Table III. Analysis of SiO_{ax} Bond Critical Points (r_b) in Silatranes[a]

n[b]	$R(Si–O_{ax})$, Å	$\rho(\mathbf{r}_b)$, au	$\nabla^2\rho(\mathbf{r}_b)$, au	d_{Si},[c] %
0	1.750 (1.709)	0.1021 (0.1096)	0.6737 (0.8216)	39.9 (40.2)
1	1.747 (1.685)	0.1034 (0.1177)	0.6774 (0.9063)	39.9 (40.2)
2	1.739	0.1063	0.6944	39.9
3	1.736	0.1090	0.6989	39.9

[a] For $n = 0, 1$ the values enclosed in parentheses arise from 6-31G(d)//6-31G(d) calculations. All other values are 6-31G(d)//AM1. [b] n = number of CH_2CH_2 bridges. [c] d_{Si} = (distance of $\mathbf{r}_b$ from Si atomic center)/$R(Si–O_{ax})$.

nature of the interaction, since such interactions are long range and fall off rather slowly.

Although the preceeding analysis is based for consistency on structures obtained with the AM1 method, similar results are obtained with the 6-31G(d) structures for $n = 0, 1$. As n increases in the 6-31G(d) structures, $\rho(\mathbf{r}_b)$ and $\nabla^2\rho(\mathbf{r}_b)$ decrease and d_{Si} increases (Table II). The $\rho(\mathbf{r}_b)$ and $\nabla^2\rho(\mathbf{r}_b)$ values are larger for these structures compared to the AM1 values because the SiN bond lengths are shorter in the 6-31G(d) structures. (Compare part b with a and d with c in Figure 1). Because of this shortening, it is expected that the 6-31G(d) $n = 2, 3$ structures will have shorter Si–N bond lengths and larger $\rho(\mathbf{r}_b)$ values than the corresponding AM1 structures.

An examination of the bonding in the $Si–O_{ax}$ bond in the silatranes allows the findings of Voronkov and co-workers[6,18] (as the Si–X bond weakens, the Si–N bond strengthens) to be tested. It has been shown that for a given bond, the value of $\rho(\mathbf{r}_b)$ increases with increasing bond order and bond strength.[24] For the AM1 structures, as n increases, $R(Si–O_{ax})$ decreases and $\rho(\mathbf{r}_b)$ and $\nabla^2\rho(\mathbf{r}_b)$ increase (Table III). The values of the ratio [$\rho(\mathbf{r}_b)$ for $Si–O_{ax}$]/[$\rho(\mathbf{r}_b)$ for Si–N] are 2.69, 2.76, 3.38, and 3.62 for $n = 0, 1, 2, 3$, respectively. Consequently, as n increases, more charge is accumulated in the $Si–O_{ax}$ bonding region and less in the Si–N bonding region. Thus, as n decreases from 3 to 0, the $Si–O_{ax}$ bond weakens and the Si–N bond strengthens, in agreement with the findings of Voronkov and co-workers.[6,18] An analysis of the $Si–O_{ax}$ and Si–N bonds in the 6-31G(d) structures ($n = 0, 1$) yields the same general conclusions as those found for the AM1 structures.

It is noteworthy that even though $\rho(\mathbf{r}_b)$ in the $Si–O_{ax}$ bond increases as n increases, the corresponding d_{Si} values remain constant (Table III). The electropositivity of Si relative to O_{ax} therefore appears to be insensitive to the number of CH_2CH_2 bridges in the system.

IV. Conclusions

The main findings of this study are the following:

(i) Even though the gas-phase silatrane Si–N internuclear distance is at least 0.25 Å longer than the corresponding distance in the solid, an Si–N bond critical point still exists in the gas phase. Thus, Si and N are directly bonded in the gas phase even for the $n = 3$ structure.

(ii) Only a small amount of energy is required to decrease the Si–N distance in hydroxysilatrane from the gas-phase value down to a value that is typical of silatrane crystal structures. Thus, it is easy to see how crystal forces are able to contract the Si–N distance.

(iii) As the number of bridges increases, the Si–N bond length increases and the $Si–O_{ax}$ bond length decreases. Concomitantly, $\rho(\mathbf{r}_b)$ in the Si–N bond decreases and $\rho(\mathbf{r}_b)$ in the $Si–O_{ax}$ bond increases. Therefore, the Si–N bond weakens and the $Si–O_{ax}$ bond strengthens.

