Organometallics 1992, 11, 2424-2435

Subsequent further substitution of the cation to give $[\eta^5\text{-}C_5H_5Cr(CO)_2(PMe_2Ph)_2][\eta^5\text{-}C_5H_5Cr(CO)_3]$ also occurs readily; this new compound was isolated and characterized spectroscopically and by elemental analyses, while the related complex, $[\eta^5\text{-}C_5H_5Cr(CO)_2(PMe_3)_2][\eta^5\text{-}C_5H_5Cr(CO)_3]$, was identified spectroscopically by comparison with data in the literature.[6h] Species of the type $[\eta^5\text{-}C_5H_5Cr(CO)_2L_2][\eta^5\text{-}C_5H_5Cr(CO)_3]$ are normally observed when disproportionation reactions occur at ambient temperature.

Although we have not carried out a kinetic study of the disproportionation reactions, the fact that they have been observed only in reactions of $\{\eta^5\text{-}C_5H_5Cr(CO)_3\}$ with the smaller phosphines and are favored by higher concentrations of reactants suggests that a mechanism of the type found for disproportionation reactions of $V(CO)_6$[15] may apply. This would involve bimolecular formation of monosubstituted radical, as in eq 2, followed by interaction of this radical with a second molecule of $\{\eta^5\text{-}C_5H_5Cr(CO)_3\}$ via a bridging isocarbonyl interaction, i.e., $\{\eta^5\text{-}C_5H_5L(OC)CrCO{:}\!\rightarrow Cr(CO)_3(\eta^5\text{-}C_5H_5)\}$.

Electron transfer would follow, a process that would be facilitated when L is a relatively small, basic ligand.

Alternatively, disproportionation may occur via the 19-electron intermediate $\{\eta^5\text{-}C_5H_5Cr(CO)_3L\}$, as in eqs 5 and 6.[4c]

$$\{\eta^5\text{-}C_5H_5Cr(CO)_3\} + L \rightarrow \{\eta^5\text{-}C_5H_5Cr(CO)_3L\} \qquad (5)$$

$$\{\eta^5\text{-}C_5H_5Cr(CO)_3L\} + \{\eta^5\text{-}C_5H_5Cr(CO)_3\} \rightarrow [\eta^5\text{-}C_5H_5Cr(CO)_3L]^+ + [\eta^5\text{-}C_5H_5Cr(CO)_3]^- \qquad (6)$$

The latter process is probably favored, since the monosubstituted cation $[\eta^5\text{-}C_5H_5Cr(CO)_3(PMePh_2)]^+$ was observed in a low-temperature NMR study.

X-ray Crystal Structure of $\eta^5\text{-}C_5H_5Cr(CO)_2(CDPP)H$. The structure of this compound is illustrated in Figure 1, while bond distances and angles are given in Table II. Although the position of the hydride ligand could not be determined, occupation of the apparent vacant site by the hydride would result in a cisoid four-legged piano stool type structure. The chromium–carbonyl and chromium–phosphorus bond lengths are similar to those in the 18-electron complexes *cis*- and *trans*-$[\eta^5\text{-}C_5Me_5Cr(CO)_2\{P(OMe)_3\}_2{}^+]$[16] and those in the 17-electron complexes $\{\eta^5\text{-}C_5H_5Cr(CO)_2(PPh_3)\}$[5a] and $\{\eta^5\text{-}C_5Me_5Cr(CO)_2(PMe_3)\}$.[5i] The OC–Cr–CO bond angle is 83.3 (2)° and the OC–Cr–P4 bond angles 86.7 (2)° (cisoid) and 106.2 (2)° (transoid); while ligand–metal–ligand bond angles are known to vary significantly in similar compounds of molybdenum,[17] few such structural data seem available for compounds of chromium.

Acknowledgment. Financial support from the Natural Sciences and Engineering Research Council of Canada (operating grants to D.H.M. and M.C.B.) made this research possible. We also thank J. A. Stone, J. R. Norton, and A. J. Poë for helpful discussions and Dr. G. Silverman, of M & T Chemicals, for gifts of CDPP and DCPP.

Supplementary Material Available: Tables of fractional coordinates and isotropic displacement parameters for all atoms and temperature factor expressions and a derivation of the rate law used (9 pages). Ordering information is given on any current masthead page.

OM9107909

---

[15] Richmond, T. G.; Shi, Q.-Z.; Trogler, W. C.; Basolo, F. *J. Am. Chem. Soc.* **1984**, *106*, 76.

[16] Salsini, L.; Pasquali, M.; Zandomeneghi, M.; Festa, C.; Leoni, P.; Braga, D.; Sabatino, P. *J. Chem. Soc., Dalton Trans.* **1990**, 2007.

[17] See footnote in ref 5f.

Mechanistic Study of Hydrogen Activation by Cationic Dinuclear (μ-Sulfido)molybdenum Complexes

Linda L. Lopez, P. Bernatis, J. Birnbaum, R. C. Haltiwanger, and M. Rakowski DuBois*

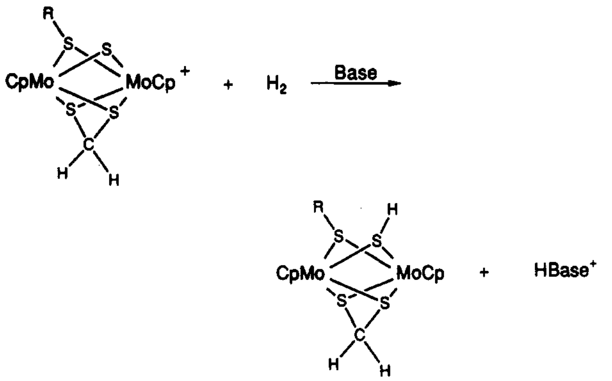
Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309

Received March 4, 1992

The cationic derivatives $[(MeCpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SR)]X$ ($R = C_4H_3S$, CH_2CO_2Me; $X = Br$, SO_3CF_3; $MeCp = C_5H_4CH_3$) have been synthesized and characterized spectroscopically. A single crystal of $[(MeCpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SC_4H_3S)]Br$ has been studied by X-ray diffraction. The complex crystallized in space group $P2_1/n$ with $a = 7.030\ (3)$ Å, $b = 19.777\ (8)$ Å, $c = 15.106\ (6)$ Å, $\beta = 90.84\ (3)°$, and $Z = 4$. The structure showed that the μ-thiophenethiolate ligand was oriented away from the adjacent sulfido ligand. The reactions of the cationic derivatives with hydrogen have been studied. The bromide salts reacted with hydrogen to form RH, $(MeCpMoS)_2S_2CH_2$, and 1 equiv of HBr. In the presence of a nitrogen base, the reactions of the cations with hydrogen proceeded to form the neutral complexes $(MeCpMo)_2(S_2CH_2)(\mu\text{-}SR)(\mu\text{-}SH)$ and 1 equiv of protonated base. The kinetics of the latter hydrogen activation reaction have been studied over a range of temperatures, hydrogen pressures, and base concentrations. The kinetic data are consistent with a rate law which is first order in cation and first order in hydrogen. For the cation where $R = CH_2CO_2Me$, the deuterium isotope effect, k_H/k_D, was found to be 2.5 at 50 °C and the following activation parameters were determined: $\Delta H^\ddagger = 84$ kJ/mol and $\Delta S^\ddagger = -9$ J/(mol K). The data seem most consistent with a heterolytic mechanism for the activation of hydrogen. Several possible mechanisms for hydrogen addition to the cation are discussed. Attempts to model the initial hydrogen addition product have been made by reacting the related neutral complexes $(CpMo)_2(S_2CH_2)(\mu\text{-}SMe)(\mu\text{-}SR)$ with 1 equiv of strong anhydrous protic acid. The reactions with acid involved either protonolysis of thiolate ligands or oxidation of the dimer, depending on the nature of thiolate substituents. However, no protonated intermediates were detected.

We have reported that some cationic molybdenum sulfide complexes of the general formula $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SR)]^+$ react with molecular hydrogen to form the final products shown in eq 1. Reaction 1 ulti-

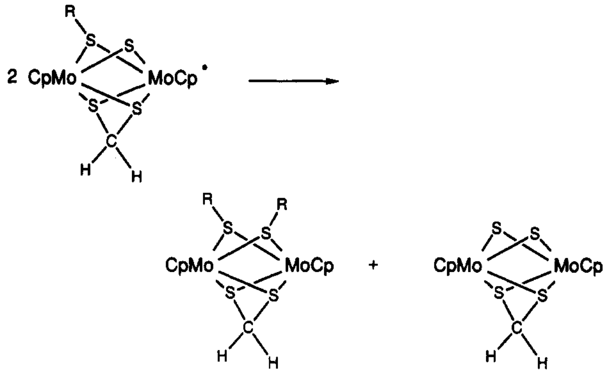
0276-7333/92/2311-2424$03.00/0

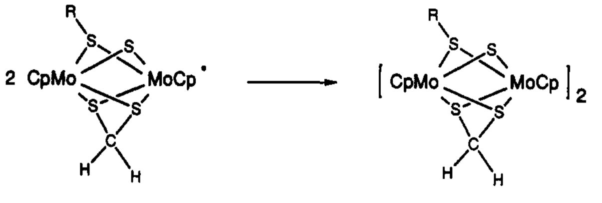

(1)

mately results in the heterolytic cleavage of H_2, but unlike other heterolytic reactions promoted by metal complexes, a ligand of the electrophilic complex accepts the hydridic atom while an uncoordinated base serves as the proton acceptor. The reactions of the molybdenum complexes with hydrogen have played a role in the reduction of many organic substrates,[2-5] and they may be relevant to hydrogen activation processes which take place on the sulfided surfaces of hydrotreating catalysts.[6,7] For these reasons we have been interested in establishing the mechanism for this unusual hydrogen activation process.

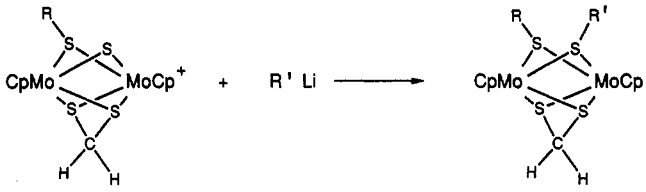
The reduction behavior of dinuclear Mo(IV) cations containing different thiolate substituents has been characterized previously for reactants other than hydrogen.[2,3,8] The chemistry was found to be quite complex but similar for each system studied. At a platinum electrode, the cations generally underwent a reversible one-electron reduction at −0.2 to −0.3 V vs SCE. Many chemical reagents have served as one-electron reductants for the cations as well. The resulting paramagnetic mixed-valence dimers have been identified by EPR spectroscopy in some cases.[2,9] Further reactions of the radical complexes occurred readily in solution, and these contribute to the overall complexity of the systems. Such reactions included disproportionation via alkyl group transfer (eq 2) and dimerization (eq 3). The structure of the tetranuclear product formed in eq 3 is unknown, but ^1H NMR data[2,10] suggest a complex of low symmetry. Molybdenum tetramers coupled through a sulfur–sulfur bond have been prepared previously by the oxidation of neutral Mo(IV) dimers.[11]

Another pertinent reaction characterized for the radical system $(MeCpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SMe)^\bullet$ was the reaction with H_2 to form $(MeCpMo)_2(S_2CH_2)(\mu\text{-}SH)(\mu\text{-}SMe)$. Studies established that the reaction was zero order in radical compound and was catalyzed by $(CpMo(\mu\text{-}S))_2S_2CH_2$, which served as the hydrogen-activating and hydrogen-transfer agent.[8]

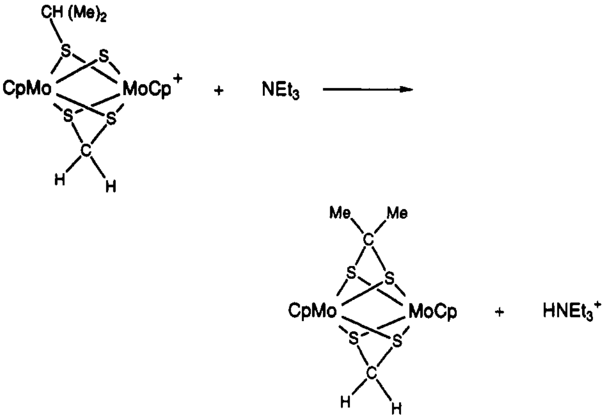

(2)


(3)

In some cases reactions of the cations with potential reducing agents did not appear to involve single electron transfer but, rather, nucleophilic attack at the μ-sulfido ligand to form neutral bis(thiolate) products (eq 4).[2,10]


(4)

Another competing pathway for the reaction of some thiolate cations with basic reagents was deprotonation of the thiolate ligand, as illustrated in eq 5.[2,3]


(5)

Definition of the reduction pathways of these cations has proven valuable in understanding mechanistic features of the hydrogen activation reaction (eq 1). In this paper we report characterization data for the reactions of hydrogen with the two complexes $[(MeCpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SR)]SO_3CF_3$ (**1**, R = C_4H_3S; **2**, R = $CH_2CO_2CH_3$). Elementary steps in the reactions have been identified, and the kinetics of the hydrogen activation step have been studied. The data are consistent with a direct interaction of hydrogen with the cation, and attempts to model this initial interaction are also described in this paper.

