactor was heated to 150 °C for 12 h. After workup as above, an NMR spectrum of the product in C_6D_6 showed a 20% conversion to **1**. A GC-MS spectrum of the volatile products confirmed the presence of OCS. Pressures of CO above about 69 atm could not be used due to the high pressure limit of the reactor (ca. 83 atm).

Attempted Reaction of 1 with CO, H_2, and Thiophene. Toluene (40 mL), thiophene (20 mL), and 100 mg of **1** were placed in the reactor which was subsequently charged with 69 atm of CO and 15 atm of H_2 as above. The reactor was heated to 150 °C for 12 h. Following workup of the product as above, an NMR spectrum of the product in C_6D_6 showed no conversion of **1** to **2**. After workup, cluster **1** was recovered unreacted.

Conversion of 1 to 2 with Methyl-Substituted Thiophenes. Cluster **1** (100 mg), 20 mL of toluene and 15 mL of one of the methyl-substituted thiophenes (2-methyl-, 3-methyl-, or 2,5-dimethylthiophene) were placed in the Parr reactor and heated to 150 °C for 3 h. The volatiles were then distilled under vacuum into a liquid nitrogen cooled trap, and the remaining solid was dissolved in C_6D_6. The conversion of **1** to **2** was determined by the areas of the CH_3 signals of **1** and **2** in the ^1H NMR spectrum. The following conversions were obtained: thiophene, 100%; 2-methylthiophene, 30%, 3-methylthiophene; 30%; 2,5-dimethylthiophene, 20%.

Attempted Reaction of 1 with Benzothiophene. A 100-mL, 3-necked flask equipped with a reflux condenser and a vacuum inlet was charged with 100 mg of **1** and 50 mL of toluene. An excess (~100 mg) of benzothiophene was added and the reaction mixture was refluxed for 12 h. No reaction was observed. The reaction mixture was transferred to the pressure reactor and heated to 165 °C for 4 h. No reaction was observed.

Reaction of 1 with Carbonyl Sulfide. $Cp'_2Mo_2Co_2S_3(CO)_4$ (0.070 g, 0.104 mmol) was dissolved in 40 mL of toluene and refluxed for 6 h under a slow stream of carbonyl sulfide. The solvent was removed and the product shown to be 50% $Cp'_2Mo_2Co_2S_3(CO)_4$ and 50% $Cp'_2Mo_2Co_2S_4(CO)_2$ by a comparison of the NMR spectrum with those of authentic samples.

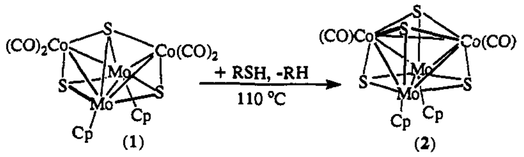
Reaction of 1 with *tert*-Butyl Isothiocyanate. $Cp'_2Mo_2Co_2S_3(CO)_4$ (approximately 10 mg), *tert*-butyl isothiocyanate (0.019 mL, 0.15 mmol), and 0.7 mL of *p*-xylene-d_{10} were loaded into an NMR tube with a J-Young valve and heated in an oil bath at 140 °C, the NMR spectrum being taken periodically to follow the reaction (Table 2S, Figure 1). The initial ratio of $Cp'_2Mo_2Co_2S_3(CO)_4$ to *tert*-butyl isothiocyanate was 1:9.58. The reaction was also conducted in an open system with 0.095 g (0.140 mmol) of $Cp'_2Mo_2Co_2S_3(CO)_4$ and 0.21 mL (1.66 mmol) of *tert*-butyl isothiocyanate in 30 mL of toluene heated to reflux under a slow stream of N_2. An NMR spectrum of the final reaction mixture showed a 3:2 ratio of the mono to bis isocyanide-substituted cubanes, **4** and **5**.

Reaction of 1 with Thiophenol. A 3-necked flask equipped with a condenser and a vacuum inlet was charged with 250 mg of **1**. Toluene (100 mL) and 1 mL of thiophenol were added and the reaction mixture was refluxed. The solution gradually turns brown and the reaction is complete after 7 h as indicated by IR. The volatiles were removed in vacuum. An NMR spectrum of the brown residue dissolved in C_6D_6 showed only cluster **2** was present. After recrystallization, cluster **2** was recovered in 80% yield. A GC-MS of the volatiles indicated the presence of benzene.