Acknowledgment. This work was supported by grants from the Air Force Office of Scientific Research (90-0052) and the National Science Foundation (CHE-8911911). The calculations reported here were performed on the CRAY 2 at Kirtland Air Force Base, on the CRAY Y-MP at the San Diego Supercomputer Center, and on the North Dakota State University IBM 3090/200E.

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Deuterium Substitution of Thiophenes by D_2: Catalytic Role of a Hydrosulfido-Bridged Molybdenum Complex

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The cationic complex $[(MeCpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SH)]SO_3CF_3$ (1; Cp′ = MeCp = $C_5H_4CH_3$) catalyzed the deuterium substitution of thiophene, methylthiophenes, and benzothiophene in dichloromethane solution at D_2 pressures of 3–4 atm and temperatures of 25–70 °C. Substitution patterns were similar to those observed for deuteration reactions carried out over sulfided molybdenum surfaces. Possible roles for 1 in the homogeneous catalytic reaction have been investigated. Evidence has been observed for the activation of D_2 by 1; when 1 was stirred under a mixture of H_2/D_2, HD was produced. However, no evidence for the interaction of 1 with thiophenes has been observed. A mechanism has been proposed for the thiophene deuteration, which involves the conversion of D_2 to D^+ by 1, followed by the electrophilic aromatic substitution of D^+ on thiophenes. Substitution patterns and kinetic information are consistent with an acid-exchange pathway. Implications of this mechanism for the surface-catalyzed reactions are discussed.

Introduction

An important characteristic of the tetrasulfur-bridged cyclopentadienylmolybdenum complexes is their ability to activate molecular hydrogen.[1-9] In some cases these reactions with hydrogen have resulted in the isolation of complexes with S–H ligands.[1-5] This reactivity appears

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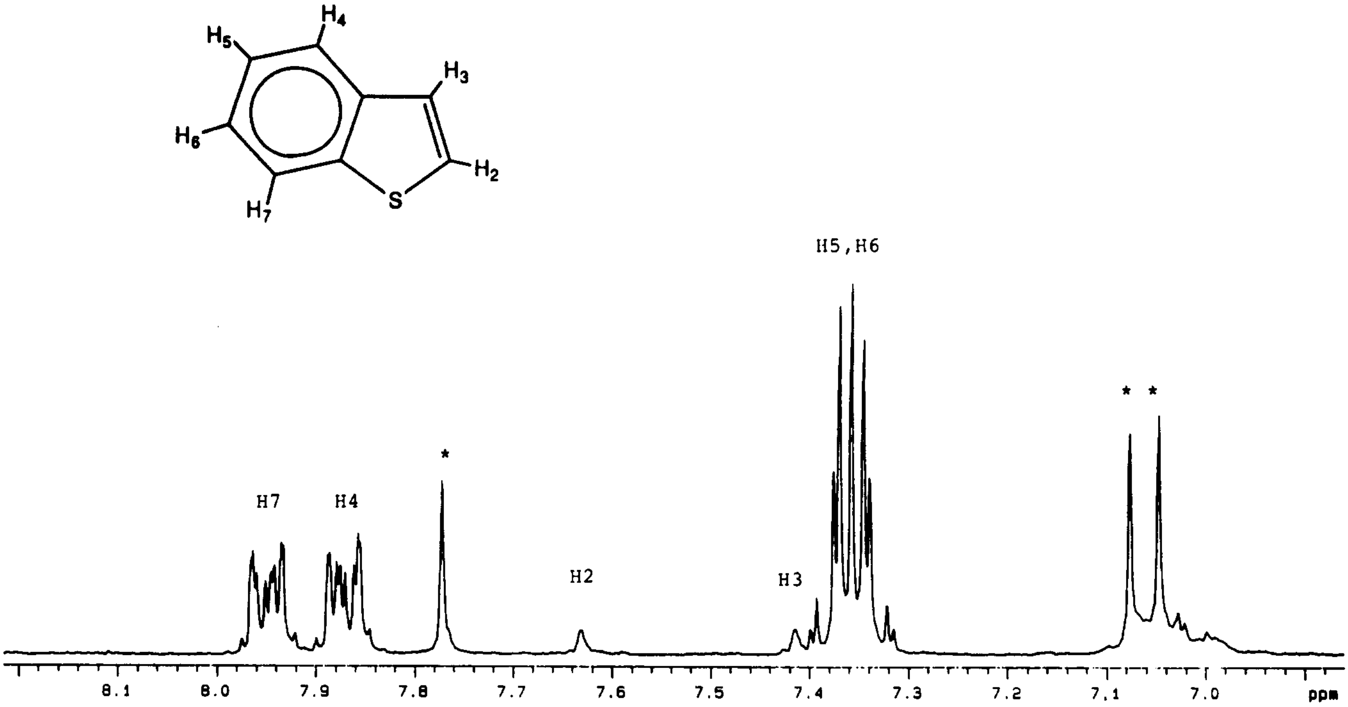