Results

Synthesis and Characterization of Cationic Derivatives. The reaction of $(MeCpMo(\mu\text{-}S))_2S_2CH_2$ with 2-

---

[1] (a) Laurie, J. C. V.; Duncan, L.; Haltiwanger, R. C.; Weberg, R. T.; Rakowski DuBois, M. *J. Am. Chem. Soc.* **1986**, *108*, 6234. (b) Gabay, J. Masters Thesis, University of Colorado, Boulder, CO, 1991.

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

[3] Coons, D. E.; Haltiwanger, R. C.; Rakowski DuBois, M. *Organometallics* **1987**, *6*, 2417.

[4] Bernatis, P.; Laurie, J. C. V.; Rakowski DuBois, M. *Organometallics* **1990**, *9*, 1607.

[5] Casewit, C. J.; Coons, D. E.; Wright, L. L.; Miller, W. K.; Rakowski DuBois, M. *Organometallics* **1986**, *5*, 951.

[6] Gates, B. C.; Katzer, J. R.; Schuit, G. C. A. *The Chemistry of Catalytic Processes*; McGraw-Hill: New York, 1979; p 422.

[7] Barbour, J.; Campbell, K. C. *J. Chem. Soc., Chem. Commun.* **1982**, 1371.

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

[9] Casewit, C. J.; Rakowski DuBois, M. *Inorg. Chem.* **1986**, *25*, 74.

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

[11] Birnbaum, J.; Godziela, G.; Maciejewski, M.; Tonker, T. L.; Haltiwanger, R. C.; Rakowski DuBois, M. *Organometallics* **1990**, *9*, 394.

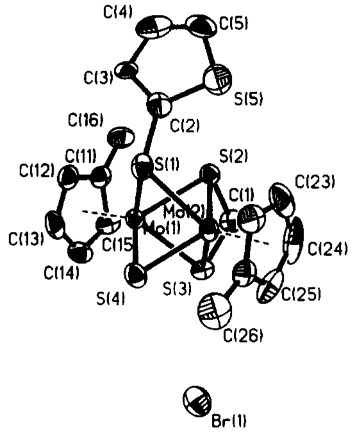


Figure 1. Perspective drawing and numbering scheme for $[(MeCpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SC_4H_3S)]Br$. Thermal ellipsoids are shown at the 50% probability level.

bromothiophene in chloroform at 50 °C resulted in a color change from blue to purple, and a purple crystalline product was isolated from this solution. Elemental analyses and spectroscopic characterization for the complex were consistent with its formulation as a bromide salt of the 2-thiophenethiolate cation. The triflate salt 1 was prepared by a reaction of the bromide derivative with silver triflate. The ^1H NMR spectrum of 1 included three multiplets for the protons on the thiophene ring at 6.78, 6.51, and 6.35 ppm. These chemical shifts are shifted upfield relative to those of free thiophene. The visible spectrum of 1 in dichloromethane solution was similar to those observed for other cationic Mo(IV) derivatives, with strong maxima observed near 520 and 820 nm. The complex obeyed Beer's law over a concentration range of 10^{-4}–10^{-3} M. The cyclic voltammogram of 1 in CH_2Cl_2 indicated that the cation underwent a reversible one-electron reduction at −0.66 V vs ferrocene and a second irreversible reduction at −1.52 V.

The synthesis and characterization of $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SCH_2CO_2Me)]Br$ have been reported previously.[3] The triflate salt 2 was prepared from the analogous methylcyclopentadienyl derivative by reaction with silver triflate. Spectroscopic and voltammetric characteristics of this cation are very similar to those of 1 and are summarized in the Experimental Section.

Crystallographic Study of $[(MeCpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SC_4H_3S)]Br$. An X-ray diffraction study of the thiophenethiolate complex was carried out in order to determine the orientation of the thiophene ring with respect to the rest of the dimer. Single crystals were isolated from a saturated CH_2Cl_2 solution. The complex crystallized in space group $P2_1/n$ with discrete cations and anions in the unit cell. A perspective drawing is shown in Figure 1, and selected bond distances and angles and positional parameters are included in Tables I and II, respectively. The structural study confirms that C(2) of the thiophene ring is coordinated to a μ-sulfide ligand of the dimer. This ring is disordered (22%) by a noncrystallographic rotational axis which exchanges S(5) and the β-carbon (C(3)). As a result of this disorder, the value obtained for the C(2)–C(3) bond distance (1.471 (6) Å) is significantly longer than the other double bond in the ring (C(4)–C(5), 1.338 (8) Å),[12] and the other C(3) and S(5) distances are also affected. The bond distances and angles of the dinuclear molybdenum–sulfur unit are similar to those observed in other thiolate-bridged cations.[1,2,10] The thiophenethiolate ligand assumes an equatorial conformation relative to the adjacent sulfido ligand. Similar equatorial isomers have been observed in the X-ray diffraction studies of several related cations where the R group of the thiolate ligand is Me,[10] $C(Ph){=}CH_2$,[1] and $CH{=}CH(Ph)$.[2] Studies of some of these related systems have shown that inversion at the thiolate sulfur from the axial to the more stable equatorial conformation occurs rapidly at room temperature.

Table I. Selected Bond Distances and Angles for $[(MeCpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SC_4H_3S)]Br$

Distances (Å)			
Mo(1)–Mo(2)	2.608 (1)	Mo(1)–S(1)	2.484 (1)
Mo(1)–S(2)	2.465 (1)	Mo(1)–S(3)	2.456 (1)
Mo(1)–S(4)	2.301 (1)	S(1)–C(2)	1.771 (4)
S(2)–C(1)	1.830 (4)	S(3)–C(1)	1.823 (4)
S(5)–C(2)	1.697 (5)	S(5)–C(5)	1.657 (6)
C(2)–C(3)	1.471 (6)	C(3)–C(4)	1.469 (7)
C(4)–C(5)	1.338 (8)		
Angles (deg)			
Mo(1)–S(1)–Mo(2)	63.5 (1)	Mo(1)–S(3)–Mo(2)	64.3 (1)
Mo(1)–S(2)–Mo(2)	63.9 (1)	Mo(1)–S(4)–Mo(2)	69.0 (1)
Mo(1)–S(1)–C(2)	112.4 (1)	Mo(2)–S(1)–C(2)	114.5 (1)
Mo(1)–S(2)–C(1)	90.9 (1)	Mo(2)–S(2)–C(1)	91.0 (1)
C(2)–S(5)–C(5)	94.0 (2)	S(1)–C(2)–S(5)	123.9 (3)
S(5)–C(2)–C(3)	111.9 (3)	C(2)–C(3)–C(4)	105.6 (4)
C(3)–C(4)–C(5)	115.7 (5)	S(5)–C(5)–C(4)	112.9 (4)
S(2)–C(1)–S(3)	95.9 (2)		

Table II. Atomic Coordinates[a] ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for $[(MeCpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SC_4H_3S)]Br$

	x/a	*y/b*	*z/c*	*U*(eq)[b]
Br(1)	1336 (1)	1485 (1)	4022 (1)	63 (1)
Mo(1)	4495 (1)	−876 (1)	3067 (1)	30 (1)
Mo(2)	5743 (1)	225 (1)	2324 (1)	32 (1)
S(1)	5275 (1)	−832 (1)	1470 (1)	40 (1)
S(2)	7913 (1)	−602 (1)	3027 (1)	33 (1)
S(3)	5331 (1)	138 (1)	3926 (1)	38 (1)
S(4)	2577 (1)	−45 (1)	2471 (1)	43 (1)
S(5)†	9453 (2)	−885 (1)	933 (1)	63 (1)
C(1)	7766 (6)	−159 (2)	4088 (2)	42 (1)
C(2)	7403 (6)	−1270 (2)	1230 (2)	45 (1)
C(3)†	7557 (5)	−2011 (2)	1186 (2)	62 (1)
C(4)	9506 (8)	−2150 (3)	901 (3)	70 (2)
C(5)	10586 (7)	−1605 (3)	754 (3)	66 (2)
C(11)	5143 (5)	−1958 (2)	3690 (3)	37 (1)
C(12)	3807 (6)	−2034 (2)	2985 (3)	44 (1)
C(13)	2130 (6)	−1684 (2)	3195 (3)	49 (1)
C(14)	2387 (6)	−1382 (2)	4019 (3)	47 (1)
C(15)	4252 (6)	−1536 (2)	4328 (3)	42 (1)
C(16)	7041 (6)	−2273 (2)	3763 (3)	53 (2)
C(21)	4932 (6)	1228 (2)	1542 (3)	39 (1)
C(22)	6303 (7)	883 (2)	1060 (3)	51 (2)
C(23)	7966 (7)	840 (3)	1547 (4)	69 (2)
C(24)	7675 (8)	1147 (3)	2366 (4)	78 (2)
C(25)	5747 (8)	1395 (2)	2376 (3)	62 (2)
C(26)	3000 (7)	1417 (3)	1228 (4)	70 (2)

[a] Atoms have occupancies of 1.0 except as marked with †: S(5), 0.86; C(3), 1.37. The thiophene moiety exhibits a 22% disorder. The occupancies of S(5) and C(3) are set to account for this disorder. [b] The equivalent isotropic *U* is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Reaction of $[(MeCpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SR)]OTf$ with Hydrogen. The reactions of the triflate salts 1 and 2 with hydrogen were initially characterized by ^1H NMR spectroscopy. When 2–3 atm of hydrogen was added to 1 or 2 in CD_2Cl_2 at room temperature, no color change was observed and new products were not detected by NMR spectroscopy. When the temperature was raised to ca. 50 °C, the reactions proceeded cleanly to form $[(MeCpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SH)]OTf$ and thiophene or

---

[12] This value is similar to that in free thiophene: (a) Bak, B.; Christensen, D.; Rastrup-Andersen, J.; Tannenbaum, E. *J. Chem. Phys.* **1956**, *25*, 892. (b) Bonham, R. A.; Momany, F. A. *J. Phys. Chem.* **1963**, *67*, 2474.

methyl acetate, respectively. These products are similar to those observed when the bromide salts of these cations were reacted with hydrogen at room temperature.[13]

The nature of the products of these reactions was changed by the addition of a nitrogen base. For example, when 1 equiv of triethylamine was added to a solution of 1, the reaction with hydrogen at 50 °C proceeded to form $(MeCpMo)_2(S_2CH_2)(\mu\text{-}SH)(\mu\text{-}SC_4H_3S)$ (3) and the triethylammonium triflate salt. Attempts to monitor the course of the reaction by NMR spectroscopy were unsuccessful, because under H_2 the spectra were broadened and resonances of 1 were not observed. A paramagnetic intermediate species was identified in room-temperature reactions and is described below. The spectral features sharpened as final products were formed. In the NMR spectrum of 3 resonances for three inequivalent protons of the coordinated thiophene ring were observed at 6.87, 6.63, and 6.23 ppm and a singlet at −1.0 ppm was assigned to the S–H proton. The spectrum was very similar to that of the analogous methanethiolate derivative $(MeCpMo)_2(S_2CH_2)(\mu\text{-}SH)(\mu\text{-}SMe)$, which has been isolated and characterized previously (δ_{SH}, −1.35 ppm; ν_{S-H}, 2380 cm^{-1}).[8] The reaction chemistry of 3 also paralleled that characterized for the methanethiolate analogue. For example, oxidation of 3 formed the paramagnetic mixed-valence dimer $(MeCpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SC_4H_3S)^\bullet$. Further reactions of this radical resulted in the formation of disproportionation products (eq 2) and coupled tetranuclear products (eq 3), which were isolated and characterized spectroscopically (see Experimental Section).