Reaction of $Cp'_2Mo_2Co_2S_3(CO)_4$ with PhSH and CO. $Cp'_2Mo_2Co_2S_3(CO)_4$ (0.109 g, 0.161 mmol), PhSH (2.00 mL, 18 mmol), and 50 mL of *p*-xylene were loaded into a Parr high-pressure reactor and pressurized to 69 atm of CO. The reactor was heated, with stirring, at 150 °C for 48 h. After the reactor was cooled, the volatiles were collected by distillation and analyzed by GC-MS (*n*-heptane as an internal standard). PhH (0.01 mmol), PhCHO (0.06 mmol), and two unknowns with molecular weights of 135 and 204 (ca. 0.03 and 0.02 mmol, respectively) were found. Sublimation of the remaining solid produced PhCOSPh (0.04 mmol), identified by GC-MS: *m/z* (relative intensity); 214 (3) $[PhSCOPh]^+$, 109 (6) $[PhS]^+$, 105 (100) $[PhCO]^+$, 77 (46) $[Ph]^+$.

Results

Cluster **1** undergoes very clean reactions with the thiols, RSH, R = *tert*-butyl, isopentyl, and phenyl. The only products detected (GC-MS, ^1H NMR) were the corresponding hydrocarbons, RH, and cluster **2** (eq 1). No rearrangement products or alkenes were observed. In the reaction with ${}^tBuSH$, the rate of disappearance of **1** may be fit to a pseudo-first-order expression with $k = 0.3$ h^{-1} under the conditions of the expreiment (115 °C, ${}^tBuSH$ in 4.5-fold excess).



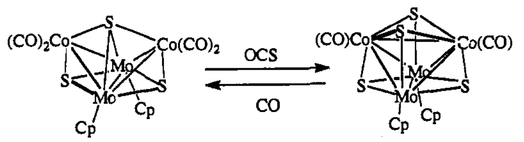
(1)

With *cis*-2,3-dimethylthiirane, the sulfur abstraction reaction was stereospecific; the only organic product was *cis*-2-butene. A black, insoluble solid was formed during the course of the reaction. No CO, M=S, or S—S stretching bands were found in the IR spectrum of the black powder.

Cluster **1** is also capable of abstracting sulfur from compounds which contain strong C=S double bonds (eq 2). The reaction of **1** with *tert*-butyl isothiocyanate, ${}^tBuN{=}C{=}S$, was followed by NMR spectroscopy in *p*-xylene-d_{10}. The initially formed ^{t}BuNC reacts further by substituting CO on the clusters. Formation of $Cp'_2Mo_2Co_2S_3(CO)_3({}^{t}BuNC)$ (**3**) and **2** was observed simultaneously (Table 2S, Figure 1). Compound **3** then slowly disappeared while the mono-isocyanide-substituted cubane cluster, $Cp'_2Mo_2Co_2S_4(CO)({}^{t}BuNC)$ (**4**), appeared. When the reaction was carried out in open system (refluxing toluene under a slow stream of nitrogen), both **4** and the bis(isocyanide) cluster, $Cp'_2Mo_2Co_2S_4({}^{t}BuNC)_2$ (**5**) were formed, an observation consistent with the dependency of the equilibrium among **2**, **4**, and **5** on the concentration of CO.

$$\left\{\begin{matrix} {}^{t}BuNCS \\ OCS \end{matrix}\right\} + 1 \longrightarrow 2 + \left\{\begin{matrix} {}^{t}BuNC \\ OC \end{matrix}\right\} \qquad (2)$$

Cluster **2** (50%) and, presumably, CO were formed when a toluene solution of **1** was heated to reflux under 1 atm of carbonyl sulfide, OCS, for 6 h. Under a high pressure of CO (70 atm, 150 °C) in a closed Parr reactor, a 20% conversion of **2** back to **1** and OCS was achieved after 12 h, thus demonstrating the equilibrium shown in eq 3.



(3)

Cluster **1** reacted with neat thiophene at 150 °C to give a quantitative conversion to the cubane cluster, **2**, and a small amount of some black insoluble material. The *quantitative* conversion of **1** to **2** and the fact that cluster **1** was recovered unreacted after heating a toluene solution of **1** to 150 °C demonstrate that **2** is not a decomposition product of **1** under these conditions. The desulfurization of thiophene was also conducted under H_2 (15 atm). In this instance, the black solid was not observed, and analysis of the head gases revealed the presence of ethane, propane, butane, and significant amounts of ethene, propene, and butene. (Our reactor design prevented us from obtaining a quantitative analysis of the volatile products.) No butadiene was observed in the reaction mixture.

