178 *J. Am. Chem. Soc.* **2000,** *122,* 178−179

Modeling Aspects of Hydrodesulfurization at Molybdenum: Carbon−Sulfur Bond Cleavage of Thiophenes by *Ansa* Molybdenocene Complexes

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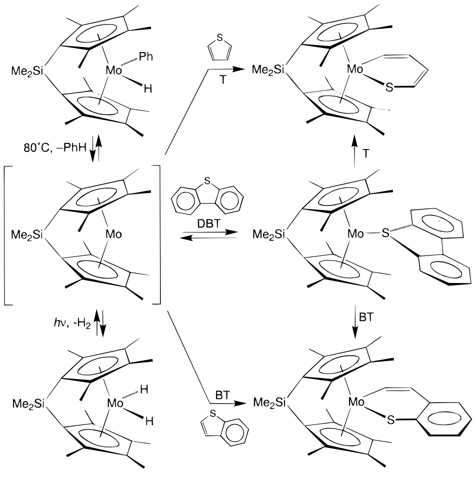
Received October 11, 1999

Hydrodesulfurization (HDS), the means by which sulfur is removed from crude petroleum feedstocks and fuels, has been cited as the largest volume and most important industrial catalytic application of transition metals.[1] Of the sulfur impurities present in crude petroleum, thiophenes are among the most resistant towards HDS. A thorough understanding of the reactivity of thiophenes towards transition metal centers is, therefore, paramount to improving existing HDS technologies. Consequently, the reactions of thiophenes with transition metal complexes have been vigorously studied by many research groups.[2,3] As a result of these pursuits, models for two of the required steps for the HDS of thiophenes, namely (i) thiophene coordination and (ii) C−S bond cleavage, have been provided. These studies, however, have focused on complexes of Mn, Fe, Co, Ni, Ru, Rh, Ir, and Pt, with studies on molybdenum, the most essential component of an HDS catalyst,[4] being almost nonexistent. We have, therefore, been prompted to investigate the reactivity of thiophenes towards molybdenum complexes in an effort to discover molybdenum chemistry of relevance to HDS.

Significantly, we have discovered that the *ansa* molybdenocene complexes, $[Me_2Si(C_5Me_4)_2]MoH_2$ and $[Me_2Si(C_5Me_4)_2]Mo(Ph)H$, exhibit reactivity that models required aspects of the mechanism for thiophene HDS. Thus, upon photolysis, $[Me_2Si(C_5Me_4)_2]MoH_2$ is capable of inducing C−S bond cleavage of thiophene (T) to give $[Me_2Si(C_5Me_4)_2]Mo(\eta^2\text{-}C,S\text{-T})$. The latter complex can also be obtained by the thermal reaction of $[Me_2Si(C_5Me_4)_2]Mo(Ph)H$ with thiophene. These reactions are not only of significance because they represent the first examples of thiophene C−S bond cleavage by a molybdenum compound, but are also of interest in view of the reports that the unsubstituted molybdenocene dihydride derivative, Cp_2MoH_2, does *not* achieve C−S bond cleavage of thiophene; in preference, Cp_2MoH_2 reacts with the α C−H bond to give a thienyl complex, $Cp_2Mo(\eta^1\text{-}C\text{-}SC_4H_3)H$.[5,6]

It is important to emphasize that the $[Me_2Si]$ *ansa* bridge plays a pivotal role in achieving the above C−S bond cleavage reaction. Thus, in the absence of a bridge, the permethylmolybdenocene counterpart, $Cp^*{}_2MoH_2$, is *unreactive* towards thiophene: i.e., photolysis of $Cp^*{}_2MoH_2$ in the presence of thiophene yields only a product of *intramolecular* C−H bond activation, namely $Cp^*(\eta^5,\eta^1\text{-}C_5Me_4CH_2)MoH$. In essence, the constraints imposed by the *ansa* bridge inhibit the $[Me_2Si(C_5Me_4)_2]$ ligand from undergoing an intramolecular deactivation reaction and thereby promote intermolecular C−S bond activation. This markedly different reactivity of thiophene towards $[Me_2Si(C_5Me_4)_2]MoH_2$ and $Cp^*{}_2MoH_2$ represents a notable example of an “*ansa* effect”.[7]