The reaction of 2 with H_2 at 40 °C in the presence of Proton Sponge (5 equiv) was also monitored by ^1H NMR spectroscopy. The reaction proceeded slowly to form $(MeCpMo)_2(S_2CH_2)(\mu\text{-}SH)(\mu\text{-}SCH_2CO_2Me)$ (4) as the major product (>90% yield). Spectroscopic data for 4 are included in the Experimental Section. In order to investigate the possibility of cations 1 and 2 reacting directly with the base, the systems were studied in the absence of hydrogen.

Reactions of 1 and 2 with Base. The addition of 1 equiv of triethylamine to 1 in the absence of H_2 also caused the NMR spectrum to broaden; a color change to orange was observed and the slow disappearance of the characteristic visible spectrum of 1 was observed. However, the change in the visible spectrum was found to be more than 1 order of magnitude slower than the changes observed under hydrogen, and the reaction with triethylamine did not significantly compete with the hydrogen activation process. Attempts to isolate a pure product resulting from larger scale reactions of 1 with triethylamine were unsuccessful; the nature of this slow interaction between amine and cation has not been identifed. Cation 1 did not appear to react with Proton Sponge when a mixture of these reagents was monitored by NMR spectroscopy.

Deprotonation of $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SCH_2CO_2Me)]Br$ by triethylamine has been reported previously.[3] However, no reaction of 2 with the more sterically hindered base Proton Sponge (5 equiv) under nitrogen was observed over a 2-h period at 40 °C when the reaction was monitored by visible spectroscopy. The reaction of 2 with hydrogen was 60–70% complete under these conditions. These studies established conditions under which the rates of the reactions with hydrogen could be monitored for cations 1 and 2 without significant competiton from reactions of the cations with base. Kinetic studies of the hydrogen activation reactions are described below.

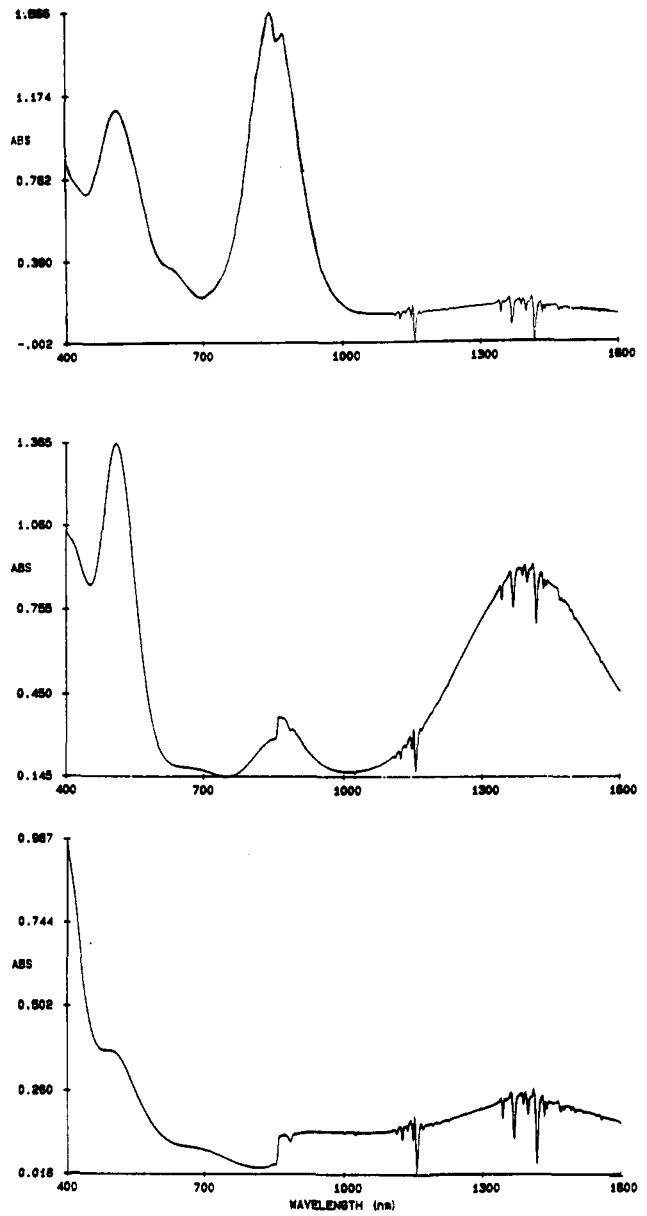


Figure 2. Optical spectra during the course of the reaction of 1 with H_2 in the presence of 1 equiv of NEt_3 and 5 (1–5 mol %) recorded in CH_2Cl_2 at room temperature: (a, top) spectrum of 1 at the beginning of the reaction (t = 0 min); (b, middle) spectrum showing near-complete conversion of 1 to $(MeCpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SC_4H_3S)^\bullet$ at t = 21 min; (c, bottom) spectrum showing near-complete conversion of $(MeCpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SC_4H_3S)^\bullet$ to $(MeCpMo)_2(S_2CH_2)(\mu\text{-}SH)(\mu\text{-}SC_4H_3S)$ (3) at t = 75 min. Absorbances of 5 at 590 and 730 nm are not detected in the spectra. A spectrometer grating change at 820 nm is responsible for the glitch at this wavelength.

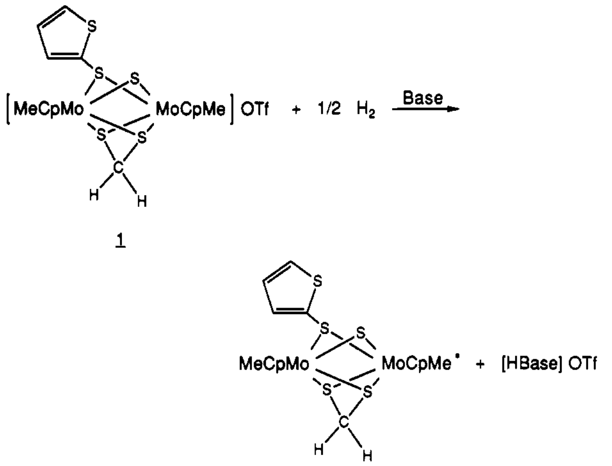
Characterization of Elementary Reaction Steps of Eq 1. When the reaction of 1 with H_2 in the presence of base was followed by visible spectroscopy at room temperature, the reaction proceeded with the disappearance of the cation absorbances at 520 and 820 nm and the growth of new bands at 510 and 1400 nm (Figure 2). These absorbances were attributed to the mixed-valence compound $(MeCpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SC_4H_3S)^\bullet$. The assignments were confirmed by an independent synthesis of this radical complex described below.

A further reaction of pure samples of the radical complex with hydrogen was not observed at room temperature even

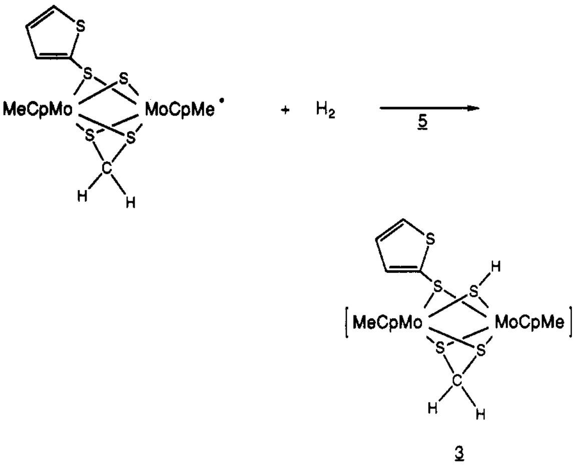
---

[13] The difference in reactivity between the bromide and triflate salts was attributed to the lower basicity of the triflate anion. Addition of better proton acceptors appeared to facilitate the hydrogen activation process.

after several days. However, upon addition of a catalytic amount (~1 mol %) of $(MeCpMo(\mu\text{-}S))_2S_2CH_2$ (**5**) to the reaction solution, the absorbance bands of the radical complex disappeared in 2–3 h in a further reaction with hydrogen. The resulting pale brown color of the final product solution and featureless visible/near-IR spectrum were characteristic of the product **3**. The identity of this compound was further confirmed by observing the characteristic oxidation chemistry of **3** described above. The reaction of **1** with hydrogen was therefore described by the sequence



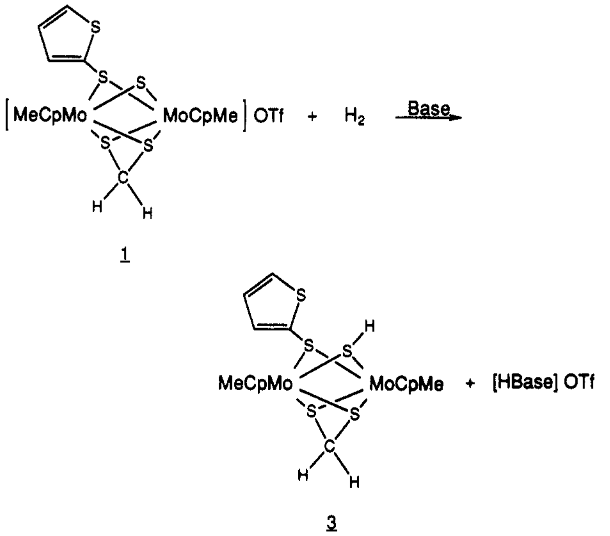
(6)



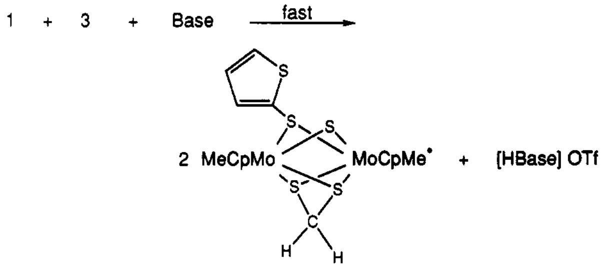
(7)

Reaction 7 has been characterized previously for the methanethiolate analogue,[8] and these results have been summarized above. The formation of the final product **3** was observed not only when catalyst **5** was added to the reaction of **1** with H_2 but also when this reaction was carried out at 50 °C in the absence of added catalyst (vide supra). Under these conditions, the higher temperature promoted disproportionation of the radical complex (eq 2), thereby producing the required catalyst **5** in situ. However, the degree of disproportionation must be small under these conditions, because **5** was generally not observed, or detected in only trace amounts, in the visible spectrum of the final products.

The reaction of hydrogen with **1** (eq 6) did not require the presence of **5** as a catalyst. The room-temperature reactions in the absence of **5** terminated in the formation of the radical complex $(MeCpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SC_4H_3S)^{\bullet}$. We were interested in defining the elementary steps of this conversion and in learning more about the mechanism of hydrogen activation. We proposed that hydrogen addition to the cation promoted by base resulted in the formation of a reduced product, such as **3**, and that rapid electron transfer between **3** and starting cation **1** led to the radical formation. This sequence (eqs 8 and 9) provided a balanced equation for the formation of the radical dimer in this system. When an authentic sample of **3** was reacted with 1 equiv of the cation **1**, we observed the immediate disappearance of the visible spectrum of **1** and the appearance of the radical dimer absorption bands at 510 and 1400 nm, as expected for eq 9. The data indicate that, while hydrogen appears to react directly with cation **1**, the neutral product **3** does not persist in the presence of excess **1**. A similar sequence is proposed to occur in the reaction of **2** with hydrogen. Radical dinuclear intermediates are detected by visible/near-IR spectroscopy (bands near 510 and 1400 nm) during the cource of this reaction as well.