Figure 1. 300-MHz ^{1}H NMR spectrum of benzothiophene deuterated at the 2- and 3-positions recorded in acetone d_6.[41] Sample was isolated from the reaction of benzothiophene with deuterium in the presence of 1. Resonances marked with an asterisk correspond to a second product formed in this reaction that has not yet been identified.

to be particularly relevant to the proposed reactions of the heterogeneous sulfided molybdenum surfaces used in the hydrodesulfurization of thiophenes and related sulfur heterocycles.[10,11] An unresolved mechanistic question in the HDS reactions is the mode of interaction between the thiophene ring and the molybdenum sulfide surface. In order to gain insight into this question, the patterns of deuterium substitution into thiophene rings have been studied with use of the heterogeneous catalysts under relatively low deuterium pressures and mild temperatures where hydrogenolysis reactions do not occur.[12-18] Similar studies of deuterium substitution patterns have been carried out with discrete model complexes containing π-bonded thiophene ligands.[18-20] In these latter systems, deuteriomethanol was used as the deuterium source.

We have found that the synthetic dinuclear complex $[(\mathrm{MeCpMo})_2(\mathrm{S_2CH_2})(\mu\text{-S})(\mu\text{-SH})]\mathrm{SO_3CF_3}$[21] catalyzes the H/D-exchange reaction of thiophenes under deuterium pressure. There are few soluble organometallic catalysts for the exchange reaction of D_2 with aromatic heterocycles.[22,23] We report here our observations on the relative substitution rates of various positions in the thiophene rings, comparisons of our data with those reported for the heterogeneous catalysts, and our proposal on the mechanism involved.

Results and Discussion

Patterns of Deuterium Substitution. When 1 was stirred in dichloromethane at 50 °C under deuterium pressure (3–4 atm) in the presence of thiophene (2–20 equiv), evidence for the slow incorporation of deuterium into the thiophene ring was observed. The reaction has been followed by ^{1}H NMR spectroscopy, and the deuterated thiophene has also been characterized by mass spectroscopy. At early stages of the reaction (1–2 days under conditions reported in the Experimental Section), the 2,5-positions in the thiophene ring were preferentially and completely substituted. After reaction periods of several days, all four positions in the ring were deuterated. No change was observed in the NMR resonances of 1 during the course of the reaction, and no intermediates were detected. A three-line pattern, assigned to HD, was observed in the spectrum at 4.6 ppm (J = 45 Hz) as the reaction proceeded. The deprotonated form of 1. $(\mathrm{MeCpMo}\mu\text{-S})_2\mathrm{S_2CH_2}$[6] (2), did not catalyze the HD exchange of thiophene under similar conditions.

Methyl-substituted thiophenes also underwent deuterium substitution in the presence of 1 under similar con-

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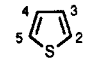
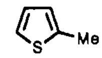
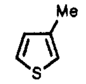
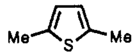
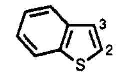
Table I. Percent Deuterations of Thiophenes

	D_2 + complex 1[a]		excess acid	D_2 + Mo/Al_2O_3[e]	
	$D_{2,5}$	60	55[c]	$D_{2,5}$	96
	$D_{3,4}$	<10	<10[c]	$D_{3,4}$	5
	D_5	68		D_5	92
	D_4	27		$D_{3,4}$	25
	D_3	45			
	D_5	66		$D_{2,5}$	90
	$D_{2,4}$	42[f]		D_4	4
	$D_{3,4}$	47		$D_{3,4}$	89
	D_2	>90[b]	70[d]		37[g]
	D_3	>90	79[d]		25

