J|A|C|S
COMMUNICATIONS

Thiophene and Butadiene−Thiolate Complexes of Molybdenum: Observations Relevant to the Mechanism of Hydrodesulfurization

Kevin E. Janak, Joseph M. Tanski, David G. Churchill, and Gerard Parkin*

Department of Chemistry, Columbia University, New York, New York 10027

Received December 31, 2001

With the advent of increasingly stringent regulations pertaining to acceptable levels for the sulfur-containing impurities in gasoline,[1] hydrodesulfurization (HDS) continues to be the largest volume and most important industrial catalytic application of transition metals.[2] Thiophenes are some of the sulfur-containing impurities that are most averse to HDS, being converted to a mixture of butadiene, butene, and butane under reaction conditions. As such, thiophene has featured prominently as a target for model studies.[3] However, of the many model studies pertaining to HDS, very few have been concerned with molybdenum chemistry, despite the fact that this is the most essential transition metal component of a typical HDS catalyst.[4] For this reason, we have recently started to investigate the reactivity of various molybdenum complexes towards thiophenes and observed the first example of C−S bond cleavage of thiophene by a molybdenum compound.[5] In this paper, we report two other reactions of relevance to HDS, namely the formation of a molybdenum thiophene adduct and a butadiene−thiolate complex, the latter resulting from both C−S bond cleavage and hydrogenation of thiophene.

The paucity of reactivity studies that have achieved C−S bond cleavage of thiophene and its derivatives by molybdenum compounds is not so much the result of a lack of effort, but is rather due to the insufficient reactivity of the molybdenum complexes studied.[6] For this reason, we have decided to focus attention on $Mo(PMe_3)_6$, which is a particularly reactive electron-rich compound that is subject to numerous ligand displacement and oxidative addition reactions.[7] Significantly, we have observed that thiophene reacts with $Mo(PMe_3)_6$ at room temperature to yield the thiophene adduct $(\eta^5\text{-}C_4H_4S)Mo(PMe_3)_3$[8] and the butadiene−thiolate complex $(\eta^5\text{-}C_4H_5S)Mo(PMe_3)_2(\eta^2\text{-}CH_2PMe_2)$, as illustrated in Scheme 1. The relative amounts of $(\eta^5\text{-}C_4H_4S)Mo(PMe_3)_3$ and $(\eta^5\text{-}C_4H_5S)Mo(PMe_3)_2(\eta^2\text{-}CH_2PMe_2)$ in the product mixture are highly dependent on reaction conditions, with the latter being favored at low temperature. It is important to note that this preference is due to a kinetic effect since isolated $(\eta^5\text{-}C_4H_4S)Mo(PMe_3)_3$ and $(\eta^5\text{-}C_4H_5S)Mo(PMe_3)_2(\eta^2\text{-}CH_2PMe_2)$ do not interconvert on the time-scale of the experiment.[9] This observation supports the notion that η^5-thiophene coordination does not necessarily facilitate C−S cleavage and that such adducts may merely represent resting states during HDS.

The formation of $(\eta^5\text{-}C_4H_5S)Mo(PMe_3)_2(\eta^2\text{-}CH_2PMe_2)$ is a result of C−S bond cleavage and hydrogenation of the thiophene ligand; the hydrogen necessary for this reduction of thiophene emanates from the PMe_3 ligand, thereby converting it to a cyclometalated $\eta^2\text{-}CH_2PMe_2$ ligand. While this transformation is irreversible, protonation of $(\eta^5\text{-}C_4H_5S)Mo(PMe_3)_2(\eta^2\text{-}CH_2PMe_2)$ with CF_3CO_2H regenerates the constitution of the PMe_3 ligand and gives $(\eta^5\text{-}C_4H_5S)Mo(PMe_3)_3(\kappa^1\text{-}O_2CCF_3)$.

