Supplementary Material Available: Spectroscopic and physical characterization of **4**, **5**, and **7** (4 pages). Ordering information is given on any current masthead page.

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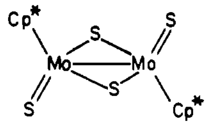
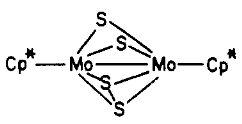
Photochemical Isomerization of $[Cp^*MoS(\mu\text{-}S)]_2$ ($Cp^* = \eta^5\text{-}(CH_3)_5C_5$) to $Cp^*{}_2Mo_2(\mu\text{-}S_2)(\mu\text{-}S)_2$ and $[Cp^*MoS]_2(\mu\text{-}S_2)$

Sir:

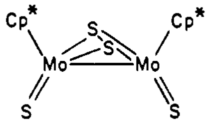
As part of our continuing study[1,2] of the ligand-to-metal charge-transfer (LMCT) photochemistry of organometallic sulfide complexes, we investigated the reactivity of the $[Cp^*MoS(\mu\text{-}S)]_2$ complex. This molecule is one of three known isomers with the formula $Cp^*{}_2Mo_2S_4$, the others being formulated as $Cp^*{}_2Mo_2(\mu\text{-}S_2)(\mu\text{-}S)_2$ and $[Cp^*MoS]_2(\mu\text{-}S_2)$.[3] The $[Cp^*MoS(\mu\text{-}S)]_2$ and $Cp^*{}_2Mo_2(\mu\text{-}S_2)(\mu\text{-}S)_2$ isomers have been structurally characterized, and their structures are shown as I and II, respectively.[3] The $[Cp^*MoS]_2(\mu\text{-}S_2)$ complex has not been structurally characterized, but the structure III has been proposed on the basis of chemical reactivity.[3] In this communication we report the stepwise photochemical interconversions of the three isomers.



I



II



III

Irradiation (λ > 450 nm) of $[Cp^*MoS(\mu\text{-}S)]_2$ in chloroform solution (~2 mM) causes a color change from orange to green.[4] An NMR spectrum of the green solution shows two new resonances in the Cp* region at δ 2.21 and 2.03, corresponding to isomers II and III, respectively. In addition, monitoring the reaction by electronic absorption spectroscopy shows that the intense $[Cp^*MoS(\mu\text{-}S)_2]$ band at 446 nm (Figure 1a) decreases in intensity while new bands appear at 620 and 790 nm (Figure 1b–d, Figure 2). Similar electronic spectral changes are observed in benzene, acetonitrile, and tetrahydrofuran solutions. Infrared spectroscopy is less informative, but it shows a decrease in the ν(Mo=S) band of the starting material at 486 cm^{-1}.[3] A comparison of the spectral and color changes described above to the data in Table I shows that all of the changes are consistent with the photochemical conversion of isomer I to isomers II and III. The quantum yield of disappearance for isomer I (λ = 436 nm) in the reaction above is 1 × 10^{-3}.[7]

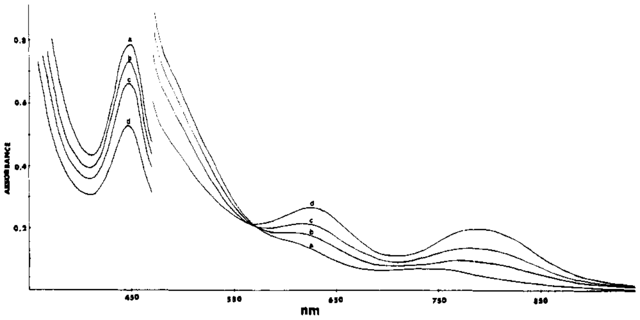


Figure 1. Electronic absorption spectral changes upon photolysis (λ > 450 nm) of $[Cp^*MoS(\mu\text{-}S)]_2$ (I) in chloroform solution (a) before irradiation (0.26 mM), (b) after 2-min irradiation, (c) after 7-min irradiation, and (d) after 15-min irradiation (absorbance ×2 at λ < 470 nm).