[a] 1.5×10^{-2} M 1, $(3-4) \times 10^{-2}$ M thiophene, ~3 atm of D_2 in CD_2Cl_2 at 50 °C for 20 h. [b] 1.0×10^{-2} M 1, $(3-4) \times 10^{-2}$ M benzothiophene, ~3 atm of D_2 in CH_2Cl_2 at 70 °C for 1 month. [c] Excess CF_3CO_2D; 1.6×10^{-1} M thiophene and 1.6 M trifluoroacetic acid-*d* in CD_2Cl_2 at 50 °C for 50 min. [d] Excess D_2SO_4; 3.7×10^{-2} M benzothiophene in 5 mL of CD_3OD plus 2.5 mL of 95% D_2SO_4 in D_2O at 50 °C for 1 week. [e] Estimate for the percent deuteration achieved over a molybdenum/Al_2O_3 catalyst at 200 °C.[19] [f] The resonances for the 2- and 4-protons are coincident in the 300-MHz NMR spectrum.[44] On the basis of percent D substitution in the 5-position, most of the deuteration of the 2,4-protons is assumed to occur at position 2. [g] Percent deuteration achieved over a $Co_{0,25}$-MoS catalyst at 300 °C.[18]

ditions. The 2- and 5-positions were again preferentially substituted if these sites were not methylated. No evidence was observed by NMR for the incorporation of deuterium into the methyl groups. Methylation of the thiophene ring appeared to increase the rate of deuterium substitution at the other positions of the ring. For example, the substitution of the 3,4-positions in 2,5-dimethylthiophene was observed to proceed with a half-life of ~24 h (see the Experimental Section for catalyst concentrations), while no significant substitution of the 3,4-positions was observed in thiophene over a 24-h period under similar conditions. A summary of typical product distributions for these homogeneous reactions is given in Table I. As indicated in the table, benzothiophene reacted very slowly with deuterium in the presence of 1 at 70 °C to form a product that was preferentially deuterated in the 2- and 3-positions. The ^1H NMR spectrum of the deuterated product isolated after ca. 1 month (Figure 1) shows the reduced intensities of the H_2 and H_3 resonances.

The distributions of deuterated thiophenes produced over the heterogeneous Co/Mo HDS catalysts have been estimated by Angelici et al.,[19] and these data are included in Table I. The trends in the relative rates of substitution for the homogeneous and heterogeneous systems are similar. In addition to the preferential substitution of 2,5-positions in thiophene and 2,3-positions in benzothiophene, the trends of increased rates of deuterium substitution for the methylated rings are similar in the two systems.

Mechanism of Deuterium Substitution. The protonated complex 1 is known to undergo reversible reactions with alkenes involving regioselective insertion into the S–H bond.[24] A reversible insertion of a double bond of thiophene into an S–D ligand of 1 could lead to selective deuterium incorporation. This pathway, however, seems unlikely because of the delocalized-aromatic character of the thiophene ring. Such an insertion product has not been detected spectroscopically. An alternate mechanism for deuterium incorporation into the thiophene ring is suggested by the reactivity of cationic molybdenum sulfide complexes under hydrogen.

Scheme I

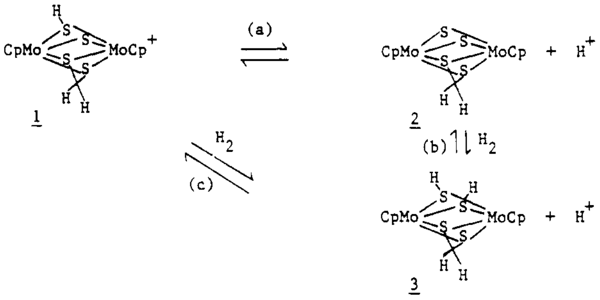
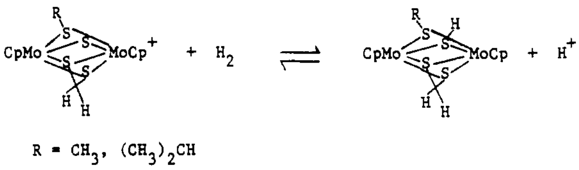


Table II. Observed Rate Constants for Reactions of Thiophenes (3×10^{-2} M) with D_2 (~3.5 atm) Catalyzed by 1 at 50 °C in CD_2Cl_2

substrate	H	[1]	$k_{obs} \times 10^5$, s^{-1}
thiophene	2,5	1.5×10^{-2}	1.1 ± 0.2
		8.4×10^{-3}	0.47
		1.5×10^{-3}	0.11
2,5-dimethylthiophene	3,4	1.5×10^{-2}	0.78