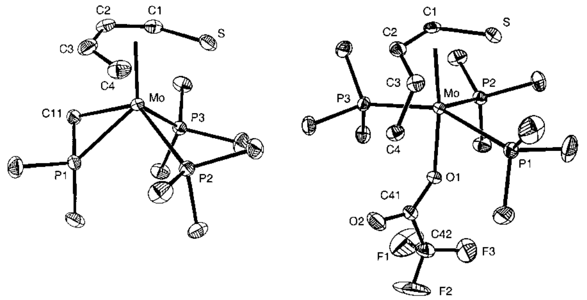
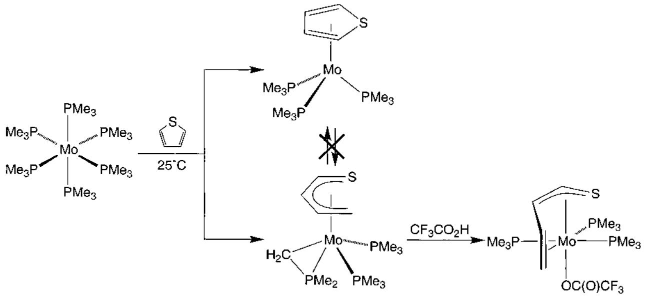


Figure 1. Molecular structures of $(\eta^5\text{-}C_4H_5S)Mo(PMe_3)_2(\eta^2\text{-}CH_2PMe_2)$ and $(\eta^5\text{-}C_4H_5S)Mo(PMe_3)_3(\kappa^1\text{-}O_2CCF_3)$. For the latter complex, the C1−C2−C3−C4 torsion angle for the latter is 122.4°.

Scheme 1



The molecular structures of the butadiene−thiolate complexes $(\eta^5\text{-}C_4H_5S)Mo(PMe_3)_2(\eta^2\text{-}CH_2PMe_2)$ and $(\eta^5\text{-}C_4H_5S)Mo(PMe_3)_3(\kappa^1\text{-}O_2CCF_3)$ have been determined by X-ray diffraction (Figure 1). The structures of these complexes are noteworthy since there are no examples of structurally characterized mononuclear transition metal butadiene−thiolate complexes listed in the Cambridge Structural Database.[10] Most interestingly, the butadiene−thiolate ligands of $(\eta^5\text{-}C_4H_5S)Mo(PMe_3)_2(\eta^2\text{-}CH_2PMe_2)$ and $(\eta^5\text{-}C_4H_5S)Mo(PMe_3)_3(\kappa^1\text{-}O_2CCF_3)$ adopt substantially different conformations. Thus, the butadiene−thiolate ligand in $(\eta^5\text{-}C_4H_5S)Mo(PMe_3)_2(\eta^2\text{-}CH_2PMe_2)$ adopts a *U*-type conformation, whereas that of $(\eta^5\text{-}C_4H_5S)Mo(PMe_3)_3(\kappa^1\text{-}O_2CCF_3)$ adopts an unusual η^5-sickle conformation.[11] Other than the geometry, the most notable difference between the *U* and sickle conformations is the relative planarity of the ligands, with the latter being distinctly nonplanar. To our knowledge the η^5-sickle coordination mode has not previously been considered for butadiene−thiolate ligands.

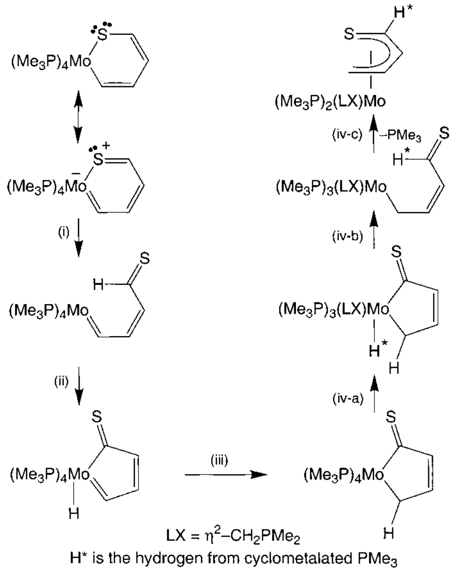
While it is the C−S cleavage and hydrogenation of thiophene that is the most important observation, it is noteworthy that $(\eta^5\text{-}C_4H_4S)Mo(PMe_3)_3$ is the first mononuclear η^5-thiophene molybdenum complex to be spectroscopically identified.[12] It is also pertinent to note that previous attempts to synthesize the related molybdenum carbonyl complex $(\eta^5\text{-}C_4H_4S)Mo(CO)_3$ were unsuccessful.[13]

---

* Address correspondence to this author. E-mail: parkin@chem.columbia.edu.