Under CO and H_2 pressures of 10–28 atm at 150 °C, **1** reacted with thiophene to give **2** as the only isolated product. Increasing the temperature to 250 °C led to cluster fragmentation and reconstruction, and the new cluster, $Cp'_3Mo_3Co(CO)S_4$, was the only isolated product.[27] At higher CO pressures (69 atm), cluster **1** failed to react with thiophene at 150 °C.

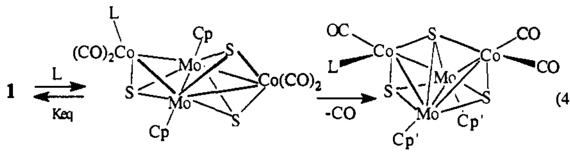
The conversion of **1** to **2** with methyl-substituted thiophenes was followed at 150 °C for a 3-h period. The observed conversions, thiophene (100%) > 2-methylthiophene (30%) ≅ 3-methylthiophene (30%) > 2,5-dimethylthiophene (20%), were used to obtain the relative rates. Cluster **1** did not react in toluene solution with benzothiophene at temperatures up to 165 °C.

Thiophenol, PhSH, was desulfurized by cluster **1** in refluxing toluene and **2** was isolated in 80% yield. A GC-MS of the organic fraction indicated that benzene was the sole organic product. Under these conditions, organic sulfides, e.g. PhSMe or $PhSCH{=}CH_2$, did not react with **1**.

In an attempt to produce a homogeneous catalytic desulfurization, **1** was reacted with thiophenol under 69 atm of CO at 150 °C in a high-pressure Parr reactor. Benzene (6% yield), benzaldehyde (36%), phenyl thiobenzoate (25%) and two unknowns with mass spectral parent ions at 134 (20%) and 204 (12%) were found in the reaction mixture. The fate of the cluster was not determined due to the instability of the products on the chromatography column.

Discussion

Desulfurization of Thiols. In the reactions of **1** with the thiols, RSH (R = ^{t}Bu, $Me_2CHCH_2CH_2$, or Ph), cluster **2** is formed in a stoichiometric reaction and the corresponding hydrocarbon, RH, is released. Serious attempts were made to detect intermediates in these desulfurization reactions so that the reaction pathways might be identified, but these efforts have not been successful. However, stronger nucleophiles, e.g. isocyanides and phosphines, add to cluster **1** to form the adducts **1·L**, in which the bond between a Co atom and the μ_4-bridging sulfide ligand is displaced by the added nucleophile, L (eq 4).[28,29] A CO ligand is displaced when the bond between the Co atom and the bridging sulfur atom is restored. It is reasonable to suppose that the reactions of **1** with sulfur-based nucleophiles follow the same pathway, but the lower nucleophilicity of the sulfur compounds translates into a much lower value for the pre-equilibirum constant, K_{eq} in eq 4. Higher temperatures are therefore necessary to affect CO substitution at a convenient rate, and the ensuing desulfurization reactions are fast compared to the rate of CO displacement at the higher temperatures. Thus, detectable concentrations of intermediates are not formed during the course of the reaction.



(4)

Even without the evidence that would be provided by the identification of intermediate complexes, some conclusions regarding the pathway(s) for desulfurization may be gleaned from the available data. The fact that the parent hydrocarbons are obtained from the thiols ^{t}BuSH and $Me_2CHCH_2CH_2SH$ and from *cis*-2,3-dimethylthiirane (see below) strongly suggests that carbocationic intermediates are *not* formed during the course of the reaction, i.e. the sulfur is not abstracted as SH^- or S^{2-}. Carbocationic intermediates would be expected to eliminate H^+ and form some alkene[30] or undergo skeletal rearrangement or isomerization in the case of *cis*-2,3-dimethylthiirane. Homolytic C–S bond cleavage is therefore a possibility for the thiols, as is an oxidative addition of a metal center to the C–S bond, followed by a reductive elimination or a homolysis of the C–M bond. It is interesting to note in this connection that deuterated alkanes were not observed when thiols were desulfurized in deuterated solvents, e.g. toluene-d_8.