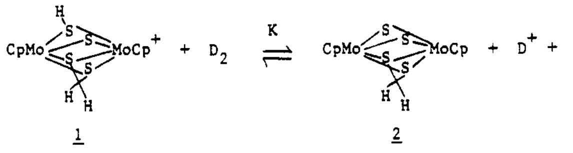
Dinuclear complexes structurally similar to 1 have been found to react with H_2 as shown in eq 1.[4,5,25] Reaction 1 has not been directly observed when R = H. However,



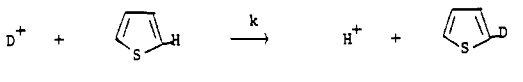
(1)

the protonated complex 1 does catalyze the slow formation of HD from a mixture of hydrogen and deuterium, and reaction 1 seems a likely pathway for this exchange. The acid dissociation constant for 1 has been determined to be 4.0×10^{-9} in acetonitrile at room temperature,[21] and therefore the reactivity of hydrogen with 2, the deprotonated form of 1, should also be considered. Studies have shown that 2 serves as a very efficient catalyst for H/D exchange under H_2/D_2 mixtures. Additional evidence for the activation of hydrogen by 2 has been discussed previously,[3] and a product of hydrogen activation containing hydrosulfido ligands, 3 in Scheme I, has been postulated, but not detected spectroscopically. Scheme I summarizes the equilibria proposed for 1 under hydrogen or deuterium pressure. The scheme provides a potential pathway by which 1 can activate deuterium and produce a steady-state concentration of D^+ under deuterium pressure.

We propose that the deuterium substitution reactions with thiophenes catalyzed by 1 involve the equilibria in Scheme I. While equilibrium a is the major source of H^+ (or D^+) in solution,[26] a combination of equilibria (eq 2) is



(2)



(3)

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required to take into account the conversion of D_2 to D^+. The D^+ ion is proposed to undergo an electrophilic aromatic substitution on thiophene (eq 3). The expression resulting from the steady-state treatment of D^+ simplifies to eq 4 if we assume that the reverse reaction of eq 2 is

$$\text{rate} = k[D^+][\text{thiophene}] = \frac{kK[1][\text{thiophene}][D_2]}{[2][HD]} \qquad (4)$$

much faster than reaction 3. Alternatively, one can assume that equilibrium 2 is established rapidly; this equilibrium is known to lie far to the left. Kinetic studies of the deuterium substitution reaction were carried out in sealed NMR tubes containing excess (2–3 atm) D_2, 3×10^{-2} M thiophene, and variable concentrations of catalyst in CD_2Cl_2 solvent. The kinetic data have confirmed that the thiophene deuteration shows a first-order dependence on thiophene under these conditions. Observed rate constants are reported in Table II. A first-order dependence on 1 was also established over a concentration range of 10^{-3}–10^{-2} M. Although the pseudo-first-order NMR tube experiments did not permit a large variation in deuterium pressure, a qualitative dependence on $[D_2]$ was also observed when deuterium pressure was varied over the range of ca. 3.4–1.4 atm. A rapid preequilibrium of the type shown in eq 2 implies that the rate of the reaction should be inversely dependent on [2]. Consistent with this proposal, the deuteration reaction was found to be inhibited by the addition of 2. For example, in the presence of 0.2 equiv of 2, deuterium incorporation into the thiophene was completely inhibited for several hours.[27] The inhibition is attributed to a shift in the acid dissociation equilibrium (a) shown in Scheme I. If the mechanism for deuterium incorporation involved reversible addition of the S–D ligand in 1 to the heterocycle, the presence of 2 would not be expected to significantly alter the rate.