Scheme 1



A more important issue, however, is concerned with why the *ansa* bridged system yields a product of C−S bond cleavage and yet the cyclopentadienyl system yields a product of C−H bond cleavage. In this regard, products of thiophene C−S bond cleavage are often considered to be more thermally stable than those of C−H bond activation,[8] but examples are known in which the order is reversed.[9] It is, therefore, not immediately apparent whether the formation of the C−S bond cleavage product $[Me_2Si(C_5Me_4)_2]Mo(\eta^2\text{-}C,S\text{-T})$ is a result of a kinetic or a thermodynamic preference. Preliminary computational studies, nevertheless, indicate that the C−S bond cleavage product is thermodynamically more favored for the *ansa* molybdenocene system than is that for the cyclopentadienyl system, with respect to their products of C−H bond activation.[10] The increased relative stability of the C−S bond cleavage product $[Me_2Si(C_5Me_4)_2]Mo(\eta^2\text{-}C,S\text{-T})$ is most likely a consequence of the shift towards η^3,η^3-coordination of the cyclopentadienyl rings that is imposed by the $[Me_2Si]$ bridge.[7,11] Specifically, whereas $Cp_2Mo(\eta^2\text{-}C,S\text{-T})$ is an 18-electron species, the electron count at the molybdenum center in $[Me_2Si(C_5Me_4)_2]Mo(\eta^2\text{-}C,S\text{-T})$ is less than 18, and would be formally 14 in the extreme that the cyclopentadienyl ligands interacted in a pure η^3-manner. As such, sulfur lone pair donation would provide an additional means of stabilization of $[Me_2Si(C_5Me_4)_2]Mo(\eta^2\text{-}C,S\text{-T})$ which is not possible for the thienyl-hydride, $[Me_2Si(C_5Me_4)_2]Mo(\eta^1\text{-}C\text{-}SC_4H_3)H$.[12]

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(1) For recent review articles, see: (a) 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. (b) Whitehurst, D. D.; Isoda, T.; Mochida, I. *Adv. Catal.* **1998**, *42*, 345−471. (c) Bianchini, C.; Meli, A. *Transition Metal Sulphides, NATO ASI Ser. 3* **1998**, *60*, 129−154. (d) Bianchini, C.; Meli, A. *Acc. Chem. Res.* **1998**, *31*, 109−116. (e) Angelici, R. J. *Polyhedron* **1997**, *16*, 3073−3088. (f) Sánchez-Delgado, R. A. *J. Mol. Catal.* **1994**, *86*, 287−307.

(2) For review articles featuring metal−thiophene chemistry, see: (a) Angelici, R. J. *Transition Metal Sulphides, NATO ASI Ser., 3* **1998**, *60*, 89−127. (b) Angelici, R. J. *Bull. Soc. Chim. Belg.* **1995**, *104*, 265−282. (c) Rauchfuss, T. B. *Prog. Inorg. Chem.* **1991**, *39*, 259−329. (d) Angelici, R. J. *Coord. Chem. Rev.* **1990**, *105*, 61−76. (e) Harris, S. *Polyhedron* **1997**, *16*, 3219−3233.

(3) For recent examples, see: (a) Iretskii, A.; García, J. J.; Picazo, G.; Maitlis, P. M. *Catal. Lett.* **1998**, *51*, 129−131. (b) Vicic, D. A.; Jones, W. D. *Organometallics* **1998**, *17*, 3411−3413. (c) Bianchini, C.; Masi, D.; Meli, A.; Peruzzini, M.; Vizza, F.; Zanobini, F. *Organometallics* **1998**, *17*, 2495−2502. (d) Dullaghan, C. A.; Zhang, X.; Greene, D. L.; Carpenter, G. B.; Sweigart, D. A.; Camiletti, C.; Rajaseelan, E. *Organometallics* **1998**, *17*, 3316−3322. (e) Reynolds, M. A.; Guzei, I. A.; Logsdon, B. C.; Thomas, L. M.; Jacobson, R. A.; Angelici, R. J. *Organometallics* **1999**, *18*, 4075−4081.

