Activation of C−S Bond Homolysis by Coordination to a Mo/Co/S-Containing Cluster

Scott H. Druker and M. David Curtis*

Willard H. Dow Laboratory, Department of Chemistry
The University of Michigan
Ann Arbor, Michigan 48105-1099

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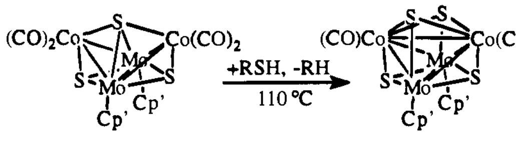
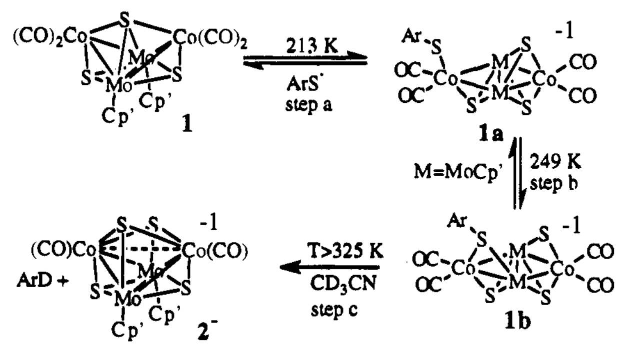
The importance of the hydrodesulfurization (HDS) process, practiced on a global scale for removal of sulfur from fossil fuels, has inspired research on the reactivity of organic sulfur compounds with organometallic complexes,[1] single crystals of metals,[2] and supported catalysts.[3] We recently reported that the cluster $Cp'_2Mo_2Co_2(\mu_3\text{-}S)_2(\mu_4\text{-}S)(CO)_4$ ($Cp' = C_5H_4Me$) (**1**) desulfurizes organic sulfur compounds in solution and is also a precursor for a heterogeneous HDS catalyst.[1b,3c] Cluster **1** is converted into the cluster $Cp'_2Mo_2Co_2(\mu_3\text{-}S)_4(CO)_2$ (**2**) in the typical desulfurization reaction (eq 1).[1b] This communication reports on the mode of coordination of organic thiols and thiolates to cluster **1**, the mobility of thiolates bound to the cluster, and the energetics and mechanism of C−S bond cleavage.



(eq. 1)

Thiolates initially coordinate to cluster **1** through a Co atom. When a solution of tetraethylammonium *p*-toluenethiolate was added to a cooled (213 K) solution of cluster **1** and the reaction was followed by ¹H-NMR spectroscopy, a deep red adduct (**1a**) was observed to form (Scheme 1, step a).[4] The Cp′ ligands in compound **1a** are equivalent: the ¹H-NMR spectrum consists of a single ABCD pattern for the Cp′ ring protons and a single peak for the Cp′ methyl protons. This spectrum is analogous to the NMR spectrum of the structurally characterized trimethylphosphine adduct of cluster **1**.[5] The adduct **1a** was rapidly converted to a new, dark green compound **1b** (Scheme 1, step b) when the temperature of the solution was increased from 213 to 249 K. Compound **1b** has inequivalent Cp′ rings as evidenced by two ABCD patterns and two methyl signals in the ¹H-NMR spectrum.[6] The decreased symmetry in compound **1b** suggests that the thiolate ligand is bridging a Co−Mo bond. Compounds containing edge-bridging thiolate ligands are well established in organometallic chemistry.[7] Elemental analysis, reactivity studies, and mass spectroscopy confirm that compound **1b** is not the CO-substituted product, $Cp'_2Mo_2Co_2S_3(CO)_3(SAr)^-$, that also would exhibit two ABCD patterns for the Cp′ protons.[8]

Scheme 1



Variable temperature ¹H-NMR spectra reveal that compound **1b** is stereochemically nonrigid. Spectra recorded between 249 and 295 K show exchange broadening (Figure 1). At 249 K, the Cp′ rings are nonequivalent as evidenced by the 2ABCD pattern and two methyl signals. At 263 K, the ring protons are broadening and the methyl signals are beginning to merge. At 295 K, the resonances for the Cp′ ring protons are broad and coalescing and only a single peak is observed for the methyl protons.[9]

A movement of the thiolate and sulfide ligands about the surface of the cluster can explain the variable temperature NMR behavior of compound **1b**. One can envision two mechanisms for the fluxional process: (1) the thiolate crosses the Mo−Mo axis or (2) the thiolate crosses the Co−Co axis. If the thiolate crossed the Mo−Mo axis, the Cp′ rings would be inequivalent and the ¹H-NMR spectrum in the fast exchange region ($T >$ 329 K) would consist of two A_2B_2 signals for the ring protons and two singlets for the methyl protons. The reactive nature of compound **1b** precluded spectra from being recorded in the fast exchange region (vide infra); nonetheless, pathway 1 could be ruled out. The 295 K spectrum shows only a single peak for the Cp′ methyl protons; hence, the Cp′ rings are equivalent. Therefore the thiolate is crossing the Co−Co axis in the fluxional process, and the barrier to this motion is 10(1) kcal/mol as determined by dynamic NMR modeling.[10]