The proposed mechanism implies that the patterns (and rates)[28] for deuterium substitution in thiophenes in the reactions catalyzed by 1 should parallel those observed for reactions with deuterated acids. In aqueous solution the exchange of thiophene with D_2SO_4 has been shown to proceed at the 2,5-positions at a rate approximately 10^3 greater than exchange at the 3,4-positions.[29] Under conditions similar to those used for the molybdenum-catalyzed reaction, dichloromethane solutions at 50 °C, the reaction of excess trifluoracetic acid-*d* with thiophene also resulted in selective exchange of the 2,5-positions. We have also confirmed that the gross substitution pattern of benzothiophene with D_2SO_4 in methanol corresponds to that catalyzed by the molybdenum complex 1, with initial exchange of the 2- and 3-positions in the heterocycle.[30]

Theoretical calculations have shown that the 2,5-positions in thiophene and the 2,3-positions in benzothiophene are the sites of highest π-electron density within these molecules;[31,32] other experimental work has verified that thiophene readily undergoes electrophilic substitution at these positions.[33] However, it is interesting to note that thiophene also undergoes nucleophilic attack preferentially at the 2,5-positions.[34] The dual reactivity of the 2- and 5-carbons in this heterocycle toward both electrophiles and nucleophiles has been attributed to similar characteristics for the LUMO and HOMO of the molecule.[35] Similarly, benzothiophene undergoes base-catalyzed, as well as acid-catalyzed H/D exchange at the 2- and 3-positions.[29,30] It is clear that the pattern of deuterium substitution of thiophenes observed for the heterogeneous Co/Mo/S catalysts cannot provide mechanistic information on the electronic characteristics of the deuterium-exchange mechanism.

The results obtained in this study also suggest that little information on the mode of thiophene interaction with the heterogeneous catalyst surface may be obtained from a study of deuterium substitution patterns. In the present system, the incorporation of deuterium into the aromatic heterocycles appeared to occur in the absence of a bonding interaction between the molybdenum sulfide complex and the thiophene ring. The heterogeneous catalysts are known to contain acidic sites,[36–39] and a similar activation of hydrogen to generate protons that react with nonchemisorbed thiophene may also take place with the heterogeneous catalysts. This suggestion is consistent with recent conclusions that the ability of a series of heterogeneous HDS catalysts to hydrogen exchange thiophene does not correlate with their relative HDS activities.[40]

Summary. The molybdenum complex 1 catalyzes the reaction of D_2 with thiophenes by a mechanism proposed to involve electrophilic aromatic substitution of D^+ on the heterocycle. This synthetic system can be compared with η^5-bonded thiophene complexes that have been deuterated by deuteriomethanol. The latter reactions are base-catalyzed and involve nucleophilic attack on the activated thiophene ligand. Both systems result in preferential substitution of the 2,5-positions in the ring and provide potential models for the H/D exchange observed for the heterogeneous Co/Mo catalysts. It was suggested several years ago that deuterium substitution patterns observed for HDS catalysts may provide information on the mode of thiophene interaction with the catalyst surface.[14–16] However, the model system discussed in this paper provides an example of HD exchange that does not require a bonding interaction of the heterocycle with the molybdenum sulfide catalyst.

Experimental Section

Materials and Instrumentation. $[(MeCpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SH)]SO_3CF_3$[21] (1) and $(MeCpMo\text{-}\mu\text{-}S)_2S_2CH_2$[6] (2) were prepared according to published procedures. Thiophene was distilled from CaH_2 before use. The 2- and 3-methylthiophene, 2,5-dimethylthiophene, benzothiophene, and all deuterated sol-

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(26) *K* values for equilibria a and b are both known to be small,[21] so *K* is very small for equilibrium c, the sum of a and b. The stoichiometric reaction of deuterated 1 with thiophene (1 equiv) under vacuum at 50 °C does produce some thiophene deuterated in the 2,5-position (approximately 8% over 4 days).

(27) Complex 2 is known to react slowly with CH_2Cl_2 under H_2 to form $(MeCpMoS_2CH_2)_2$ and 2 HCl.[6] After ~10–12 h, under deuterium pressure, we began to observe evidence for deuterium substitution of thiophene, presumably due to the formation of DCl in the reaction described above. Over a period of 10–20 h the Cp resonance for $(MeCpMoS_2CD_2)_2$ (5.7 ppm) increased in intensity in the NMR spectrum.

(28) We have not attempted to compare second-order rate constants for the two systems since a value for the acid dissociation constant of CF_3CO_2D in CH_2Cl_2 was not found in the literature.

(29) Ostman, B.; Olsson, S. *Ark. Kemi* **1960**, *15*, 275.