10.1021/ja012771o CCC: $22.00 © 2002 American Chemical Society

Scheme 2



LX = η^2–CH_2PMe_2
H* is the hydrogen from cyclometalated PMe_3

The formation of the thiophene adduct (η^5-C_4H_4S)Mo(PMe_3)$_3$ and the butadiene−thiolate complex (η^5-C_4H_5S)Mo(PMe_3)$_2$(η^2-CH_2PMe_2) is of potential relevance to HDS, since both thiophene and butadiene−thiolate species have been invoked as intermediates. Ascertaining the mechanism for formation of a butadiene−thiolate species is of particular interest. Two mechanistic possibilities that exist in the literature are distinguished according to whether C−S cleavage occurs prior to addition of hydrogen,[14] or vice versa,[15] with the latter involving the participation of an η^4-allyl-thioether intermediate followed by ring opening.[16] Regardless of which of these mechanisms operates, the hydride emanating from the PMe_3 ligand would be expected to terminate in the CH_2 group of the butadiene−thiolate ligand. Accordingly, Rauchfuss[15a] and Angelici[15b] have reported that the reactions of D^+ and D^- with thiophene complexes generate η^5-butadiene−thiolate ligands in which the deuterium is located in the terminal CH_2 group (anti and syn, respectively). However, a deuterium labeling study employing C_4D_4S demonstrates that the hydrogen from the PMe_3 ligand is transferred *selectively to the carbon adjacent to the sulfur* of the η^5-butadiene−thiolate ligand of (η^5-C_4H_5S)Mo(PMe_3)$_2$(η^2-CH_2-PMe_2). Such an observation is most unexpected and indicates that a new mechanism is required to describe the formation of (η^5-C_4H_5S)Mo(PMe_3)$_2$(η^2-CH_2PMe_2).

A possible mechanism that accounts for selective transfer of the hydrogen from the PMe_3 to the carbon adjacent to the sulfur η^5-butadiene−thiolate ligand is illustrated in Scheme 2 which, for simplicity, starts with Mo(PMe_3)$_4$(η^2-SC_4H_4) as a postulated intermediate. The essential features of this mechanism are (i) rearrangement of the metallathiacycle ring to give a molybdenum alkylidene species with an incipient thioaldehyde fragment,[17] (ii) oxidative-addition of the thioaldehyde C−H bond giving a five-membered metallacycle, (iii) α-H migration to the alkylidene carbon atom, and (iv) a sequence involving hydrogen transfer from the PMe_3 ligand to the thioacyl carbon atom via the molybdenum center. Of these steps, it is the proposed involvement of an alkylidene species that ultimately enables selective hydrogen transfer to the carbon adjacent to the sulfur of the butadiene−thiolate ligand. Experimental evidence for alkylidene intermediates in the hydrogenation of thiophene C−S bond cleavage products has not previously been reported,[18] and the present study suggests that such species may facilitate thiophene hydrogenation during HDS.

In summary, the reaction of Mo(PMe_3)$_6$ with thiophene has provided the first examples of η^5-thiophene coordination and C−S cleavage and hydrogenation by a molybdenum compound. Deuterium labeling studies suggest that the hydrogenation of thiophene may involve an alkylidene intermediate, an observation that has ramifications for the mechanisms of HDS.

Acknowledgment. We thank the U.S. Department of Energy, Office of Basic Energy Sciences (DE-FG02-93ER14339) for support of this research.