(8)



(9)

The reactivity of **5**, discussed above, suggests that **5** should also catalyze the disappearance of **1** under hydrogen. For example, a reduced form of **5** readily formed under hydrogen, such as $(MeCpMo)_2(S_2CH_2)(\mu\text{-}SH)_2$, should behave as an electron-transfer agent similar to **3**. Indeed, rates of reactions of **1** with H_2 were increased by the addition of **5**. For example, the addition of 1 mol % of **5** gave a k_{obs} value at room temperature of 3.4×10^{-4} s^{-1} for the disappearance of **1**, while the analogous reaction in the absence of **5** gave $k_{obs} = 2.3 \times 10^{-4}$ s^{-1} (details of kinetic studies are described below). Larger amounts of **5** led to faster reactions. Significantly, the nature of the final products in the catalyzed and uncatalyzed reactions differed. Conversion of the radical complex to **3** at room temperature (eq 7) was not observed in the uncatalyzed reactions even after several days. Slow formation of **3** would be expected if trace impurities of **5** were solely responsible for the reaction of **1** with H_2.

Kinetic Studies of Hydrogen Activation. The kinetics of the initial reactions of **1** and **2** with a large excess of hydrogen in the presence of base (e.g. eq 8) were followed by visible spectroscopy. A spectroscopic cell equipped with an attached 25-mL reservoir and Teflon stopcock was used to prepare solutions of the cations under hydrogen pressure. Reactions were carried out at various

Table III. Observed Rate Constants for the Disappearance of 1 and 2 in Reactions with Hydrogen and Base

SR	[cation], M	P_{H_2}, atm	base (amt, equiv)	T, K	k_{obs}, s^{-1}
Cation Dependence					
SC_4H_3S	1.5×10^{-3}	3.0	NEt_3 (1)	298	3.61×10^{-4}
	1.5×10^{-4}	3.0	NEt_3 (1)	298	3.72×10^{-4}
SCH_2CO_2Me	1.0×10^{-3}	3.0	PS (5)[a]	313	1.58×10^{-4}
	3.0×10^{-4}	3.0	PS (5)	313	1.53×10^{-4}
Base Dependence					
SC_4H_3S	1.5×10^{-3}	3.0	NEt_3 (1)	298	3.61×10^{-4}
	1.6×10^{-3}	3.0	PS (10)	298	4.32×10^{-4}
	1.6×10^{-3}	3.0	PS (20)	298	4.25×10^{-4}
Hydrogen Dependence					
SC_4H_3S	1.5×10^{-3}	3.0	NEt_3 (1)	298	3.61×10^{-4}
	1.5×10^{-3}	0.79	NEt_3 (1)	298	1.34×10^{-4}
	1.5×10^{-3}	0.39	NEt_3 (1)	298	6.39×10^{-5}
SCH_2CO_2Me	1.1×10^{-3}	3.0	PS (5)	293	1.06×10^{-5}
	1.1×10^{-3}	0.80	PS (5)	293	1.72×10^{-6}
	1.1×10^{-3}	0.45	PS (5)	293	9.29×10^{-7}
Hydrogen vs Deuterium					
SCH_2CO_2Me	1.1×10^{-3}	0.78 (H_2)	PS (5)	323	2.90×10^{-5}
	1.1×10^{-3}	0.78 (H_2)	PS (5)	323	3.25×10^{-5}
	1.1×10^{-3}	0.78 (H_2)	PS (5)	323	3.17×10^{-5}
	1.1×10^{-3}	0.78 (D_2)	PS (5)	323	1.25×10^{-5}
	1.1×10^{-3}	0.78 (D_2)	PS (5)	323	1.24×10^{-5}
Temperature Dependence					
SCH_2CO_2Me	1.1×10^{-3}	3.0	PS (5)	293	2.11×10^{-5}
	1.1×10^{-3}	3.0	PS (5)	313	1.56×10^{-4}
	1.1×10^{-3}	3.0	PS (5)	324	8.95×10^{-4}
	1.1×10^{-3}	3.0	PS (5)	336	1.63×10^{-3}
SC_4H_3S	1.0×10^{-3}	3.0	PS (5)	273	3.88×10^{-6}
	1.0×10^{-3}	3.0	PS (5)	273	4.04×10^{-6}
	1.0×10^{-3}	3.0	PS (5)	294	3.59×10^{-5}
	1.0×10^{-3}	3.0	PS (5)	294	3.49×10^{-5}
	1.0×10^{-3}	3.0	PS (5)	312	2.66×10^{-4}
	1.0×10^{-3}	3.0	PS (5)	312	2.62×10^{-4}
	1.0×10^{-3}	3.0	PS (5)	319	5.27×10^{-4}
	1.0×10^{-3}	3.0	PS (5)	319	5.14×10^{-4}

[a] PS is Proton Sponge, 1,8-bis(dimethylamino)naphthalene.

temperatures with constant shaking or vigorous stirring, and the rates were determined by periodically monitoring the disappearance of the near-IR absorbance of each cation at 840 nm. Plots of the natural logarithm of this absorbance vs time were linear, and a first-order dependence on each cation was further verified by determining that k_{obs} was independent of the initial concentration of the cation (e.g., Figure 3). Observed rate constants[14] for the disappearance of 1 and 2 under H_2 under various conditions are given in Table III.

In the reaction of 1 with H_2, the rate was not dependent on the nature or excess concentration of the nitrogen base. For example, the observed rate constants were identical regardless of whether triethylamine or Proton Sponge was used as the proton acceptor, and no change in k_{obs} was observed, within experimental error, when the base concentration was varied over the range of 1 equiv (per equiv of 1) to 20 equiv (Table III). The data indicate that the base is not involved in the rate-determining step.

Initial rates of the reactions of 1 and 2 with hydrogen were monitored for initial hydrogen pressures ranging from ca. 0.4 to 3 atm (Table III). A plot of the observed rate constant as a function of hydrogen pressure was linear for each reaction (e.g., Figure 4). The data support a first-order dependence on hydrogen for these reaction conditions. The rate of the reaction of 2 with deuterium (1 atm) was also monitored at 50 °C. The average k_{obs} value for the deuterium reactions was compared to the k_{obs} value determined for reactions of 2 with hydrogen under identical conditions (Table III). The ratio of the average rate constants k_H/k_D was found to be 2.5 at this temperature.

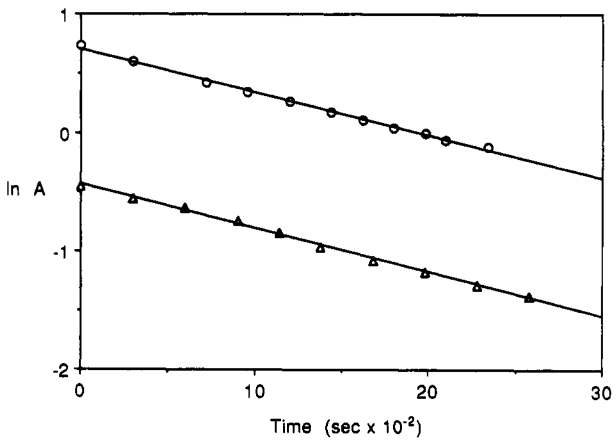


Figure 3. Plots of the natural logarithm of the absorbance of 1 vs time obtained during the reaction of 1 with H_2 in the presence of NEt_3 (1 equiv) in CH_2Cl_2 at room temperature: (○) initial concentration of 1 1.0 × 10^{-3} M; (△) initial concentration of 1 1.0 × 10^{-4} M.

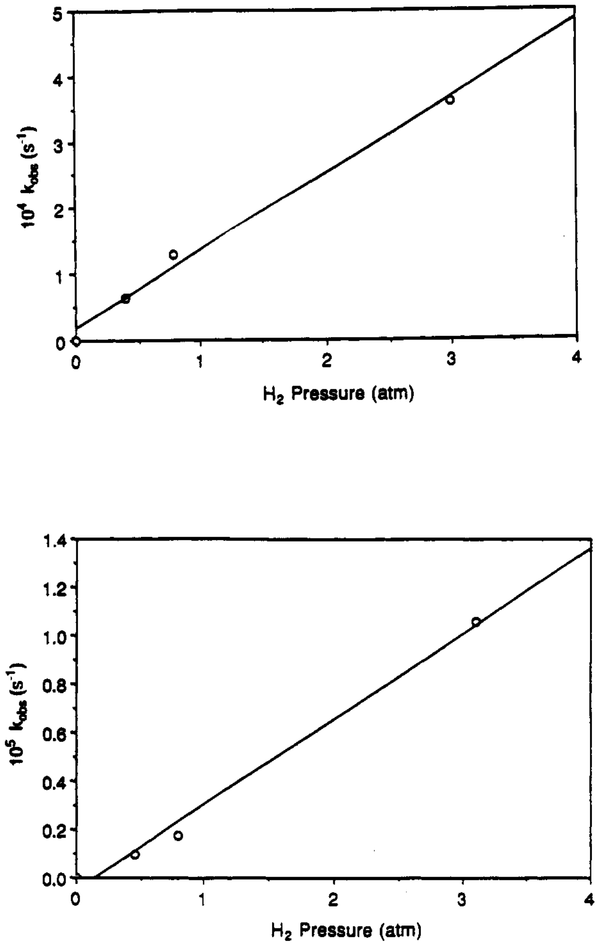


Figure 4. Plots of k_{obs} vs H_2 pressure obtained for the reactions of (a, top) 1 and (b, bottom) 2 with H_2 in the presence of base at room temperature.

Initial rates of the reactions of 2 with hydrogen were also determined as a function of temperature over a range of 20–60 °C. Observed rate constants are included in Table III. By using an estimated solubility of H_2 in CH_2Cl_2 (see

---

[14] According to the mechanistic scheme proposed in eqs 7 and 8, k_{obs} for the disappearance of 1 is 2 times the pseudo-first-order k value for eq 8.

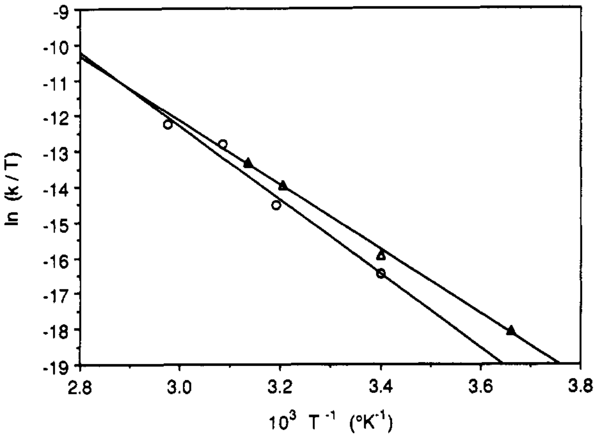


Figure 5. Eyring plots for the reaction of 1 (△) and 2 (○) with H_2 in the presence of base.

Experimental Section), corresponding second-order rate constants k_2 were calculated. A plot of k_2/T vs $1/T$, shown in Figure 5, permitted the calculation of $\Delta H^{\ddagger} = 84$ kJ/mol and $\Delta S^{\ddagger} = -9$ J/(K mol). A similar set of experiments with 1 led to $\Delta H^{\ddagger} = 75$ kJ/mol.