The reaction of thiolates with cluster **1** has provided the first insight into the mechanism by which cluster **1** cleaves C−S bonds. When a solution of the bridging thiolate complex, $[(C_6H_5CH_2)N(CH_3)_3][\mathbf{1}\cdot SC_6H_4CH_3]$ (**3**) in CD_3CN (0.7 mL), was heated to reflux, desulfurization of the bound thiolate occurred and a new organometallic compound, the radical anion of cluster **2** (**2⁻**), was formed, along with the only organic product detected, toluene-d_1 (Scheme 1, step c). The molecular structure of the radical anion was confirmed by single-crystal X-ray analysis (Figure 2).[11] The increase in the Co−Co distance, from 2.56 Å in **2**[12] to 2.75 Å in **2⁻**, is consistent with the added electron residing in a Co−Co σ^* orbital. Formation of toluene-d_1 results from homolytic cleavage of the C−S bond, followed

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[1] (a) Adams, R. D.; Pompeo, M. P.; Wu, W.; Yamamoto, J. H. *J. Am. Chem. Soc.* **1993,** *115,* 8207. (b) Curtis, M. D.; Curnow, O. J.; Riaz, U. *J. Am. Chem. Soc.* **1994**, *116*, 4357. (c) Angelici, R. J. *Acc. Chem. Res.* **1988**, *21*, 387. (d) Luo, S.; Ogilvy, A. E.; Rauchfuss, T. B.; Rheingold, A. L.; Wilson, S. R. *Organometallics* **1991**, *10*, 1002. (e) Jones, W. D.; Chin, R. M. *J. Am. Chem. Soc.* **1994**, *116*, 198. (f) Bianchini, C.; Meli, A.; Peruzzini, M.; Vizza, F.; Moneti, S.; Herrera, V.; Sánchez-Delgado, R. A. *J. Am. Chem. Soc.* **1994**, *116*, 4370.

[2] (a) Review: Wiegand, B. J.; Friend, C. M. *Chem. Rev.* **1992**, *92*, 491. (b) Jaffey, D. M.; Madix, R. J. *J. Am. Chem. Soc.* **1994**, *116*, 3012.

[3] (a) Topsøe, H.; Clausen, B. S.; Topsøe, N.-Y.; Pedersen, E.; Niemann, W.; Müller, A.; Bögge, H.; Lengeler, B. *J. Chem. Soc., Faraday Trans.* **1987**, *83*, 2157. (b) Markel, E. J.; VanZee, J. W. *J. Mol. Catal.* **1992**, *73*, 335. (c) Curtis, M. D. *Appl. Organomet. Chem.* **1992**, *6*, 429.

[4] Synthesis of **1a**: A resealable NMR tube was charged with a solution of cluster **1** (17 mg, 0.025 mmol) in $(CD_3)_2CO$. A solution of $(NEt_4)(SC_6H_4CH_3)$ (13 mg, 0.051 mmol) in $(CD_3)_2CO$ was added to the frozen solution of cluster **1**. The tube was placed immediately into a cooled (213 K) NMR probe and a spectrum recorded. ¹H-NMR of **1a** ($(CD_3)_2CO$): δ 7.30 (d, 2H), 6.72 (d, 2H), 2.10 (s, 3H); CpH, δ 5.29 (m, 2H), 5.21 (m, 2H), 5.07 (m, 2H), 4.92 (m, 2H); $CpCH_3$, δ 1.96 (s, 6H).

[5] Curnow, O. J.; Kampf, J. W.; Curtis, M. D.; Mueller, B. L. *Organometallics* **1992**, *11*, 1984.

[6] ¹H-NMR of compound **1b** ($(CD_3)_2CO$): δ 7.35 (d, 2H), 6.76 (d, 2H), 2.14 (s, 3H); CpH protons, δ 5.71 (m, 1H), 5.51 (m, 1H), 5.47 (m, 1H), 5.28 (m, 1H), 5.20 (m, 1H), 5.16 (m, 1H), 4.98 (m, 1H), 4.83 (m, 1H); $CpCH_3$, δ 2.00 (s, 3H), 1.97 (s, 3H).

[7] Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; John Wiley & Sons Inc.: New York, 1988; p 531.