In order to determine which isomer results from the irradiation of isomer I, we synthesized isomers II and III[3b] and irradiated each. The electronic spectrum of each isomer is shown in Figure 2. When II is irradiated (λ > 450 nm) in chloroform-*d*, the NMR spectral changes are consistent with the initial formation of III (Φ(disappearance, 436 nm) = 3 × 10^{-3}).[8] Continued irradiation eventually yields small amounts of I. Isomer III initially yields I on irradiation (λ > 450 nm) (Φ(appearance, 436 nm) = 2 × 10^{-3}).[9] Prolonged irradiation of the reaction solution eventually yields some of

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[1] Bruce, A. E.; Bruce, M. R. M.; Tyler, D. R. *J. Am. Chem. Soc.*, in press.

[2] (a) Bruce, A. E.; Bruce, M. R. M.; Sclafani, A.; Tyler, D. R., submitted for publication in *Organometallics*. (b) Bruce, M. R. M.; Kenter, A.; Tyler, D. R. *J. Am. Chem. Soc.* **1984**, *106*, 639–644.

[3] (a) Rakowski Dubois, M.; Dubois, D. L.; VanDerveer, M. C.; Haltiwanger, R. C. *Inorg. Chem.* **1981**, *20*, 3064–3071. (b) Brunner, H.; Meier, W.; Wachter, J.; Guggolz, E.; Zahn, T.; Ziegler, M. L. *Organometallics* **1982**, *1*, 1107–1113.

[4] All preparative and photochemical reactions were done under an argon or nitrogen atmosphere. Solvents were dried with the appropriate drying agent and distilled under nitrogen.[5] Literature methods were used to synthesize isomers I,[3a] II, and III.[3b] Electronic absorption spectra were recorded on a Cary 17 spectrophotometer in 1-cm quartz cuvettes of ~3-mL cell volume. ^1H NMR spectra were obtained on a Varian XL 200 or a Bruker WM 250 instrument. Infrared spectra were obtained on a Perkin-Elmer 983 spectrophotometer equipped with a Perkin-Elmer data station. A 200-W Oriel high-pressure mercury arc lamp was used for the photochemical experiments. Corning glass cutoff filters (3-72, λ > 450 nm; 3-70, λ > 490 nm; 2-61, λ > 610 nm; 3-68 + 7-39, λ > 700 nm) and a 436-nm interference filter from Edmund Scientific were used to isolate the wavelengths of irradiation. For quantum yield measurements, solutions were irradiated at room temperature in 1.0-cm quartz cells and were stirred during irradiation. Each isomer was irradiated at 436 nm, and the spectral change was monitored at 446 nm for I and III and at 800 nm for II. The lamp intensity was measured by Reinecke's salt actinometry.[6] Photochemical experiments monitored by proton NMR or infrared were done as follows. (a) ^1H NMR: 1–2 mM solutions of each isomer in $CDCl_3$ were irradiated (directly in the NMR tube) in an ice–water bath for short time intervals (1–5 min). The spectrum was recorded after each irradiation. Typical irradiation times were 12 min for I, 25 min for II, and 14 min for III. (b) Infrared: A 2 mM solution of I in $CHCl_3$ was irradiated for 12 min in a 6 mm path length polyethylene cell.

[5] Perrin, D. D.; Armarego, W. L.; Perrin, D. R. "Purification of Laboratory Chemicals"; Pergamon Press: Oxford, England, 1966.

[6] Wegner, E. E.; Adamson, A. W. *J. Am. Chem. Soc.* **1966**, *88*, 394.

[7] The photochemistry of I is wavelength dependent. When a 5.4 × 10^{-4} M solution of I in $CHCl_3$ is irradiated in the two lowest energy absorption bands (λ > 700 nm, ~2 h), there was a very slight decrease in the absorbance at 750 nm, but the bands due to isomer II did not appear. However, irradiation of I in $CHCl_3$ at wavelengths ranging from λ > 610 to λ > 330 nm leads to the efficient formation of II (~5 min; λ > 330 nm; ~15 min, λ > 610 nm).