(4) Typical HDS catalysts are comprised of a mixture of MoS_2 and Co_9S_8 supported on Al_2O_3. See ref 1.

(5) Samat, A.; Sala-Pala, J.; Guglielmetti, R.; Guerchais, J. *Nouv. J. Chem.* **1978**, *2*, 13−14.

(6) Jones, W. D.; Chin, R. M.; Crane, T. W.; Baruch, D. M. *Organometallics* **1994**, *13*, 4448−4452.

(7) For other examples of the “*ansa* effect” in this system, see: Churchill, D.; Shin, J. H.; Hascall, T.; Hahn, J. M.; Bridgewater, B. M.; Parkin, G. *Organometallics* **1999**, *18*, 2403−2406.

(8) See, for example: (a) Bianchini, C.; Casares, J. A.; Osman, R.; Pattison, D. I.; Peruzzini, M.; Perutz, R. N.; Zanobini, F. *Organometallics* **1997**, *16*, 4611−4619 and references therein. (b) Dong, L.; Duckett, S. B.; Ohman, K. F.; Jones, W. D. *J. Am. Chem. Soc.* **1992**, *114*, 151−160.

(9) Paneque, M.; Taboada, S.; Carmona, E. *Organometallics* **1996**, *15*, 2678−2679.

(10) Bridgewater, B. M.; Friesner, R. A.; Parkin, G. Unpublished results.

(11) Lee, H.; Desrosiers, P. J.; Guzei, I.; Rheingold, A. L.; Parkin, G. *J. Am. Chem. Soc.* **1998**, *120*, 3255−3256.

10.1021/ja9936316 CCC: $19.00

C−S bond cleavage is also observed in the photochemical reactions of $[Me_2Si(C_5Me_4)_2]MoH_2$ and $[Me_2Si(C_5Me_4)_2]Mo(Ph)H$ with benzothiophene (BT) giving $[Me_2Si(C_5Me_4)_2]Mo(\eta^2\text{-}C,S\text{-}BT)$. In contrast, dibenzothiophene (DBT) yields an adduct $[Me_2Si(C_5Me_4)_2]Mo(\eta^1\text{-DBT})$ under comparable conditions;[13] it is likely that an adduct of this type is also formed in the corresponding reactions of T and BT, but in the case of DBT the C−S bond cleavage reaction is inhibited.

The reactions of $[Me_2Si(C_5Me_4)_2]MoH_2$ and $[Me_2Si(C_5Me_4)_2]Mo(Ph)H$ with thiophenes are postulated to occur via a common molybdenocene intermediate $\{[Me_2Si(C_5Me_4)_2]Mo\}$ that is obtained by reductive elimination of H_2 (photochemical) and PhH (thermal), respectively. The molybdenocene intermediate $\{[Me_2Si(C_5Me_4)_2]Mo\}$ so obtained is subsequently trapped by thiophene to give initially an η^1-thiophene adduct which, in the cases of thiophene and benzothiophene, evolves to the products of C−S bond cleavage. Competition studies indicate that benzothiophene is kinetically more susceptible to C−S bond cleavage than is thiophene; at 80 °C, the selectivity is 3:1 in the reaction of $[Me_2Si(C_5Me_4)_2]Mo(Ph)H$ in cyclohexane.[14]

The dibenzothiophene ligand of $[Me_2Si(C_5Me_4)_2]Mo(\eta^1\text{-DBT})$ is labile, which is in line with the fact that no structurally characterized molybdenum thiophene derivatives are listed in the Cambridge Structural Database.[15,16] Thus, $[Me_2Si(C_5Me_4)_2]Mo(\eta^1\text{-DBT})$ reacts thermally with H_2 and excess benzene to regenerate $[Me_2Si(C_5Me_4)_2]MoH_2$ and $[Me_2Si(C_5Me_4)_2]Mo(Ph)H$, respectively. Furthermore, treatment of $[Me_2Si(C_5Me_4)_2]Mo(\eta^1\text{-DBT})$ with thiophene or benzothiophene at room temperature yields $[Me_2Si(C_5Me_4)_2]Mo(\eta^2\text{-}C,S\text{-T})$ and $[Me_2Si(C_5Me_4)_2]Mo(\eta^2\text{-}C,S\text{-BT})$, respectively.