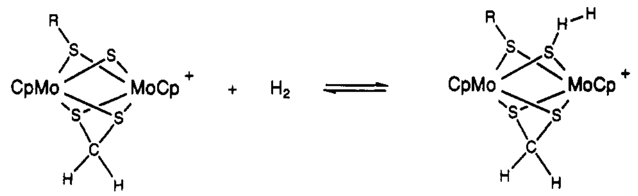
Discussion

Implications of Kinetic Data. The kinetic data for eq 8 under the conditions studied here are consistent with the second-order rate law rate = k[cation][H_2] and suggest a direct interaction of the cations with hydrogen. The addition of hydrogen to 1 or 2 would initially produce a cation for which a number of different structures could be proposed (see below). Rapid deprotonation of such a species produces 3, or an electronically similar structure, which undergoes rapid electron transfer to 1. Because of this formation of paramagnetic species, NMR spectroscopy does not provide any information on the structure of intermediates. As mentioned above, spectra of the molybdenum complexes are broadened under a hydrogen atmosphere even at low temperatures.

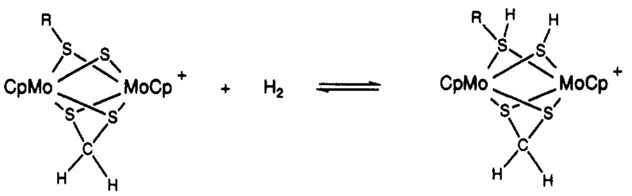
Some information on the mechanism of hydrogen activation may be obtained by comparing the activation parameters determined for the molybdenum complex to those reported for other metal complexes that react with molecular hydrogen. These data, primarily for reactions with group 8–10 metals, have been collected by James in a recent review.[15] He notes that the values of the activation parameters cannot be used to unequivocally assign a mechanism of hydrogen activation, but some trends have been observed. Well-defined oxidative addition of hydrogen to a single metal center is generally characterized by a relatively low activation enthalpy (<50 kJ/mol), while activation enthalpies >50 kJ/mol have been reported for reactions which are proposed to involve the heterolytic cleavage of hydrogen. The values of $\Delta H^{\ddagger}$ determined for the reactions of the molybdenum complexes are most consistent with those of other proposed heterolytic reactions. While insufficient data are available to reliably correlate kinetic isotope effects with hydrogen activation mechanisms,[15,16] the deuterium isotope effect of 2.5 observed for these molybdenum systems is larger than the values of 1–1.5 which have been associated in some cases with a concerted oxidative-addition process.[15–19] These data provide support for the tentative[20] conclusion that the reactions of the cations with hydrogen do not involve oxidative addition of H_2 to a single molybdenum ion. An alternate interaction which results in the heterolytic cleavage of H_2 seems to be favored.

Possible Modes of Hydrogen Addition to the Cations. Extended Hückel calculations on the cationic derivative $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SH)]^+$ have established that the LUMO of the cation is composed primarily of contributions from metal d orbitals with a significant (20%) component from the orbitals of the μ-sulfide ligand and a smaller contribution from the adjacent thiolate sulfur orbital.[21] We consider here three possible modes of hydrogen addition to the cations which are consistent with the kinetic data and with the molecular orbital description of the cations.[22]

End-on addition of hydrogen to a sulfido ligand in cation 1 or 2 provides one potential description of the hydrogen addition process (eq 10).[24] Deprotonation by external base, which should occur readily, would form the known complex 3 or 4. Alternatively, sites within the molybdenum dimer might serve as the initial Brønsted base in the heterolytic hydrogen cleavage. Addition of H_2 to the sulfur sites, as shown in eq 11, would produce a mercaptan-bridged structure which would readily deprotonate in the presence of base to give 3 or 4. The analogous reversible addition of ethene to the sulfur sites of an alkanethiolate cation has been characterized recently.[25] This reaction



(10)



(11)

---

[15] James, B. R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982; Vol. 8, Chapter 51, pp 285–302.

[16] Zhou, P.; Vitale, A. A.; San Filippo, J., Jr.; Saunders, W. H., Jr. *J. Am. Chem. Soc.* **1985**, *107*, 8049.

[17] Wink, D.; Ford, P. C. *J. Am. Chem. Soc.* **1985**, *107*, 1794.

[18] Low, J. J.; Goddard, W. A. *J. Am. Chem. Soc.* **1984**, *106*, 6928.

[19] Reamey, R. H.; Whitesides, G. M. *J. Am. Chem. Soc.* **1984**, *106*, 81.

[20] Ambiguities in assigning heterolytic mechanisms for hydrogen activation have been discussed: Brothers, P. J. *Prog. Inorg. Chem.* **1980**, *28*, 1.

[21] DuBois, D. L.; Kvietok, F.; Rakowski DuBois, M. Submitted for publication.

[22] Other structures of hydrogen-addition products could obviously be proposed, including addition across a M–M bond.[15] Suggestions made by reviewers included (a) H_2 addition to M and S with cleavage of the metal–sulfur bond and (b) initial H_2 addition across the C–S bond of the dithiolate ligand. Formation of a terminal SH ligand (path a) seems unlikely in view of its bridging ability and the stability of the Mo_2S_4 core. Path b seems unlikely on the basis that reaction of 1 with D_2, characterized by ^2H NMR spectroscopy, did not result in deuterium incorporation into the methanedithiolate ligand. Initial formation of a molecular H_2 adduct has also been suggested by a reviewer, but activation enthalpies for η^2-H_2 complex formation have been found to be significantly lower than those observed here.[23]

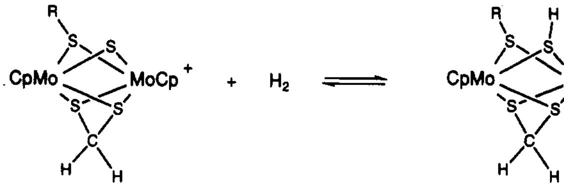
[23] Miller, J. M.; Kastrup, R. V.; Melchior, M. T. Horvath, I. T.; Hoff, C. D.; Crabtree, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 9643.

[24] End-on addition of H_2 to a metal has been proposed; E.g.: Gell, K. I.; Schwartz, J. *J. Am. Chem. Soc.* **1978**, *100*, 3246.

[25] Birnbaum, J.; Haltiwanger, R. C.; Teachout, C.; Parker, K.; Bernatis, P.; Rakowski DuBois, M. *Organometallics* **1991**, *10*, 1779.

gives a precedent for the addition of a molecule to the sulfur sites in such cations and provides support for this proposed pathway of hydrogen addition.

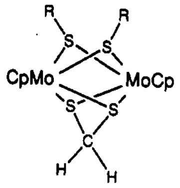
An alternate mechanism for the initial interaction of the cation with hydrogen could involve a stepwise addition of hydrogen across a molybdenum–sulfide bond (eq 12).



(12)

Nucleophilic attack on the sulfido ligand in such cations has been observed (eq 5). Although most molybdenum hydrides are not very acidic in nature, the positive charge on the product proposed in eq 12 and the multiple coordination by electronegative sulfur ligands may permit deprotonation of this complex to give a neutral reduced species such as 3 or 4.

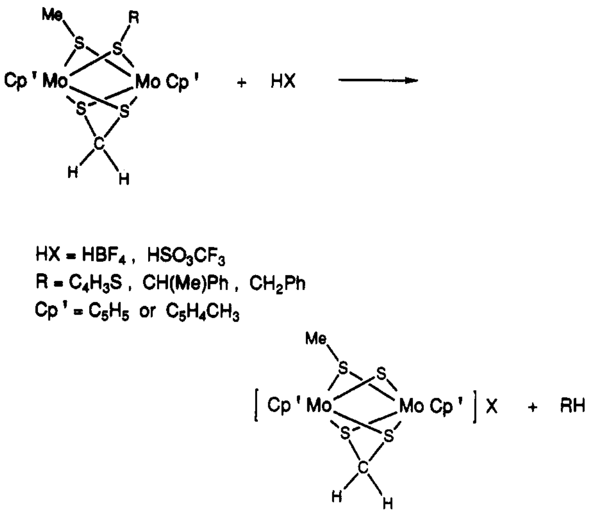
It should be possible to probe the relative basicities of a thiolate ligand and of a molybdenum ion in neutral molybdenum(III) derivatives in order to compare the stabilities of the products proposed in eqs 11 and 12. Neutral dinuclear molybdenum complexes of the formula $(MeCpMo)_2(S_2CH_2)(\mu\text{-SR})(\mu\text{-SH})$ have been prepared, and their protonation might give access to one or both of the desired products of eqs 11 and 12. However, protonation of such SH complexes has been observed to lead to hydrogen elimination,[8] and this reaction may prevent observation of an intermediate protonation product. In addition, the SH ligands in the neutral complexes are extremely prone to oxidation and other side reactions; we have therefore studied the protonation of more stable analogues with two thiolate ligands (structure A).



A

Reactions of $(CpMo)_2(S_2CH_2)(\mu\text{-SR})_2$ with Protic Acid at Room Temperature. The reactions of a strong anhydrous acid with neutral molybdenum(III) dimers of type A were initially investigated at room temperature. Two different reactions were observed with 1 equiv of acid, depending on the nature of the thiolate ligand substituents. For example, the reaction of $(MeCpMo)_2(S_2CH_2)(SMe)(SC_4H_3S)$ with 1 equiv of HBF_4 at room temperature resulted in rapid cleavage of the C–S bond of the thiophenethiolate ligand as shown in eq 13. Free thiophene was identified in the NMR spectrum of the product solution. No evidence for cleavage of the methyl group in the methanethiolate ligand was observed. The methanethiolate cation was isolated in high yield and identified by comparison of spectroscopic data with those of the known iodide salt.[10] This facile protonolysis of the neutral molybdenum(III) thiolate complex appears to be related to the observed reaction of the bromide or triflate salts of the thiophenethiolate cation with hydrogen in the absence of a strong nitrogen base. The latter reaction also resulted in the formation of free thiophene.

The protonolysis reactions for the relatively low-valent Mo(III) complexes appeared to be favored for thiolate substituents with electron-withdrawing character, which shift electron density from metal and sulfur to stabilize carbanionic character in the thiolate carbon. In previous studies of metal thiolates, Boorman and co-workers found that the cleavage of S–C bonds of coordinated thiolates in high-valent M complexes was accomplished by hydridic reagents.[26] These reactions were facile when electron-donating thiolate substituents stabilized carbonium ion character at the thiolate substituent as shown in eq 14.



(13)

(14)

An alternate reaction pathway was observed for molybdenum thiolate complexes with electron-donating thiolate substituents. For example, the room-temperature reaction of 1 equiv of triflic acid with $(CpMo)_2(S_2CH_2)(SMe)(SR)$, where R = Me and i-Pr, did not result in alkane formation but, rather, led to the rapid one-electron oxidation of the complex. The one-electron-oxidation products of the molybdenum dimers gave very broad NMR resonances characteristic of the paramagnetic cations. Such products were further identified by mass spectroscopy. The identification of H_2 as the second product in these redox reactions is described in the Experimental Section.

Low-Temperature Protonation Reactions. The two different reaction pathways observed at room temperature suggested to us that the sites of protonation in the complexes differed. For example, we postulated that protonation at a thiolate sulfur may precede RH elimination from the ligand, while protonation at a metal ion may initiate oxidation. In an attempt to detect initial protonated intermediates in these reactions, we carried out the reactions with triflic acid at −70 °C in sealed NMR tubes and monitored the reactions by NMR spectroscopy at this temperature.

When the complexes $(CpMo)_2(S_2CH_2)(SMe)(SR)$ (R = Me, CH_2Ph, CH(Me)Ph) were protonated at −70 °C, evidence was observed for the rapid formation of the oxidized paramagnetic cations and of molecular hydrogen. Intermediate protonation products were not detected. As the reaction mixtures were warmed to room temperature, the stability of the oxidized cations $[(CpMo)_2(S_2CH_2)(\mu\text{-}$

---

[26] Boorman, P. M.; Freeman, G. K. W. *Abstracts of Papers*, 199th National Meeting of the American Chemical Society, Boston, MA, 1990; American Chemical Society: Washington, DC, 1990; INOR 468. Freeman, G. K. W. Ph.D. Thesis, University of Calgary, Calgary, Alberta, Canada, 1990.