Desulfurization of *cis*-2,3-Dimethylthiirane. The desulfurization of *cis*-2,3-dimethylthiirane was stereospecific; *cis*-2-butene was the sole organic product (eq 5). This process could be concerted or stepwise, provided the second C–S bond is cleaved quickly relative to the rate of *cis–trans* isomerization of the intermediate. The desulfurization of *cis*-2,3-dimethylthiirane by phosphines has been reported to occur by a stereospecific, concerted process known as a linear chelotropic reaction.[31] Although alkene episulfides are often used as sulfur atom donors to metal complexes, the commonly used ones, e.g. ethene, propene, or cyclohexene episulfides impart no stereochemical information via the product alkenes.[18c,19,32,33f]

The data in Table 1 show a clean pseudo-first-order behavior with $k = 1.4\ h^{-1}$ at 120 °C for the disappearance of cluster **1**, but

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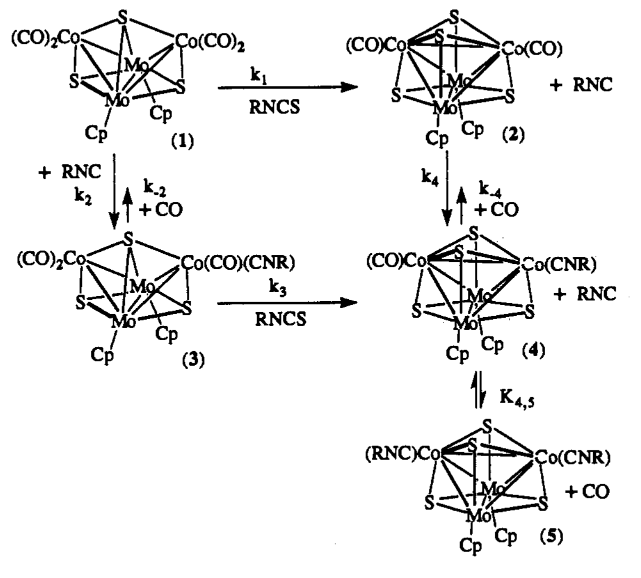
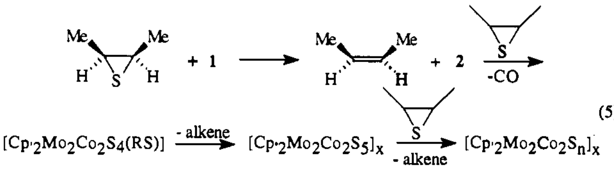
Scheme 1



it is obvious that only a fraction of the cluster product appeared as **2**. Furthermore, the amount of *cis*-2-butene produced was approximately 2.5 times the amount of cluster **1** reacted, and the consumption of the 2,3-dimethylthiirane was nearly 3.5 times the initial quantity of cluster **1**. The alkene sulfides are much more reactive sulfur atom donors than thiols and can react further with the initial product, cluster **2**, to form a black, insoluble product. An analogous black product has been prepared by reaction of **1** or **2** with cyclohexene episulfide in refluxing toluene. The microanalysis was consistent with the formula $Cp'_2Mo_2Co_2S_4(C_6H_{10}S)$ (assuming no O atoms to be present and a 1:1 Mo:Co ratio), i.e., CO was lost upon an apparent oxidative addition of the alkene episulfide to cluster **2**. Upon further reaction with excess alkene episulfide, these insoluble materials release alkene and form polysulfide clusters, $[Cp_2Mo_2Co_2S_n]_x$ ($n > 5$) (eq 5).[34]


(5)

Desulfurization of RNCS and OCS. Even multiply bonded sulfur is cleanly removed from alkyl isothiocyanates, RNCS, or carbonyl sulfide by reaction with **1** under mild conditions. The corresponding alkyl isocyanide, RNC, or CO is formed along with the cubane cluster **2**. Some information about the reaction pathway may be obtained from the concentration profiles shown in Figure 1. Early in the reaction, the rates of formation of cubane cluster **2** and substituted cluster **3** are nearly identical (see Scheme 1). Since the only source of ^{t}BuNC for the formation of **3** is the desulfurization step in which **2** is formed, the rate of CO substitution on **1** by ^{t}BuNC must be rapid compared to the rate of desulfurization of ^{t}BuNCS. Thus, two molecules of **1** are converted (to **2** and **3**) for each molecule of ^{t}BuNCS reacted, and the *initial* rate of disappearance of **1** is $2k_1$, where $k_1 = 0.30$ h^{-1} (assuming a pseudo-first-order rate law, Scheme 1).