In contrast to the facile thermal displacement of DBT, the C−S cleavage products $[Me_2Si(C_5Me_4)_2]Mo(\eta^2\text{-}C,S\text{-T})$ and $[Me_2Si(C_5Me_4)_2]Mo(\eta^2\text{-}C,S\text{-BT})$ are inert towards reductive elimination of thiophene and benzothiophene, respectively. Thus, $[Me_2Si(C_5Me_4)_2]Mo(\eta^2\text{-}C,S\text{-T})$ is inert towards substitution by benzothiophene at 120 °C; correspondingly, $[Me_2Si(C_5Me_4)_2]Mo(\eta^2\text{-}C,S\text{-BT})$ is inert towards thiophene. Furthermore, $[Me_2Si(C_5Me_4)_2]Mo(\eta^2\text{-}C,S\text{-T})$ and $[Me_2Si(C_5Me_4)_2]Mo(\eta^2\text{-}C,S\text{-BT})$ do not react with benzene at ca. 150 °C to give $[Me_2Si(C_5Me_4)_2]Mo(Ph)H$. The latter result provides an interesting contrast to the observation that cyclopentadienyl tungsten analogue, $Cp_2W(\eta^2\text{-}C,S\text{-T})$, reacts with benzene to give $Cp_2W(Ph)H$.[6]

The molecular structures of $[Me_2Si(C_5Me_4)_2]Mo(\eta^2\text{-}C,S\text{-T})$ (Figure 1), $[Me_2Si(C_5Me_4)_2]Mo(\eta^2\text{-}C,S\text{-BT})$, and $[Me_2Si(C_5Me_4)_2]Mo(\eta^1\text{-DBT})$ (Figure 2) have been determined by X-ray diffraction.[17,18] Thiophenes are known to bind to metal centers with a variety of coordination modes, of which the η^5-mode is the most prevalent; however, it is the less common η^1-mode that is considered to be a necessary interaction to achieve subsequent C−S bond cleavage.[2] As such, the synthesis of $[Me_2Si(C_5Me_4)_2]Mo(\eta^1\text{-DBT})$, the first structurally characterized molybdenum thiophene complex, is significant.

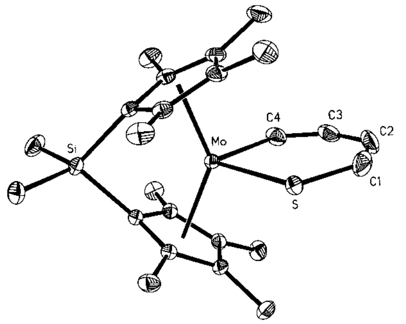

Figure 1. Molecular structure of $[Me_2Si(C_5Me_4)_2]Mo(\eta^2\text{-}C,S\text{-T})$. Selected bond lengths (Å): Mo−S$_{av}$ 2.43, Mo−C4$_{av}$ 2.22, Mo−C$_{Cp}$ 2.269(2)−2.470(2).

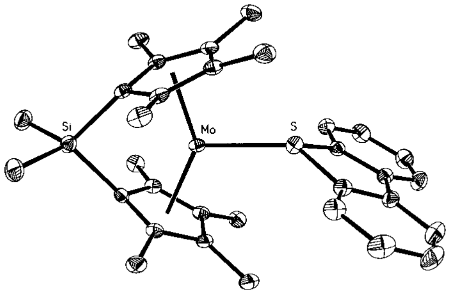

Figure 2. Molecular structure of $[Me_2Si(C_5Me_4)_2]Mo(\eta^1\text{-DBT})$. Selected bond lengths (Å): Mo−S 2.353(1), Mo−C$_{Cp}$ 2.246(4)−2.356(4).