[8] Elemental analysis performed on the compound $[(C_6H_5CH_2)N(CH_3)_3][Cp'_2Mo_2Co_2S_3(CO)_4\cdot SC_6H_4CH_3]$. Anal. Calcd for $C_{33}H_{37}Co_2Mo_2NO_4S_4$: C, 41.70; H, 4.05; N, 1.52. Found: C, 42.51; H, 4.10; N, 1.46. Reaction of compound **1b** with triflic acid yielded the cluster **1** and the free thiol. MS (ESI, 3V, *m/e*): 799 (M^+), 771 ($M^+ - CO$), 743 ($M^+ - 2CO$), 715 ($M^+ - 3CO$).

[9] ¹H-NMR at 295 K (CD_3CN): CpH, δ 5.50 (m, 2H) plus five broad peaks between 4.9 and 6.0 ppm; $CpCH_3$, δ 2.04 (s, 6H).

[10] Quantum Chemistry Program Exchange, Indiana University, Bloomington, IN, Program No. 365.

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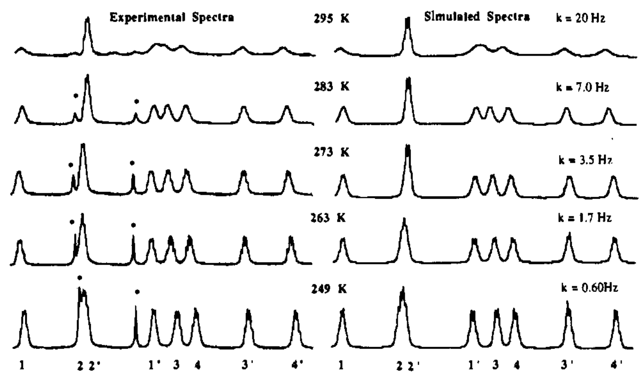

Figure 1. Exchange-broadened ^{1}H-NMR spectra for **1b** in the Cp′ ring proton region between 4.9 and 6.0 ppm. Peaks marked with an asterisk are due to a second, symmetrical product (bis(thiolate) adduct?) that reversibly forms at low temperature. Experimental spectra are on the left; simulated spectra with corresponding rate constants are on the right.

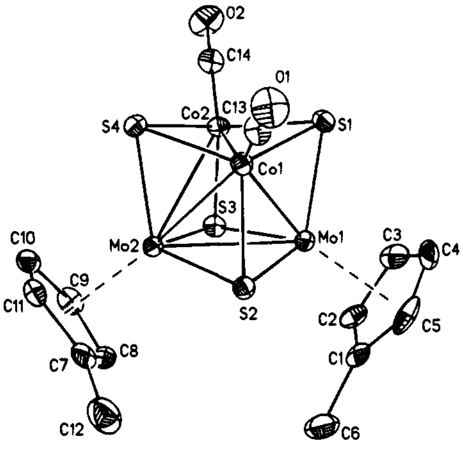

Figure 2. ORTEP diagram of the anion $Cp'_2Mo_2Co_2S_4(CO)_2^-$ ($\mathbf{2}^-$). Thermal ellipsoids are drawn at the 50% probability level. Some relevant interatomic distances (Å): Mo–Mo, 2.8384(5); Mo–Co (av), 2.744(3); Co–Co, 2.746(1); Co–S (av), 2.22(4); Mo–S (av), 2.33(1).

by abstraction of a deuterium atom from the solvent by the *p*-tolyl radical (Scheme 1, step c). The desulfurization of Na-^{t}BuS by cluster **1** gave isobutane but no butenes, a result that is consistent with a free radical mechanism for C–S bond cleavage.[13]

Desulfurization of lithium cyclopropylmethylthiolate, Li[$SCH_2(c\text{-}C_3H_5)$], provided additional support for homolytic C–S bond cleavage. The cyclopropylmethyl radical, $^\bullet CH_2(c\text{-}C_3H_5)$, is known to rapidly rearrange to the butenyl radical.[14] Desulfurization of Li[$SCH_2(c\text{-}C_3H_5)$] by cluster **1** in CD_3CN gave cluster $\mathbf{2}^-$ and 1-butene-d_1.[15a] No other products were detected.

Cluster **1** also cleaves the C–S bond in thiols via an apparent free radical mechanism. Desulfurization of the thiol ($c\text{-}C_3H_5$)CH_2SH in toluene-d_1 yielded the cluster **2** and 1-butene.[15b] The lack of deuterium incorporation in the butene product implies that the butenyl radical abstracts a hydrogen atom from the cluster–thiol complex before the radical has a chance to abstract a deuterium atom from the solvent.