SMe)(μ-SR)]$^+$ varied depending on the nature of R. Further reactions of such cations did not lead to quantitative RH formation but, rather, to intermolecular alkyl transfer between dimers. These reactions will be described in more detail in a separate paper.

Summary

Kinetic studies of the reactions of cationic thiolate-bridged molybdenum(IV) complexes with hydrogen indicate that the addition of hydrogen to the cation is the rate-determining step. This is followed by rapid deprotonation of the cationic hydrogen-addition product by an external base and electron transfer between reduced product and starting cation. The activation enthalpy determined for the hydrogen activation is higher than those observed for most oxidative additions of hydrogen to a single metal center and seems more consistent with a heterolytic cleavage mechanism. Attempts were made to model the hydrogen-addition product by protonating neutral molybdenum(III) thiolate complexes. Protonated intermediates were not observed in these reactions, which proceeded by one of two pathways depending on the nature of the thiolate substituent. Complexes with electron-withdrawing substituents underwent cleavage of the C–S bond of a thiolate ligand when protonated at room temperature, while complexes with electron-donating substituents underwent a one-electron oxidation.

Because the initial site of protonation of the neutral dimers may determine their subsequent reactivity as well as shed light on the mode of hydrogen addition to the cations, we have made further efforts to identify protonated or alkylated intermediates by exploring reactions of electrophiles with a series of related dithiolate complexes of molybdenum. This work, which provides evidence for electrophilic attack at both molybdenum and sulfur sites, is discussed in the following paper.

Experimental Section

Materials and Instrumentation. (MeCpMo(μ-S))$_2$S$_2$CH$_2$ was prepared according to the published procedure.[27] Potassium graphite and Proton Sponge (1,8-bis(dimethylamino)naphthalene) were purchased from Alfa. The latter was recrystallized from EtOH. Triethylamine was distilled from sodium hydride. Dichloromethane, acetonitrile, and THF were distilled from CaH$_2$, toluene was distilled from Na/benzophenone, and chloroform was passed through basic alumina prior to use. Reagent grade hydrogen and deuterium (99.8%) were purchased from Matheson. All other reagents were purchased from commercial suppliers and used without further purification.

Electronic spectra were recorded on either a Hewlett-Packard 8451A diode array spectrophotometer or a Perkin-Elmer Lambda 9 spectrophotometer. Proton NMR spectra were recorded on a Varian VXR-300 NMR spectrometer. Chemical shifts were referenced to Si(CH$_3$)$_4$ by using the deuterated solvent as the secondary reference. Mass spectra were obtained on a VG Analytical 7070 EQ-HF mass spectrometer. Elemental analyses were performed by Spang Microanalytical Laboratories. All electrochemical measurements were carried out under a nitrogen atmosphere using either 0.1 M n-Bu$_4$NBF$_4$ or n-Bu$_4$NClO$_4$ in dichloromethane. Cyclic voltammograms were recorded using either a BAS 100 or a Cypress Systems Model CYSY-1 electrochemical analyzer with a Pt-wire or Pt-disk working electrode, Pt-wire-mesh auxiliary electrode, and Pt- or Ag-wire reference electrode. Potentials are reported vs the ferrocene couple (+0.42 V vs SCE), which was used as an internal reference.

Synthesis of [(MeCpMo)$_2$(S$_2$CH$_2$)(μ-S)(μ-SC$_4$H$_3$S)]Br. (MeCpMo(μ-S))$_2$S$_2$CH$_2$ (0.696 g, 1.4 mmol) was dissolved in 20 mL of CHCl$_3$ in a 100-mL Schlenk flask. The solution was freeze–pump–thaw-degassed three times, and 2-bromothiophene (407 μL, 4.2 mmol) was vacuum-distilled into the vessel. The frozen sample was charged with 600 mm of nitrogen at 77 K, the vessel was sealed, and the mixture was stirred while being heated in a 50 °C oil bath for 3 days. The solvent was removed under vacuum, and the remaining oil was extracted with methanol and the extract filtered. The volume of the filtrate was reduced under vacuum, and following slow addition of Et$_2$O, the red-purple product crystallized. Yield: ca. 70%. ^{1}H NMR (CDCl$_3$; δ ppm): 6.98 (m, 8 H, Cp), 6.78 (m, 1 H, C$_4$H$_3$S), 6.51 (m, 1 H, C$_4$H$_3$S), 6.35 (m, 1 H, C$_4$H$_3$S), 4.69 (s, 2 H, S$_2$CH$_2$), 2.54 (s, 6 H, CH$_3$Cp). FAB-MS (m/e): 655 (P$^+$ of salt), 575 (P – Br), 529 (P – Br – SCH$_2$), 446 (P – Br – SCH$_2$ – C$_4$H$_3$S). $E_{p/2}$ (V vs Cp$_2$Fe): –0.66 (ΔE_p = 70 mV), –1.52 (ΔE_p = 100 mV). Anal. Calcd for Mo$_2$C$_{17}$H$_{19}$S$_5$Br: C, 31.15; H, 2.92; S, 24.45; Br, 12.20. Found: C, 31.09; H, 3.11; S, 24.39; Br, 12.20.

Table IV. X-ray Data Collection Parameters for [(MeCpMo)$_2$(S$_2$CH$_2$)(μ-S)(μ-SC$_4$H$_3$S)]Br

formula	C$_{17}$H$_{19}$S$_5$BrMo$_2$
fw	655.4
space group	$P2_1/n$
unit cell dimens	
a, Å	7.030 (3)
b, Å	19.777 (8)
c, Å	15.106 (6)
β, deg	90.84 (3)
V, Å^3	2100.0 (15)
Z	4
calcd density, g/cm^3	2.073
cryst size, mm	0.18 × 0.20 × 0.36
μ, mm^{-1}	3.531
λ, Å	0.710 73 (Mo Kα)
temp, °C	22
scan type	θ–2θ
2θ range, deg	4.0–50.0
scan speed, deg/min	2.93–58.59
index ranges	$-8 \le h \le 8$, $0 \le k \le 23$, $-18 \le l \le 18$
no. of obsd reflns	3102 ($F > 6\sigma(F)$)
no. of unique reflns	3714 (R_{int} = 2.69%)
data-to-param ratio	13.7:1
R, %	3.64
R_w, %	3.60

X-ray Diffraction Study of [(MeCpMo)$_2$(S$_2$CH$_2$)(μ-S)(μ-SC$_4$H$_3$S)]Br. Crystals were obtained by slow diffusion of hexanes in a methanol solution. Details of the crystal data and experimental conditions and a summary of solution and refinement details are given in Table IV.

The structure was solved by direct methods followed by Fourier techniques. For the final model, all atoms except hydrogens were refined independently with anisotropic displacement parameters. Hydrogen atoms were included in idealized positions riding on the atom of attachment. Hydrogen atom isotropic thermal parameters were set to equal 1.1 times the equivalent values for the attached atom. Complete experimental details and structural data are given in the supplementary material.

Reduction of [(MeCpMo)$_2$(S$_2$CH$_2$)(μ-S)(μ-SC$_4$H$_3$S)]Br. The title complex (0.056 g, 0.086 mmol) was placed in a 100-mL side-arm round-bottom flask, and under a nitrogen atmosphere, approximately 1.5 equiv of potassium graphite (29% K) was added. Approximately 40 mL of THF was cannulated into the flask, and the slurry was stirred at ambient temperature. After 36 h the solution appeared homogeneous and was red-brown. The solvent was rotary evaporated to give a dark red-brown solid, and the crude product was chromatographed on alumina with dichloromethane eluent. The first yellow-brown fraction was collected in fairly good yield and was further purified by rechromatographing on alumina with THF eluent. A single yellow band was collected and was identified as the bis(thiophenethiolate) complex [(MeCpMo)$_2$(S$_2$CH$_2$)(μ-SC$_4$H$_3$S)$_2$]. ^{1}H NMR (CDCl$_3$; δ, ppm): 6.89 (m, 2 H, SC$_4$H$_3$S), 6.62 (m, 2 H, SC$_4$H$_3$S), 6.42 (m, 2 H, SC$_4$H$_3$S), 5.59 (m, 10 H, Cp + S$_2$CH$_2$), 2.12, 2.10 (2 s, 6 H, CH$_3$Cp). FAB-MS (m/e): 658 (P$^+$), 575 (P – C$_4$H$_3$S), 529 (P – C$_4$H$_3$S – SCH$_2$), 492 (P – 2 C$_4$H$_3$S), 448 (P – 2 C$_4$H$_3$S – SCH$_2$). CV $E_{p/2}$ (V vs Cp$_2$Fe): –0.14 (ΔE_p = 160 mV), +0.61 (ΔE_p = 100 mV), –0.64 (irrev). The second band was the major fraction, yielding a pink solid with unknown structure and the proposed

---

[27] McKenna, M.; Wright, L. L.; Miller, D. J.; Tanner, L.; Haltiwanger, R. C.; Rakowski DuBois, M. *J. Am. Chem. Soc.* **1983**, *105*, 5329.

tetrameric formulation $[(MeCpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SC_4H_3S)]_2$. ^1H NMR ($CDCl_3$; δ ppm): 6.91 (m, 2 H, SC_4H_3S), 6.65 (m, 2 H, SC_4H_3S), 6.28 (m, 10 H, Cp + S_2CH_2), 5.71 (m, 12 H, Cp + S_2CH_2 + SC_4H_3S), 2.41 (s, 6 H, CH_3Cp), 1.99 (m, 6 H, CH_3Cp). FAB-MS (*m/e*): 575 ($P^+/2$), 529 ($P/2 - SCH_2$), 493 ($P/2 - C_4H_3S$), 446 ($P/2 - SCH_2 - C_4H_3S$). $E_{p/2}$ (V vs Cp_2Fe): −0.68 (ΔE_p = 50 mV), −1.58 (irrev). The third fraction was identified by ^1H NMR spectroscopy as the methanedithiolate-bridged complex $(MeCpMo(\mu\text{-}S))_2S_2CH_2$ (5).

Synthesis of $[(MeCpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SC_4H_3S)]SO_3CF_3$ (1). $[(MeCpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SC_4H_3S)]Br$ (0.295 g, 0.449 mmol), 10 mL of acetonitrile, and silver triflate (0.14 g, 0.55 mmol) were placed in a 100-mL side-arm round-bottom flask. The resulting slurry was degassed, purged with nitrogen, and stirred at room temperature. After 24 h a white solid (AgBr) had formed in the solution. The reaction mixture was filtered through Celite-545, and the filtrate was reduced in volume. Addition of diethyl ether gave a dark purple-red, microcrystalline solid that was isolated in 90% yield. ^1H NMR (CD_3CN; δ, ppm): 7.27 (m, 1 H, C_4H_3S), 6.96 (m, 8 H, Cp), 6.82 (m, 1 H, C_4H_3S), 6.73 (m, 1 H, C_4H_3S), 4.01 (s, 2 H, S_2CH_2), 2.51 (s, 6 H, CH_3Cp). UV–vis (CH_3CN; λ_{max}, nm): 516 ($\epsilon = 871\ M^{-1}\ cm^{-1}$), 590 ($\epsilon = 389\ M^{-1}\ cm^{-1}$), 820 ($\epsilon = 1186\ M^{-1}\ cm^{-1}$). The complex was found to obey Beer's law over a concentration range of $1 \times 10^{-3} - 1 \times 10^{-4}$ M in dichloromethane solution. Anal. Calcd for $C_{18}H_{20}Mo_2S_6F_3O_3$: C, 29.79; H, 2.78; S, 26.51. Found: C, 29.67; H, 2.60; S, 26.47.