As the concentration of **3** builds up, the rate of conversion, **3** → **4** becomes important and provides additional isocyanide to convert **1** into **3**. Once started, nearly all the desulfurization is channeled through the substituted cluster **3**, and the concentration of **2** levels off since it is not being produced at a competitive rate from **1**. Nearly all the substituted cubane cluster **4** is formed by the autocatalytic reaction of **3** desulfurizing ^{t}BuNCS, i.e. $k_4[^t\text{BuNC}] \ll k_3[^t\text{BuNCS}] < k_2[^t\text{BuNC}]$ (Scheme 1). The reaction pathways shown in Scheme 1 strongly suggest that the isothiocyanate is coordinated to the cluster only through the terminal sulfur atom since the isocyanide apparently is released to the solution immediately upon desulfurization. An η^1-bound RNCS ligand is also consistent with the general substitution scheme shown in eq 4.

The data plotted in Figure 1 were obtained from a reaction conducted in a sealed NMR tube, in which the concentration of CO increased with time and affected the final distribution of products. In an open system that allowed CO to escape, the final products were the mono- and disubstituted cubanes $Cp'_2Mo_2Co_2S_4(^t\text{BuNC})(CO)$ (**4**) and $Cp'_2Mo_2Co_2S_4(^t\text{BuNC})_2$ (**5**). The effects of these equilibria, coupled with the unknown concentrations of ^{t}BuNC and CO in solution, thwarted any quantitative fitting of the curves in Figure 1 to obtain values for the various rate constants. Compounds **4** and **5** have been prepared independently by reaction of **2** with 1 and 2 equiv of ^{t}BuNC, respectively, while **3** was prepared by reaction of **1** with 1 equiv of ^{t}BuNC.[28]

Desulfurization of isothiocyanates have been observed before.[33,35] Puddephatt *et al.* have studied a trimetallic system which behaves in a fashion similar to that of **1**: a weak adduct with the isothiocyanate is initially formed, followed by desulfurization with loss of isocyanide and then replacement of a carbonyl ligand by an isocyanide ligand.[35]

Reactions of 1 with Thiophenes. The reaction pathways involved in the desulfurization of thiophene have not been determined to date, and the reaction may proceed through quite different mechanisms depending on whether or not hydrogen is present, since hydrogen is required in this case for the formation of volatile hydrocarbons. In the absence of H_2, a trace of dark solid is produced that presumably contains the carbonaceous residue resulting from the desulfurization. In the presence of hydrogen, the desulfurization pathway must involve the hydrogenation of an intermediate complex since starting cluster **1** did not react with H_2 (100 psi, 150 °C) even in the presence of Me_3NO to facilitate the removal of CO. (A separate experiment showed that **1** did not react with Me_3NO.)

The cluster-mediated desulfurization has some elements in common with the HDS of thiophene over conventional Co/Mo/S catalysts. At low conversions, the primary organic products from the heterogeneous HDS of thiophene at 350 °C are 1-butene and its isomerization products, *cis*- and *trans*-2-butene.[36] "Cracking" occurs, so that some C_2–C_3 alkenes and alkanes are always produced. In the desulfurization mediated by cluster **1**, the proportion of cracking products appeared to be greater even though the reaction was conducted at a much lower temperature.

The cracking reaction may be rationalized if MC_4 metallacycles are formed during the desulfurization. There is ample precedent in the organometallic literature for the fragmentation of MC_4 rings into C_1, C_2, and C_3 hydrocarbons,[37] and metallacycles are formed in the reactions of thiophenes with metal surfaces and

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Table 2. Relative Binding Constants for Methyl Thiophenes on Metal Centers and Relative Rates of Desulfurization of Methyl-Substituted Thiophenes

compd	bonding type	2-MeT	3-MeT	2,5-Me2T	ref
A. Relative Binding Constants (1 for Thiophene)					
$CpRu(T)^+$	η^5-	6	7	35 (36)[b]	42
$CpRe(CO)_2(T)$	S-	33	2.5	230 (1090)[b]	*a*
$CpRu(CO)(PPh_3)(T)^+$	S⁻	4.1	6.3	2.8 (17)[b]	43a
$CoMoS/Al_2O_3$ cat.	η^5- (?)	1.6	1.7	2.5 (2.6)[b]	41
B. Relative Desulfurization Rates (1 for Thiophene)					
$CoMoS/Al_2O_3$ cat.		1.5	1.9	2.0	41
1/Al_2O_3 cat.		2.2	2.1	1.7	22b
1 (homogeneous)		0.3	0.3	0.2	*c*