The most notable feature of the structure of $[Me_2Si(C_5Me_4)_2]Mo(\eta^1\text{-DBT})$ is that, by comparison to other η^1-thiophene complexes, the metal center is significantly less displaced from the thiophene plane; for example, the M−S−cent. angle is only 26° (where cent. is the centroid of the thiophene nucleus). In contrast, the angle at sulfur in other η^1-thiophene complexes ranges from 37 to 61°, with the smallest angle being for $[IrH_2(PPh_3)_2(\eta^1\text{-T})_2][PF_6]$.[19,20] Although the more planar nature of the Mo−DBT interaction in $[Me_2Si(C_5Me_4)_2]Mo(\eta^1\text{-DBT})$ is most probably a consequence of steric interactions with the cyclopentadienyl methyl groups, it nevertheless serves to indicate that the coordination mode of a unidentate thiophene ligand is more flexible than previously realized.

In summary, the reactions of $[Me_2Si(C_5Me_4)_2]MoH_2$ and $[Me_2Si(C_5Me_4)_2]Mo(Ph)H$ towards thiophenes provide the first well-defined examples of thiophene coordination and C−S bond cleavage by molybdenum. This reactivity differs significantly from that of Cp_2MoH_2 and $Cp^*{}_2MoH_2$, thereby underscoring the important role that *ansa* bridges may play in directing reaction pathways.

Acknowledgment. We thank the U.S. Department of Energy, Office of Basic Energy Sciences (No. DE-FG02-93ER14339) for support of this research, and also the National Science Foundation and the U.S. Department of Energy for support via the Environmental Molecular Sciences Institute at Columbia University (NSF CHE-98-10367). Professor Roberto Sánchez-Delgado is thanked for stimulating discussions and Mark Rubinshtein is thanked for technical assistance.

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.

JA9936316

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[12] In addition to this thermodynamic influence, the barrier for C−H bond activation may be greater for the *ansa* molybdenocene system than that for the cyclopentadienyl system, due to increased steric demands inhibiting the "perpendicular" orientation that favors thiophene C−H bond cleavage. See, for example: Sargent, A. L.; Titus, E. P. *Organometallics* **1998**, *17*, 65−77.

[13] Spectroscopic evidence suggests that small quantities of products resulting from C−H bond activation are also obtained.

[14] Angelici has also reported that the equilibrium constant for binding benzothiophene to $[CpRuL(CO)]^+$ (L = CO, PPh_3) is greater than that for thiophene. See: (a) Benson, J. W.; Angelici, R. J. *Organometallics* **1993**, *12*, 680−687. (b) Benson, J. W.; Angelici, R. J. *Organometallics* **1992**, *11*, 922−927.

[15] Cambridge Structural Database (Version 5.17). Allen, F. H.; Kennard, O. 3D Search and Research Using the Cambridge Structural Database. In *Chem. Design Automation News* **1993**, *8* (1), 1, 31−37.

[16] Angelici has recently reported $(CO)_5Mo(\eta^1\text{-DBT})$ and $(CO)_3Mo(\eta^1\text{-DBT})$, but the complexes were not structurally characterized due to their pronounced thermal instability. See ref 3e.

[17] For discussions on the structures of six-membered metallathiacycles derived from thiophenes, see ref 2e and: (a) Palmer, M.; Carter, K.; Harris, S. *Organometallics* **1997**, *16*, 2448−2459. (b) Blonski, C.; Myers, A. W.; Palmer, M.; Harris, S.; Jones, W. D. *Organometallics* **1997**, *16*, 3819−3827.

[18] The Mo atom in $[Me_2Si(C_5Me_4)_2]Mo(\eta^2\text{-}C,S\text{-T})$ is displaced by ca. 0.15 Å from the plane defined by $SC_1C_2C_3C_4$.

[19] Sánchez-Delgado, R. A.; Herrera, V.; Bianchini, C.; Masi, D.; Mealli, C. *Inorg. Chem.* **1993**, *32*, 3766−3770.

[20] The pyramidal geometry at sulfur in η^1-thiophene complexes has been attributed to reducing antibonding interactions between the sulfur π lone pair and filled d-orbitals on the metal. See, for example: (a) Rincón, L.; Terra, J.; Guenzburger, D.; Sánchez-Delgado, R. A. *Organometallics* **1995**, *14*, 1292−1296. (b) Palmer, M.; Carter, K.; Harris, S. *Organometallics* **1997**, *16*, 2448−2459. (c) Harris, S. *Organometallics* **1994**, *13*, 2628−2640.