(30) The gross pattern of deuterium substitution of benzothiophene at the 2,3-positions is observed for both base-catalyzed and electrophilic exchange. Studies seem to indicate that the former pathway results in slightly higher substitution at the 2-position while the latter pathway results in a slight preference for H_3 exchange. Scrowton, R. M.; *Adv. Heterocycl. Chem.* **1981**, *29*, 171. Relative rates of substitution of the 2- and 3-positions in benzothiophene have not yet been determined for the model system involving 1.

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vents were purchased from Aldrich and used without further purification. Dichloromethane and *tert*-butyl chloride (Aldrich) were distilled from CaH_2. Deuterium gas (99.8% D) was purchased from Isotech Inc. The 95% D D_2SO_4 solution in D_2O and the 95% D CF_3COOD (Aldrich) were used without further purification.

^1H NMR spectra were obtained on a Varian VXR-300 NMR spectrometer. Chemical shifts were referenced to $Si(CH_3)_4$ by using the deuterated solvent as a secondary reference. Mass spectra were obtained on a VG Analytical 7070 EQ-HF mass spectrometer.

Deuterium Exchange Reaction of Thiophene Catalyzed by 1. Complex 1 (0.010 g, 0.016 mmol) was placed in an NMR tube. A thiophene (0.032 mmol) and *tert*-butyl chloride (0.5 μL) were syringed into 1 mL of CD_2Cl_2, and the resultant mixture was added to the tube. The solution was freeze–pump–thaw degassed three times and charged with 1 atm of D_2 at 77 K. The frozen sample was flame-sealed and thawed, and an initial ^1H NMR spectrum was taken. The tube was placed in a 50 °C oil bath, and the reaction was monitored by NMR spectroscopy. Resonances in the ^1H NMR spectra were integrated and normalized relative to the *tert*-butyl chloride signal, which was used as a *relative* internal standard. In the reaction of 2-methylthiophene with 1 and D_2, the chemical shifts for MeCp and methylthiophene resonances coincided at 2.46 ppm; resonances for a ring hydrogen and the Cp ligand overlapped (6.8 ppm). In this case the volatiles were vacuum-distilled after the reaction. By comparison of the ^1H NMR spectra before and after distillation, percent deuteration of the originally obscured hydrogen in the spectrum could be estimated. Typical deuteration percents are given in Table I. The spectra showed that there was no deuterium incorporation into the methyl groups of the thiophene. The NMR spectrum of the molybdenum complex recovered after the reaction was unchanged.

Reactions with a large excess of thiophene (20 equiv/equiv of 1) with excess deuterium have been carried out in a Schlenk flask. Aliquots were analyzed periodically by NMR. The observation of 45% deuteration at the 2,5-positions after 3 days further confirmed the catalytic nature of this reaction.

Deuterium Exchange Reaction of Benzothiophene Catalyzed by 1. Complex 1 (0.034 g, 0.053 mmol), dissolved in 5 mL of CH_2Cl_2, and benzothiophene (0.025 g, 0.186 mmol) were placed in a Schlenk tube. The solution was freeze–pump–thaw degassed three times and charged with 700 mm of D_2 at 77 K. The tube was placed in a 70 °C oil bath and was allowed to stir for approximately 1 month. After the reaction mixture was cooled to room temperature, the solvent was removed and the remaining solid was chromatographed on Al_2O_3 with CH_2Cl_2. The benzothiophene eluted before the molybdenum complexes. The ^1H NMR spectrum of the product was recorded in acetone-d_6.[41] Integrations of the benzothiophene resonances showed constant relative values for all protons except those in the 2- and 3-positions. Percent deuterations of these are given in Table I. A new organic product (or products) was also observed in the NMR spectrum with multiplets at 7.06 and 6.86 ppm and a singlet at 7.78 ppm. This product has not yet been identified.

Kinetic Measurements of Deuterium Exchange of Thiophene. A CD_2Cl_2 solution of complex 1, 10^{-2}–10^{-3} M, and thiophene, (3–4) × 10^{-2} M, was placed in an NMR tube, and an internal standard of *tert*-butyl chloride (1 μL) was added by syringe. The solution was freeze–pump–thaw degassed three times, and 1 atm of D_2 was added at −196 °C. The tube was flame-sealed and placed in a 50 °C oil bath. The reaction tubes were kept in a stationary oil bath and shaken only periodically. Similar deuteration experiments carried out in Schlenk tubes at 50 °C with constant stirring showed no differences in the observed rate data. NMR spectra were recorded at room temperature at periodic time intervals (every 3–4 h) over approximately 30 h. The thiophene resonance of interest was integrated relative to the *tert*-butyl chloride signal[42] with a pulse delay parameter of 20 s between NMR irradiations. The fraction of deuteration that occurred, F, was determined by comparing the normalized integration of this resonance with that at time 0. Plots of ln $(1 - F)$ vs time for several runs thru 60–80% deuteration were linear with correlation coefficients in the range 0.98–0.99+. Observed rate constants are given in Table II.