[a] Calculated from the data in ref 43b. [b] Calculated as $[K_{eq}(2\text{-MeT})]^2$. [c] This work.

organometallic reagents.[14c,38,39] Cluster **1** reacts with alkynes to form an interesting cluster that contains a molybdenacyclopentadiene coordinated to the two cobalt atoms,[40] thus showing that cluster **1** can support metallacycle formation, although this type of complex was not detected in the course of the thiophene desulfurization reactions.

The relative rates of desulfurization of methyl-substituted thiophenes by cluster **1** do not parallel either the rates of HDS of methyl thiophenes over conventional catalysts or the relative binding constants of methyl thiophenes to transition metal centers. Methyl substitution increases the rate of thiophene HDS over conventional heterogeneous catalysts or from catalysts made from cluster **1** as a precursor (Table 2).[22b,41] Angelici has shown that this trend in rates follows the increase in equilibrium constants (K_{eq}, eq 6,Table 2) for displacement of η^5-thiophene (T) from

$$CpRu(\eta^5\text{-}T)^+ + Me_xT \rightleftharpoons CpRu(\eta^5\text{-}Me_xT)^+ + T \qquad (6)$$

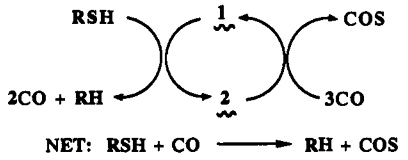
$CpRu(\eta^5\text{-}T)^+$ by methyl-substituted thiophenes, Me_xT,[42] and Zdrazil has shown that the adsorption coefficients on the conventional Co/Mo/S catalyst also increase with methyl substitution (Table 2).[41] For η^5-bound thiophenes in well-defined complexes, the effect of the methyl substituents on K_{eq} is additive ($K_{eq}[2.5\text{-}Me_2T] \approx K_{eq}{}^2[2\text{-MeT}]$) and nearly independent of substituent position on the ring. Since the adsorption coefficients on the heterogeneous catalysts follow the same pattern, η^5 bonding of the thiophenes to the catalyst surface is indicated.

Table 2 also gives the K_{eq} values for the analogous displacement series for S-bound thiophene on $CpRu(CO)(PPh_3)(T)^+$.[43a] We also include in Table 2 a set of calculated "pseudo" equilibrium constants for the reaction shown in eq 7. Angelici has shown that the displacement of methyl-substituted thiophenes, Me_xT, by PPh_3 from $CpRe(CO)_2(Me_xT)$ proceeds by a pathway in which the rate-determining step is the dissociation of the thiophene (eq 8).[43b] Hence, the K_{eq} for reaction 7 should equal the ratio of the first-order dissociation rate constants determined for the displacement reaction in eq 8, $K_{eq} = k_1(\text{T-dissociation})/k_1(Me_xT\text{-dissociation})$.

$$CpRe(CO)_2(\eta^1\text{-}T) + Me_xT \rightleftharpoons CpRe(CO)_2(\eta^1\text{-}Me_xT) + T \qquad (7)$$

$$CpRe(CO)_2(\eta^1\text{-}Me_xT) \underset{-\,Me_xT}{\overset{k_1}{\rightleftharpoons}} CpRe(CO)_2 \xrightarrow[PPh_3]{fast} CpRe(CO)_2(PPh_3) \qquad (8)$$

Scheme 2



In contrast to the behavior of the η^5-complexes, the effect of methyl substitution in the S-bound complexes is not at all additive, $K_{eq}[2,5\text{-}Me_2T] \ll K_{eq}{}^2[2\text{-MeT}]$. The electronic effect (increased basicity) of methyl substitution depends greatly on the substituent position and is highest at the 2-position. This beneficial effect is damped in the more bulky phosphine-substituted complex, $CpRu(CO)(PPh_3)(Me_xT)^+$, because the increased steric demand of the phosphine ligand cancels the increased basicity caused by methyl substitution. This cancellation effect is not observed in reactions of the less sterically congested complex $CpRu(CO)_2(Me_xT)$.[43] Therefore, we argue that a coordination site with sufficiently demanding steric repulsion could completely negate the positive effect of methyl substitution and could lower the binding constants and rates of desulfurization of the methyl thiophenes.