[8] The thermal conversion of isomer II to III requires stirring at 45 °C for 3 days.[3b] A control reaction showed that there is no thermal conversion of II to III under the conditions used in our photochemical experiment.[4]

[9] The extinction coefficient of isomer III at 446 nm is approximately two-thirds that of isomer I (see Table I). Thus as III is irradiated and I grows in, the absorbance increases at 446 nm.

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Table I. Spectral Data for $Cp^*{}_2Mo_2S_4$ Isomers I-III

complex (color)	^1H NMR, δ_{CH_3}[a]	λ_{max}, nm (ϵ, $M^{-1}\,cm^{-1}$)[b]	IR, cm^{-1} Mo=S	IR, cm^{-1} Mo-S-Mo
$[Cp^*MoS(\mu\text{-}S)]_2$ (I, orange-brown)	2.07	900 (50) sh	488 s	447 m[c]
		740 (170) sh		
		600 (610) sh		
		485 (2740) sh		
		446 (5980)	486 s	445 m[d]
		335 (10 250)		
$[Cp^*{}_2Mo_2(\mu\text{-}S_2)(\mu\text{-}S)_2]$ (II, blue)	2.21	803 (1500)		420 w[c]
		630 (2000)		
		550 (760) w sh		
		440 (670) sh		
		330 (3030) sh		
$[Cp^*MoS]_2(\mu\text{-}S_2)$ (III, green-brown)	2.03	800 (40) w sh	485 s	442 w[c]
		635 (420)		
		550 (590)		
		490 (1730) w sh		
		446 (3580)		
		390 (3170) w sh		
		365 (4790) w sh		
		335 (8210) sh		

[a] $CDCl_3$ solution, internal reference $(CH_3)_4Si$. [b] $CHCl_3$ solution. [c] KBr pellet, this work and ref 3. [d] $CHCl_3$ solution, polyethylene cell.

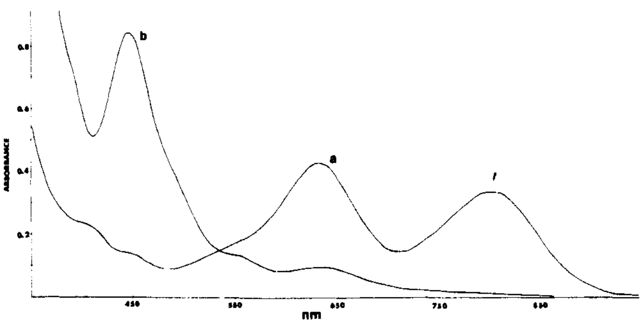

Figure 2. Electronic absorption spectra of (a) $Cp^*{}_2Mo_2(\mu\text{-}S_2)(\mu\text{-}S)_2$ (II), 0.22 mM in chloroform, and (b) $[Cp^*MoS]_2(\mu\text{-}S_2)$ (III), 0.24 mM in chloroform.

isomer II. The sequence of reactions is thus best described by eq 1, although it should be noted that the occurrence of the photochemical back-reactions (e.g. II → I) cannot be excluded by our observations. The important point, however, is that irradiation of any isomer eventually yields the other two isomers.

$$\begin{tikzcd} \mathrm{I} \arrow[r, "h\nu"] & \mathrm{II} \arrow[r, "h\nu"] & \mathrm{III} \arrow[ll, bend left, "h\nu"] \end{tikzcd} \qquad (1)$$

The photochemical isomerization of I to II is logical when viewed as resulting from an LMCT excited state involving the terminal sulfur: the Mo atoms are reduced from oxidation state V to IV and the S^{2-} ligands are oxidized and form a disulfide bridge. Theoretical and experimental studies are under way in our laboratory to elucidate the exact mechanisms of the isomerization reactions.[10]

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(10) We found that the analogous complex $[(\eta^5\text{-}CH_3C_5H_4)MoS(\mu\text{-}S)]_2$ undergoes a similar photochemical isomerization on the basis of electronic absorption, infrared, and ^1H NMR spectral changes.

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