Reaction of Thiophene with Excess Trifluoroacetic Acid-*d*. Thiophene (10 μL, 0.125 mmol) was syringed into 0.8 mL of CD_2Cl_2 and the mixture placed in an NMR tube. The solution was freeze–pump–thaw degassed three times, and then deuterated trifluoroacetic acid (100 μL, 1.25 mmol) was vacuum-distilled into the tube at 77 K. The tube was sealed under vacuum at −196 °C. Approximately 5 min elapsed between the time the sample was thawed and data collection in the 50 °C probe was begun. The reaction was followed by NMR spectroscopy over a period of 50 min (55% of 2,5-positions deuterated). The 2,5-thiophene resonance was integrated and normalized relative to the proton impurity in CD_2Cl_2 or relative to the resonance of the 3,4-position of thiophene. Rates were very dependent on the amount of water impurity in the sample, and this varied considerably for commercial sources of CF_3CO_2D. For the most anhydrous system, the plot of ln $(1 - F)$ vs time was linear with a correlation coefficient of 0.996 and a slope, k_{obs}, of 2.6 × 10^{-4} s^{-1}.

Reaction of Benzothiophene with Excess Sulfuric Acid-*d*. Benzothiophene (0.025 g, 0.186 mmol) was dissolved in 5 mL of CD_3OD and the mixture placed in a Schlenk tube. To this was added 2.5 mL of a 95% solution of D_2SO_4 in D_2O. The solution was freeze–pump–thaw degassed three times, sealed under nitrogen, and allowed to stir in a 50 °C oil bath. After 1 week, an aliquot of the reaction mixture was removed. The deuterated benzothiophene product was recrystallized, rinsed with D_2O, and dried for several hours under vacuum. The ^1H NMR spectrum was recorded in acetone-d_6, and the 2,3-resonances were integrated relative to the other positions in the ring. Results are given in Table I.

Reaction of 1 or 2 with H_2 and D_2. Complex 1 or 2 (~0.1 mmol) was dissolved in 5 mL of CH_2Cl_2. The solution was freeze–pump–thaw degassed three times, and 290 mm of H_2 and 330 mm of D_2 were added at −196 °C. Mass spectral analysis of the volatiles in the tube indicated a ratio of 10 parts of H_2 to 9 parts of D_2. The solution containing 1 was stirred at 50 °C for 24 days. The m/e 2–4 region of the mass spectrum indicated a mixture of H_2, HD, and D_2 in a 10/4.2/1.4 ratio. The solution containing 2 was stirred at room temperature for 5 days. The mass spectrum of the volatiles showed a 6.8/10/4.4 ratio of H_2, HD, and D_2. This is the ratio expected for an equilibrium mixture; K_{eq} = 3.3.[43]

Reaction of Thiophene with Excess Deuterium in the Presence of 1 and 2. Complex 1 (0.012 g, 0.018 mmol) and 0.2 equiv of complex 2 (0.002 g, 0.004 mmol) were placed in an NMR tube. Thiophene (3 μL, 0.036 mmol) was syringed into 0.8 mL of CD_2Cl_2 and the mixture added to the tube. The solution was freeze–pump–thaw degassed three times and charged with ~1 atm of D_2 at 77 K. The tube was placed in a 50 °C oil bath, and the reaction was monitored by ^1H NMR. No change was observed in the integrated areas of the ^1H NMR resonances for the 2- and 5-positions of thiophene over 11 h. In analogous experiments in the absence of 2, approximately 40% of the 2,5-protons are deuterated in this time period.

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[41] Chemical shift assignments for benzothiophene in this solvent have been published previously.[18]

[42] The same rate constant was obtained in several cases when the resonance of the 3,4-protons of thiophene at 6.8 ppm or of the proton impurity in CD_2Cl_2 (5.34 ppm) was used as an internal standard.

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