Synthesis of $[(MeCpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SCH_2CO_2CH_3)]CF_3SO_3$ (2). $[(MeCpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SCH_2CO_2CH_3)]Br$ (0.6 g, 0.9 mmol) was reacted with silver triflate in a procedure similar to that described above. The dark burgundy product was recrystallized from dichloromethane/hexanes. Yield: ca. 90%. ^1H NMR (CD_3CN; δ, ppm): 6.89 (m, 8 H, Cp), 4.14 (s, 2 H, S_2CH_2), 3.64 (s, 3 H, OCH_3), 2.64 (s, 2 H, $SCH_2CO_2CH_3$), 2.47 (s, 6 H, CH_3Cp). $E_{p/2}$ (V vs Cp_2Fe): −0.67 (ΔE_p = 72 mV), −1.67 (irrev), +1.02 (irrev). UV–vis (CH_2Cl_2; λ_{max}, nm): 484 ($\epsilon = 985\ M^{-1}\ cm^{-1}$), 820 ($1660\ M^{-1}\ cm^{-1}$). Plots of absorbance (λ = 484 nm) vs concentration of 2 in dichloromethane were linear over the concentration range of 1.7×10^{-3}–3.8×10^{-4} M with correlation coefficients of 0.999. Anal. Calcd for $C_{17}H_{21}Mo_2S_5F_3O_5$: C, 28.57; H, 2.97; S, 22.43. Found: C, 28.50; H, 2.98; S, 22.30.

Reaction of $[(MeCpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SC_4H_3S)]Br$ with H_2. The title complex (0.007 g, 0.01 mmol) was dissolved in 1 mL of $CDCl_3$ in an NMR tube. The solution was freeze–pump–thaw-degassed three times and charged with 600 mm of hydrogen at 77 K. After 1 day at ambient temperature a color change from red-purple to blue was observed, and the ^1H NMR spectrum showed clean formation of $(MeCpMo(\mu\text{-}S))_2S_2CH_2$ and free thiophene (δ 7.34, 7.15). HBr was presumably formed but was not detected spectroscopically. The volatile portion of the reaction mixture was vacuum-distilled into a second NMR tube, and the ^1H NMR spectrum of this fraction confirmed the presence of free thiophene.

Reaction of 1 or 2 with H_2. Complex 1 or 2 (0.009 g, 0.01 mmol) was dissolved in 1 mL of CD_2Cl_2 in an NMR tube. The solution was freeze–pump–thaw-degassed three times, and the tube was charged with 600 mm of hydrogen at 77 K. After the tube was shaken for 1 week at ambient temperature, no change in the ^1H NMR spectrum was observed, and no reaction with hydrogen had occurred. When the reaction mixture was heated at 50 °C for 2 days, the reaction proceeded to form $[(MeCpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SH)]OTf$ and thiophene or methyl acetate, respectively.

Reaction of 1 with Hydrogen and Base. (a) Low-Temperature NMR Experiment. Complex 1 (0.01 g, 0.014 mmol) was placed in an NMR tube fitted with a high-vacuum valve and Teflon stopcock. Triethylamine (2 μL, 0.014 mmol) was combined with 1 mL of CD_2Cl_2 in a 10-mL Schlenk tube and degassed. The solvent mixture was vacuum-transferred into the NMR tube at −196 °C, 600 mm of hydrogen was added, and the tube was sealed. The tube was thawed in a dry-ice–acetone bath at −77 °C and immediately inserted into the −70 °C spectrometer probe. The reaction was monitored over a temperature range of −70 to 0 °C over 2 h. The spectra appeared very broad, and resonances due to starting material disappeared after 30 min, suggesting a paramagnetic product. A similar spectrum was observed at room temperature. No evidence for a hydrosulfido ligand was observed.

(b) Visible/Near-IR Experiment. Complex 1 (0.004 g, 0.006 mmol) was dissolved in 5 mL of dichloromethane in a spectrometer cell equipped with a high-vacuum valve and a glass reservoir, and triethylamine (0.8 μL, 0.006 mmol) was added to the solution. The solution was degassed in two freeze–pump–thaw cycles, and 600 mm of hydrogen was added at −196 °C. The reaction mixture was thawed, and an initial absorbance spectrum was recorded. The cell was placed on a shaker at ambient temperature and periodically removed to monitor the optical spectrum. The absorbance of 1 at 820 (and 520) nm gradually disappeared, while new bands at 510 and 1400 nm grew in (see Figure 2). The latter are assigned to $(MeCpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SC_4H_3S)^{\bullet}$. No further change in the spectrum was observed over a several-day period.

When 1 mole % of 5 was added in the above experiment, similar results were initially observed. However, the intermediate bands at 510 and 1400 nm disappeared over a 3-h period to give the featureless visible spectrum associated with 3. The plot of Abs_{1400} vs time for the latter reaction was linear with a correlation coefficient of 0.995.

Synthesis of $[(MeCpMo)_2(S_2CH_2)(\mu\text{-}SH)(\mu\text{-}SC_4H_3S)]$ (3). The bromide or triflate salt of the thiophenethiolate cation (0.071 g, 0.13 mmol) was placed in a Schlenk flask. Triethylamine (18 μL, 0.16 mmol) was combined with 5 mL of deuteriotoluene and added to the flask. The reaction mixture was degassed with three freeze–pump–thaw cycles, and the flask was charged with 600 mm of hydrogen at −196 °C. The slurry was stirred at 50 °C, and after 4 h a color change from red-purple to dark brown was noticed and a white precipitate had formed. The brown solution was filtered away from the solid under hydrogen purge and transferred into an NMR tube fitted with a high-vacuum valve and Teflon stopcock. The tube was sealed under a hydrogen atmosphere. ^1H NMR (CD_2Cl_2; δ, ppm): 6.87 (m, 1 H, C_4H_3S), 6.63 (m, 1 H, C_4H_3S), 6.23 (m, 1 H, C_4H_3S), 5.59 (m, 10 H, Cp + S_2CH_2), 2.08 (m, 6 H, CH_3Cp), −1.0 (s, 1 H, SH). Visible spectrum (nm): 400 (sh). The same molybdenum product was formed when the reaction was carried out in the presence of an alternate base such as Proton Sponge. When the hydrogen was removed and the tan-brown solution exposed to air, the color of the solution rapidly changed to red, characteristic of $[(MeCpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SC_4H_3S)]^{\bullet}$, which has been identified by visible spectroscopy (λ_{max} 510, 1400 nm) and by its decomposition products (see above).

The white solid product filtered from the reaction mixture was redissolved in CD_3CN and was identified by ^1H NMR spectroscopy as the triethylammonium salt (δ 3.12 (m), 1.41 (m)).

Reaction of $[(MeCpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SCH_2CO_2CH_3)]CF_3SO_3$ (2) with Hydrogen and Base. Complex 2 (0.009 g, 0.012 mmol) was dissolved in 1 mL of CD_2Cl_2 in an NMR tube fitted with a high-vacuum valve and Teflon stopcock. Proton Sponge (0.013 g, 0.061 mmol) was added to the tube, and the mixture was degassed with three freeze–pump–thaw cycles. The tube was flame-sealed under 600 mm of hydrogen at −196 °C and placed in a 40 °C oil bath. The tube was shaken periodically, and after 1 day a color change from red-purple to tan-brown was observed, with the formation of a brown precipitate. The ^1H NMR spectrum of the reaction mixture identified the major product as the neutral hydrosulfido-bridged product $[(MeCpMo)_2(S_2CH_2)(\mu\text{-}SH)(\mu\text{-}SCH_2CO_2CH_3)]$ (4). ^1H NMR (CD_2Cl_2; δ, ppm): 5.75 (s, S_2CH_2); 5.43 (m, Cp); 3.59 (s, OCH_3); 2.49 (s, SCH_2); 2.02 (s, CH_3Cp); −1.2 (s, SH). A second unassigned methoxy singlet was observed at 3.64 ppm with less than 0.1 of the intensity of the resonance of 4. Resonances for the ammonium salt of Proton Sponge were broadened and shifted downfield from those of the neutral base.

Reaction of 1 with Base under a Nitrogen Atmosphere. Complex 1 (0.004 g, 0.006 mmol) was dissolved in 5 mL of freshly distilled dichloromethane in a volumetric flask. Triethylamine (0.85 μL, 0.006 mmol) was added to the solution, and the mixture was transferred to a UV–visible spectrometer cell equipped with a high-vacuum valve and a glass reservoir. The solution was degassed with two freeze–pump–thaw cycles and the cell charged with 600 mm of nitrogen at 77 K. The reaction mixture was thawed, and an initial absorbance spectrum was recorded. The tube was placed on a shaker at ambient temperature and periodically removed to monitor the disappearance of the near-IR absorbance at 840 nm. After 90 min, this absorbance was diminished by less than 14%. When the identical experiment was run under a hydrogen atmosphere, the near-IR absorbance at 840 nm was more than 90% diminished over 90 min of reaction time.

Reaction of 2 with Base under a Nitrogen Atmosphere. Complex 2 (0.005 g, 0.007 mmol) was dissolved in 5 mL of freshly distilled dichloromethane in a volumetric flask. Proton Sponge (0.008 g, 0.035 mmol) was added to the solution, and the reaction mixture was placed under hydrogen and monitored as described previously. After the mixture was stirred for 2 h at 40 °C, the near-IR absorbance at 840 nm was diminished by less than 5%. When the identical experiment was run under a hydrogen atmosphere, the near-IR absorbance was 70% diminished over the same reaction time.

Synthesis of $(MeCpMo)_2(S_2CH_2)(\mu\text{-}SCH_3)(\mu\text{-}SR)$. A typical procedure is given for R = C_4H_3S. The bromide salt of the thiophenethiolate cation (0.119 g, 0.182 mmol) was placed in a 50-mL Schlenk flask with 10 mL of freshly distilled THF. Approximately 2 equiv of CH_3Li (1.4 M in Et_2O) was syringed into the slurry. The solution was degassed with three freeze–pump–thaw cycles, and the tube was sealed under nitrogen. After it was stirred for 1 day at ambient temperature, the solution appeared homogeneous and was dark brown. Volatiles were evaporated, and the remaining brown, oily product was extracted with dichloromethane and chromatographed on alumina with CH_2Cl_2/hexanes as eluent. The first orange-brown band, the desired product, was isolated as an oil, and further attempts to crystallize it were unsuccessful. Estimated yield: 50–60%. ^1H NMR ($CDCl_3$; δ, ppm): 6.9 (m, 1 H, C_4H_3S), 6.6 (m, 1 H, C_4H_3S), 6.41 (m, 1 H, C_4H_3S), 5.60 (m, 10 H, Cp + S_2CH_2), 2.09 (s, 6 H, CH_3Cp), 1.46 (s, 3 H, SCH_3). FAB-MS (*m/e*): 590 (P^+), 575 (P – CH_3), 529 (P – CH_3 – SCH_2), 446 (P – CH_3 – SCH_2 – C_4H_3S). Exact mass: calcd for $Mo_2C_{18}H_{22}S_4$ 593.8433, found 593.8436.

Similar procedures were followed for R = Me, Me_2CH, CH_2Ph, and CH(Me)Ph. ^1H NMR data are given in the supplementary material.[28]

Reaction of $(MeCpMo)_2(S_2CH_2)(\mu\text{-}SCH_3)(\mu\text{-}SR)$ with Acid at Room Temperature. A typical procedure is given for R = C_4H_3S. To a brown solution of the molybdenum complex (~0.4 mmol) in 1 mL of $CDCl_3$ was added a slight excess of $HBF_4 \cdot Et_2O$ (~150 μL, 0.6 mmol). The solution was degassed by three freeze–pump–thaw cycles and stirred at ambient temperature. After several hours, the solution had turned red-purple. The volatile portion of the reaction mixture was vacuum-transferred, and a ^1H NMR spectrum confirmed the presence of free thiophene (δ 7.34, 7.15). The red-purple solid was redissolved in $CDCl_3$, and by comparison of its ^1H NMR spectrum with that of the known iodide salt,[10] the product was identified as $[(MeCpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SMe)]BF_4$.

Quantitative formation of RH and the methanethiolate cation was also observed in the protonation of the title complex where R = CH(Me)Ph. Formation of RH and the methanethiolate cation was observed in the protonation when R = CH_2Ph, but a second insoluble molybdenum product was also formed. RH products were identified by ^1H NMR and GC–mass spectroscopic data.