The data in Table 2 show that the rates of desulfurization of methyl-substituted thiophenes by cluster **1** do not follow the trends in K_{eq} exhibited by the S-bound or η^5-bound thiophene ligands in the model complexes. If the relative rates indeed reflect the "K_{ads}" of the thiophenes on the cluster, then (according to the above argument) steric effects are much more important on the cluster surface than on the mononuclear model compounds or even the surface of the heterogeneous catalysts. An alternate explanation is that the rate-determining step in the desulfurization by the cluster is later in the reaction pathway and is not related to the relative binding constants.

Toward a Homogeneous HDS Cycle: Desulfurization Reactions in the Presence of CO. In conventional HDS catalysis, sulfur is abstracted from the substrate and the surface of the catalyst is thereby sulfided. Removal of the surface-bound sulfur as H_2S replenishes the vacancies necessary for the next turnover cycle. Since cluster **1** cleanly abstracts sulfur from various organic sulfur compounds, it should be possible to construct a *homogeneous* catalytic cycle provided there were some means of converting the product cluster **2** back to the starting cluster **1**. Simple sulfur extraction with H_2 is not feasible in this case because cluster **1** contains two more carbonyl groups than cluster **2**. We therefore investigated the reactions of cluster **1** with mixtures of H_2 and CO. Cluster **2** did not react with a mixture of H_2 (8 atm) and CO (32 atm) at 150 °C. Increasing the pressure of CO to 69 atm gave a 20% conversion to cluster **1** and OCS (eq 3). The hydrogen was unnecessary and the same result was obtained in its absence. To our knowledge, this represents the first example of the use of carbon monoxide as a desulfurization agent for an organometallic sulfide.

The combination of the sulfur abstraction reaction (e.g. eq 1) and the conversion of cluster **2** back to cluster **1** (eq 3) constitutes a cycle for the catalytic "carbonyl desulfurization" (CDS) of organic sulfides (Scheme 2). However, starting materials were recovered after thiophene was heated with cluster **1** to 150 °C under 69 atm of CO and 15 atm of H_2 for 12 h. Apparently, the high CO concentration inhibits coordination of the thiophene to the cluster. In fact, under these conditions, CO adds to cluster **1** and forms an adduct, $Cp'_2Mo_2Co_2S_3(CO)_5$.[28b]

The reaction was repeated with thiophenol in the hope that the more nucleophilic thiol could compete with CO for a coordination site. Excess thiophenol did react with **1** at 150 °C in the presence of 69 atm of CO. The fate of the cluster was not established due to the decomposition of the organometallic products on the chromatography column, but cluster **2** was *not* formed in a significant quantity. The organic products were benzene (6%),

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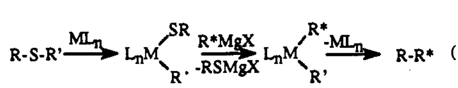
benzaldehyde (36%), the phenyl thiobenzoate, PhC(O)SPh (25%), in addition to diphenyl disulfide, PhSSPh (288%, all yields based on cluster **1**). These carbonyl-containing products strongly suggest the formation of benzoyl intermediates by insertion of CO into metal–phenyl bonds during the course of the reaction (eq 9, M_n represents the cluster). Cleavage of aryl–sulfur bonds on metal clusters has been observed previously;[44] the significance here is the implication for the addition of a metal center to the C–S bond.