Supporting Information Available: Experimental details, spectroscopic data, and crystallographic data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Beginning in 2004, U.S. federal regulations will restrict refineries to manufacture gasoline with a maximum sulfur level of 300 ppm; by 2006, the maximum cap will be reduced to 80 ppm. See: U.S. Environmental Protection Agency, Air and Radiation, Office of Mobile Sources (EPA420-F-99-051; December 1999).
(2) For recent review articles, see: (a) Stirling, D. *The Sulfur Problem: Cleaning up Industrial Feedstocks*; RSC Clean Technology Monographs, 2000. (b) Topsøe, H.; Clausen, B. S.; Massoth, F. E. Hydrotreating Catalysis. In *Catalysis: Science and Technology*; Anderson, J. R., Boudart, M., Eds.; Springer-Verlag: New York, 1996; Vol 11.
(3) Angelici, R. J. *Organometallics* **2001**, *20*, 1259−1275.
(4) Typical HDS catalysts are comprised of a mixture of MoS_2 and Co_9S_8 supported on Al_2O_3. See ref 1 and: Lauritsen, J. V.; Helveg, S.; Laegsgaard, E.; Stensgaard, I.; Clausen, B. S.; Topsoe, H.; Besenbacher, F. *J. Catal.* **2001**, *197*, 1−5.
(5) Churchill, D. G.; Bridgewater, B. M.; Parkin, G. *J. Am. Chem. Soc.* **2000**, *122*, 178−179.
(6) For an example in which a molybdenum complex reacts preferentially with the C−H bond of thiophene, see: Jones, W. D.; Chin, R. M.; Crane, T. W.; Baruch, D. M. *Organometallics* **1994**, *13*, 4448−4452.
(7) Murphy, V. J.; Parkin, G. *J. Am. Chem. Soc.* **1995**, *117*, 3522−3528.
(8) It is noteworthy that the thiophene ligand of (η^5-C_4H_4S)Mo(PMe_3)$_3$ is fluxional on the NMR time-scale at room temperature, but is frozen out at −70 °C.
(9) For example, (η^5-C_4H_5S)Mo(PMe_3)$_2$(η^2-CH_2PMe_2) shows no evidence for isomerization to (η^5-C_4H_4S)Mo(PMe_3)$_3$ after heating at 60 °C for ca. 40 h, while solutions of (η^5-C_4H_4S)Mo(PMe_3)$_3$ decompose upon heating at 60 °C for ca. 3 h.
(10) The structure of a substituted 1,4-dimethylbutadiene−thiolate complex of ruthenium, CpRu(η^5-$SC_4H_3Me_2$), has been reported. See: Hachgenei, J. W.; Angelici, R. J. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 909−910.
(11) The η^5-*U* and η^5-sickle conformations for the butadiene−thiolate ligand are analogous to those of the pentadienyl ligand. See, for example: Ernst, R. D. *Comm. Inorg. Chem.* **1999**, *21*, 285−325.
(12) For reviews of thiophene coordination modes, see: (a) Rauchfuss, T. B. *Prog. Inorg. Chem.* **1991**, *21*, 259−329. (b) Angelici, R. *Coord. Chem. Rev.* **1990**, *105*, 61−76.
(13) Ruette, F.; Valencia, N.; Sanchez-Delgado, R. *J. Am. Chem. Soc.* **1989**, *111*, 40−46.
(14) See, for example: Bianchini, C.; Meli, A.; Peruzzini, M.; Vizza, F.; Frediani, P.; Herrera, V.; Sánchez-Delgado, R. A. *J. Am. Chem. Soc.* **1993**, *115*, 2731−2742.
(15) See for example: (a) Luo, S.; Rauchfuss, T. B.; Gan, Z. *J. Am. Chem. Soc.* **1993**, *115*, 4943−4944. (b) Hachgenei, J. W.; Angelici, R. J. *J. Organomet. Chem.* **1988**, *355*, 359−378.
(16) Rauchfuss has demonstrated that the interconversion of η^4-allyl-thioether and η^5-butadiene−thiolate ligands is facile on a ruthenium center. See ref 15a.
(17) It is possible that oxidative addition of the C−H bond could occur without complete dissociation of the thioaldehyde fragment.
(18) Angelici has reported thienylcarbene complexes of thiophene that do not involve C−S bond cleavage. See: (a) Robertson, M. J.; White, C. J.; Angelici, R. J. *J. Am. Chem. Soc.* **1994**, *116*, 5190−5195. (b) White, C. J.; Angelici, R. J. *Organometallics* **1994**, *13*, 5132−5140.

JA012771O