For the complex with R = CH_3, protonation with triflic acid led to formation of $[(CpMo)_2(S_2CH_2)(SMe)_2]OTf$, which was precipitated with petroleum ether (bp 35–60 °C) and recrystallized from CH_2Cl_2–Et_2O. Yield: 53%. FAB–MS (*m/e*): 494 (P of cation) 479 (P^+ – CH_3) 464 (P^+ – 2 CH_3), 446 (P^+ – SCH_3), 433 (P^+ – CH_3 – SCH_2). When the reaction was carried out in an NMR tube, broad resonances were observed for the molybdenum product and a sharp singlet at 4.6 ppm was assigned to H_2. Similar results were observed for the complex with R = $(CH_3)_2CH$.[28]

Protonation of $(CpMo)_2(S_2CH_2)(SMe)(SR)$ (R = Me, CH_2Ph, CH(Me)Ph) at –70 °C. Triflic acid (1 μL, 0.01 mmol) was combined with 1 mL of CD_2Cl_2 and placed in an NMR tube. The solution was degassed with two freeze–pump–thaw cycles and frozen in an *n*-pentane ice bath at –131 °C. The molybdenum dimer (0.010 mmol) was dissolved in a minimal amount of CD_2Cl_2 and was added to the frozen acid mixture under a nitrogen purge. The tube was sealed under N_2, thawed in a –77 °C cold bath, and inserted into the spectrometer probe at –70 °C. NMR spectra showed very broad resonances characteristic of oxidized dimers and a sharp singlet at 4.6 ppm assigned to H_2. Intermediate protonated species were not identified. When R = CH(Me)Ph, additional products, including ethylbenzene, and products resulting from further reactions of $[(CpMo)_2(S_2CH_2)(SMe)(SCH(Me)Ph)]^+$ were detected in the low-temperature spectrum. These will be discussed elsewhere.

Rate Studies of the Reactions of H_2 with Molybdenum Cations. Stock solutions of 1 or 2 and base (~5 equiv of Proton Sponge or, for 1, 1 equiv of NEt_3) in dichloromethane were prepared with known cation concentrations over the range of 1×10^{-4}–1×10^{-3} M. Approximately 5 mL of the solution was added to a 1 cm path length spectrometer cell equipped with a high-vacuum valve and an attached 25-mL glass reservoir. The solution was degassed with two freeze–pump–thaw cycles, and 600 mm of hydrogen or deuterium gas was added at 77 K. After the mixture was warmed to room temperature, an initial absorbance spectrum was recorded. The reaction mixture was shaken vigorously on a Barnstead/Thermolyne rotating mixer for ambient-temperature experiments or placed in a constant-temperature bath and stirred vigorously. Samples were removed from the mixer or stirrer for 1–2 min at periodic time intervals over the course of the reaction in order to monitor the disappearance of the near-IR absorbance at 840 nm. Plots of the natural logarithm of this absorbance vs time were linear, checked through 90% reaction for 1 and 78% reaction for 2, with correlation coefficients of 0.98 to 0.99+. Rate constants obtained for individual samples of 1, used in comparative rate studies, showed good reproducibility, as indicated in Table III, but absolute values of k_{obs} varied somewhat for different samples of 1. We later determined that variations depended on the amount of $(MeCpMo(\mu\text{-}S))_2S_2CH_2$ (5) present in the sample. Samples of 1 could be obtained free of 5 by chromatographing on acidic alumina with acetonitrile eluent. The burgundy fraction from the column was recrystallized by the addition of diethyl ether to an acetonitrile solution of the complex. Rate constants obtained for reactions of purified samples of 2 showed good reproducibility (see Table III).

Dependence of Reaction Rates on Temperature. Four solutions of 2 in CH_2Cl_2 were prepared from two different stock solutions, and a procedure similar to that described above was followed. The cells were placed in oil baths of different temperatures, and reaction mixtures were stirred vigorously. Cells were removed momentarily from the oil baths at 5-min intervals to monitor the disappearance of the absorbance at 840 nm. Hydrogen solubility in dichloromethane was estimated[29] as described below in order to convert observed rate constants to second-order rate constants ($k_2 = k_{obs}/[H_2]$). A plot of ln (k_2/T) vs inverse temperature was linear with a correlation coefficient of 0.989. From the slope and intercept of this line the ΔS and ΔH values of activation were calculated to be 84 kJ/mol and –9 J/(mol K), respectively.

Hydrogen solubilities (at 760 and 2280 mm) at 19.0 °C were compared in $CDCl_3$ and CD_2Cl_2 by ^1H NMR spectroscopy using a standard amount of *t*-BuCl as an internal reference. Integrations were compared for data collected with a 20-s pulse delay. The average of several determinations of two independent experiments gave a ratio of H_2 concentration in CD_2Cl_2 vs that in $CDCl_3$ of 1.06 ± 0.08 at both 1 and 3 atm. Using the reported solubility of H_2 in $CDCl_3$ (1 atm at 19 °C) of 2.61×10^{-3} M,[30] we calculated the solubility in CD_2Cl_2 at 19 °C as 2.77×10^{-3} M at 1 atm and 8.31×10^{-3} M at 3 atm. Comparison of ^1H NMR data at 1 and 3 atm showed good agreement with Henry's law. Rate constants were not corrected for differences in hydrogen solubility over the temperature range employed.[29]

Solutions of 1 and Proton Sponge (5 equiv) from a stock solution were degassed and reacted with H_2 as described above at the four temperatures indicated in Table III. Reaction rates for this entire series of experiments were reproducible but significantly slower than normal (see Table III). The reactions were found to be inhibited by base impurities. A plot of ln (k_2/T) vs inverse

---

[28] Birnbaum, J. Ph.D. Thesis, University of Colorado, Boulder, CO, 1990.

[29] Solubility data for H_2 in dichloromethane were not found, but the solubility of 1 atm of H_2 in chloroform was reported to vary by <10% over a temperature range of 1–26 °C.[30]

[30] Linke, W. F. *Solubilities of Inorganic and Metal Organic Compounds*, 4th ed.; American Chemical Society: Washington DC, 1958; Vol. 1, p 1089.

Organometallics **1992**, *11*, 2435–2443

temperature was linear with a correlation coefficient of 0.999. From the slope $\Delta H^{\ddagger}$ was calculated to be 75 kJ/mol.

Acknowledgment. This work was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research, U.S. Department of Energy. We thank Prof. Cortlandt Pierpont and his research group for the use of their spectrometer.

Supplementary Material Available: Tables of all bond distances and angles, positional parameters, and complete crystal data, data collection conditions, and solution and refinement details for $[(MeCpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SC_4H_3S)]Br$ and a table of ^1H NMR data for $(CpMo)_2(S_2CH_2)(SMe)(SR)$ derivatives (10 pages). Ordering information is given on any current masthead page.

OM920117Z

Sites of Electrophilic Attack in Neutral Dithiolate-Bridged Molybdenum Complexes

Paul Bernatis, R. C. Haltiwanger, and M. Rakowski DuBois*

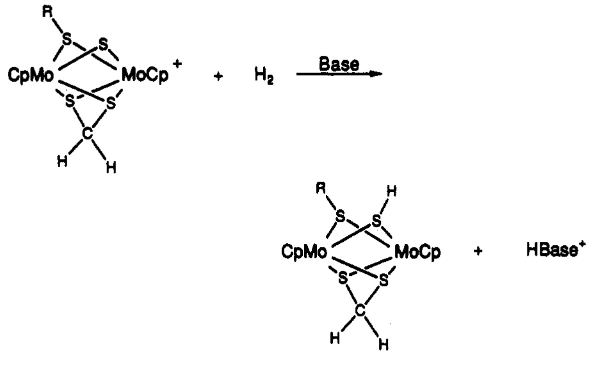
Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309

Received March 3, 1992

The reaction of $[CpMoS_2CH_2]_2$ (1) with 1 equiv of triflic acid at −70 °C resulted in the formation of a diamagnetic product which was formulated as $[CpMo(H)(S_2CH_2)_2MoCp]SO_3CF_3$ (2) on the basis of ^1H NMR data. When 2 was warmed above −50 °C, an intermolecular redox reaction occurred to form $[CpMoS_2CH_2]_2SO_3CF_3$ and $^1/_2$ mol of H_2. Similar chemistry was characterized for the related derivatives $[CpMoS_2CRR']_2$, where R = R′ = Me and R = Me, R′ = Ph. The reaction of 1 with methyl triflate resulted in alkylation of a sulfur ligand to form $[(CpMo)_2(S_2CH_2)(SCH_2SCH_3)]SO_3CF_3$ (6). Complex 6 was unstable in solution and rearranged to form $[CpMo(S_2CH_2)(\mu\text{-}SMe)(\mu\text{-}SCH_2)MoCp]SO_3CF_3$ (7). Complex 7 crystallized in space group *Pbca* with cell dimensions $a = 14.287$ (3) Å, $b = 14.374$ (3) Å, $c = 20.045$ (3) Å, $V = 4116.5$ (14) Å^3, and $Z = 8$. The crystal structure of 7 showed that the cation contained a bridging thioformaldehyde ligand which was η^1-bonded to one metal ion and η^2-bonded to the second. The protonated and alkylated products may be related to species formed in the addition of H_2 to the cations $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SR)]^+$. Chemical properties and reactivities of the cationic models of the hydrogen addition products are discussed.

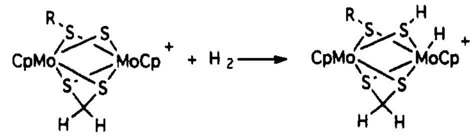
Introduction

In previous work we have reported that certain cationic thiolate-bridged molybdenum dimers reacted with hydrogen in the presence of base to form neutral products such as that shown in eq 1.[1] A kinetic study, described

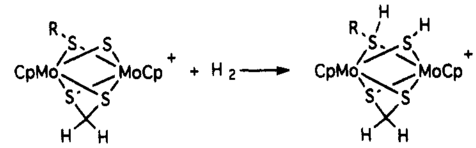


(1)

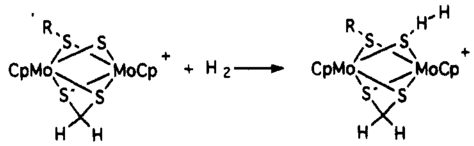
in the preceding paper,[2] determined that the rate of reaction 1 was first order in molybdenum cation, first order in hydrogen, and independent of external base. Activation enthalpies determined for reaction 1 seemed most consistent with a heterolytic cleavage of hydrogen. Potential structures for the species resulting from initial hydrogen addition to the cation were discussed in the preceding paper, and some possibilities are reviewed in eqs 2–4.



(2)

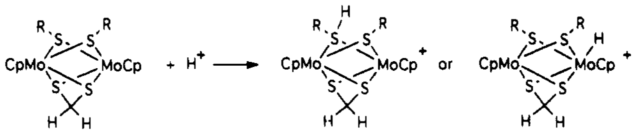


(3)



(4)

We wish to learn more about the mechanism of hydrogen activation in this system. Attempts to spectroscopically detect a hydrogen-addition product have been unsuccessful. An indirect method of assessing the relative stabilities of the products in eqs 2 and 3 may be to identify the site(s) of protonation in related neutral dimers, e.g. eq 5. For example, if the molybdenum ion served as a



(5)

Brønsted base, this might model the role of the metal ion in heterolytic hydrogen cleavage. Conversely, if the pro-

---

[1] (a) Laurie, J. C. V.; Duncan, L.; Haltiwanger, R. C.; Weberg, R. T.; Rakowski DuBois, M. *J. Am. Chem. Soc.* **1986**, *108*, 6234. (b) Gabay, J. Masters Thesis, University of Colorado, Boulder, CO, 1991.

[2] Lopez, L. L.; Bernatis, P.; Birnbaum, J.; Haltiwanger, R. C.; Rakowski DuBois, M. *Organometallics*, preceding paper in this issue.