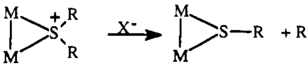
$$\begin{gathered} M_n(SR) \longrightarrow M_{n-1}(S)M\text{-}Ph \xrightarrow{CO} M_{n-1}(S)M\text{-}CO\text{-}Ph \\ \xrightarrow{PhSH} M_n(S) + PhCHO + PhC(O)SPh \end{gathered} \qquad (9)$$

Comparison with Other HDS Model Systems. Several metal-based systems have evolved for desulfurizing organic compounds, and several basic mechanistic pathways are now evident. One type of mechanism, common with low valent transition metal compounds, involves the oxidative addition of the metal into the C–S bond of allyl or aryl sulfides. The resulting metal–thiolate bond is then displaced by an anionic reagent, e.g. hydride or carbanion, and reductive elimination then gives a desulfurized product (eq 10).[45]



(10)

A second general mechanism is the nucleophilic displacement of a sulfur atom of an organic sulfide bonded to two or more metals (eq 11). In effect, the multi-hapto coordination mode of the sulfur increases its positive charge and makes the sulfur a better leaving groups.[17,46]

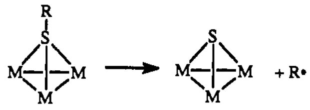


(11)

X = H, Cl, R, etc.

Desulfurization of thiophene has special characteristics because the complexing ability of the π-bonds rivals or exceeds that of the sulfur atom in this heteroaromatic structure. Initially formed η^2, η^4, or η^5 complexes may undergo oxidative insertion of the metal in C–H or C–S bonds,[12–16] but these reactions typically do not lead to desulfurization of the carbon skeleton. At higher temperatures, decomposition to metal sulfides and sulfur free fragments or complexes may occur; multi-hapto coordination of the sulfur atom may be required to promote the desulfurization process.[47] Sulfur is an excellent bridging ligand, and dimerization of mononuclear complexes through sulfur bridges is known to occur. Hence, the nuclearity of a complicated desulfurization process is not immediately apparent from the nuclearity of the starting complexes.[15e,h] Another special aspect of thiophene coordination is that η^4 or η^5 bonding renders the thiophene ring susceptible to attack by nucleophiles[12,14f,16f] or by proton sources.[48] Thus, valuable insights on the effects of thiophene coordination on its reactivity have been gained, but the mechanisms for the complete *desulfurization* of thiophenes remains an open question.

Finally, coordination of thiolates to metal centers can activate the C–S bond to homolytic scission (eq 12).[49] The C–S bond



(12)

energy is the difference between the energies of final and initial states, and stabilization of the sulfur fragment by coordination lowers the apparent C–S bond dissociation energy. In this connection, clusters that offer multi-nuclear coordination sites that promote the η^3-coordination mode for the thiolate sulfur are especially effective in activating homolytic cleavage of C–S bonds.[50]

The efficacy of cluster **1** for desulfurization reactions can be traced to two factors: (1) relative ease of substitution reactions on **1** (i.e. getting the substrate onto the cluster),[29b] and (2) the generation of multi-nuclear coordination sites by changing the coordination modes of the sulfide ligands (η^4 to η^3, etc.). Substitution reactions are facile because cluster **1** is electronically unsaturated (60 electrons *vs.* the 62 required for a butterfly cluster).[24] The abstracted sulfur ends up as an η^3 sulfide ligand in the product cluster **2**, and it is probable that multi-point attachment of the thiolate sulfur facilitates the C–S bond breaking. Although desulfurization reactions with **1** are considerably more facile than those mediated by a dinuclear $Cp_2Mo_2S_4$ derivative,[18c] and although the Co atom in **1** is most likely the site of initial nucleophilic attack of the sulfur-containing substrate, it is premature to ascribe any special role to cobalt *per se* in the desulfurization process. The overall structural and electronic features of the cluster are probably more important than the elemental identity.

Conclusions

A Mo/Co/S cluster is capable of cleaving strong carbon–sulfur bonds at temperatures several hundred degrees below that used in the conventional HDS of petroleum feed stocks. The C–S bond activation does not appear to be heterolytic, and the desulfurization of PhSH under CO suggests the intermediate formation of metal–phenyl bonds. The results furthermore suggest that C–S bond activation is not likely to be rate determining over a heterogeneous catalyst at 350 °C, and efforts to upgrade the activity of HDS catalysts should be focused on increasing the rate of sulfide removal from the catalyst surface. The sulfur abstraction reactions mediated by cluster **1** are exceptionally clean and may have synthetic value. Work directed toward elucidating the mechanism(s) of the reactions reported here is in progress.

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Supplementary Material Available: Tables 1S and 2S, relative concentrations of reactants and products in the reactions of ${}^tBuSH$ and ${}^tBuNCS$ with **1** vs time and Figures 1S and 2S, first-order kinetic plots for the reactions of ${}^tBuSH$ and *cis*-2,3-dimethylthiirane with cluster **1** (3 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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