The discovery that nucleophiles react with cluster **1** to yield an adduct led us to investigate the kinetics of the desulfurization of several aryl and alkyl thiols. The rates of thiol desulfurization were first-order in cluster and first-order in thiol concentrations. Added CO did not affect the rate of the desulfurization reaction.[16] Therefore, the rate law for the formation of cluster **2** is $d[\mathbf{2}]/dt = k[\mathbf{1}][\text{thiol}]$. This rate law and the calculated negative values for the activation parameter $\Delta S^\ddagger$ (−5 to −22 cal/(mol K)) suggest a mechanism for desulfurization in which the rate-determining step is initial coordination of the thiol to the cluster. Such a mechanism also explains why aryl and alkyl thiols are desulfurized with almost equal facility even though the aryl sulfur bond is stronger than the alkyl sulfur bond.

The activation enthalpy $\Delta H^\ddagger$ provides a value for the upper limit of the homolytic bond dissociation energy (BDE) for a thiol coordinated to cluster **1**. The value for the homolytic BDE of the C–S bond in C_6H_5SH is approximately 83 kcal/mol.[17] The value of $\Delta H^\ddagger$ for the cleavage of the C–S bond in C_6H_5SH mediated by cluster **1** is 27 kcal/mol. Cluster **1** effectively lowers the strength of the C–S bond by nearly 75% by stabilizing the sulfur-containing fragment by μ_3-coordination of the S atom and by delocalization of the unpaired electron (cf. eqs 2 and 3).

(2)

$$\mathrm{ArSH} \xrightarrow{\Delta H\,=\,\text{C-S BDE}} \mathrm{HS}^\bullet + \mathrm{Ar}^\bullet \qquad (3)$$

The reaction of cluster **1** with thiols and thiolates has provided a deeper understanding of the mechanism (Scheme 1) by which C–S bonds are activated by coordination to metal centers. The results of these reactivity studies provide valuable insight into processes, e.g., substrate coordination and mobility, C–S bond cleavage, and C–H formation, that may occur on heterogeneous HDS catalysts.

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Supplementary Material Available: Tables of rate constants and crystallographic statistics, ORTEP figure of $PhCH_2NMe_3{}^+\mathbf{2}^-$ with numbering scheme, and table of fractional coordinates (6 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(11) A GC/MS analysis of the NMR solution gave an $m/e = 93$ value for the organic product. The structure of $(PhCH_2NMe_3)\cdot\mathbf{2}^-$ was determined from the analysis of 3417 unique reflections. $R_1 = 0.033$, $wR_2 = 0.092$, $a = 9.868(3)$ Å, $b = 12.590(3)$ Å, $c = 13.105(4)$ Å, $\alpha = 84.19(2)°$, $\beta = 69.89(2)°$, $\gamma = 88.99(2)°$, $\rho(\text{calc}) = 1.83$ g/cm^3. Details of the structure will be reported in due course.

(12) Riaz, U. Ph.D. Thesis, University of Michigan, Ann Arbor, MI, 1989.

(13) A resealable tube was charged with cluster **1** (20 mg, 0.30 mmol), Na^{t}BuS (4.0 mg, 0.30 mmol), and CH_3CN (10 mL). The solution was heated to 80 °C for 2.5 h. GC/MS analysis of head gas: *m/e* 58 (isobutane).

(14) Newcomb, M.; Curran, D. P. *Acc. Chem. Res.* **1988**, *21*, 206.

(15) (a) A resealable NMR tube was charged with ($c\text{-}C_3H_5$)CH_2SLi (10 mg, 0.11 mmol), cluster **1** (20 mg, 0.07 mmol), and CD_3CN (0.7 mL). The solution was heated to reflux, and the progress of the reaction was monitored periodically by ^{1}H-NMR spectroscopy. GC/MS analysis of head gas revealed 1-butene-d_1 (*m/e* 57). All volatile compounds in the NMR solution was transferred under vacuum and analyzed by GC/MS. No products other than 1-butene-d_1 were detected. (b) ^{1}H-NMR ($C_6D_5CD_3$): 1-butene; δ 0.85 (t, 3H), 1.91 (m, 2H), 4.96 (m, 1H), 5.01 (m, 1H), 5.77 (m, 1H). GC/MS of NMR solution: *m/e* 56.

(16) The rate constant for the desulfurization of C_6H_5SH conducted under CO was identical within experimental error to the rate constant for the desulfurization under N_2 ($0.86(6) \times 10^{-3}$ M^{-1} s^{-1} vs 0.92×10^{-3} M^{-1} s^{-1}).

(17) The homolytic bond dissociation energy was calculated using thermochemical data listed in the following reference: Griller, D.; Kanabud-Kaminsks, J. M.; Maccoll, A. *J. Mol. Struct. (THEOCHEM)* **1988**, *163*, 125.