

# Metal-Catalyzed “On-Demand” Production of Carbonyl Sulfide from Carbon Monoxide and Elemental Sulfur\*\*

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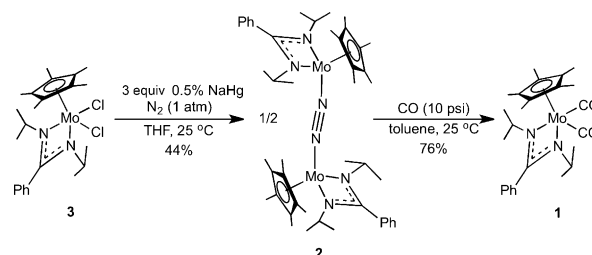
**Abstract:** The group 6 molybdenum(II) cyclopentadienyl amidinate (CPAM) bis(carbonyl) complex  $[\text{Cp}^*\text{Mo}\{\text{N}(\text{iPr})\text{C}(\text{Ph})\text{N}(\text{iPr})\}(\text{CO})_2]$  ( $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$ ) serves as a precatalyst for the high-yielding photocatalytic production of COS from CO and  $\text{S}_8$  under near-ambient conditions (e.g., 10 psi, 25 °C). Further documented is the isolation and structural characterization of several key transition-metal intermediates which collectively support a novel molybdenum(IV)-based catalytic cycle as being operative. Finally, in the presence of an excess amount of a primary amine, it is demonstrated that this catalytic system can be successfully used for the “on-demand” generation and utilization of COS as a chemical reagent for the synthesis of ureas.

Carbonyl sulfide (COS),  $\text{O}=\text{C}=\text{S}$ , occurs as a product of highly energetic natural events, such as volcanism, and as a greenhouse gas, it is thought to have kept an early Earth warm while the young sun was still faint.<sup>[1,2]</sup> In a prebiotic world, COS might have also played a critical role as a reagent for the coupling of amino acids to peptides under conditions that were physiologically favorable for life.<sup>[3,4]</sup> More recently, COS is obtained for industrial purposes through a rather lengthy and inefficient process of separation and purification from a complex mixture of products arising from the reaction of potassium thiocyanate with sulfuric acid.<sup>[5]</sup> Quite surprisingly, while the direct reaction of carbon monoxide (CO) with elemental sulfur ( $\text{S}_8$ ) is also known to produce COS at high temperatures and pressures, until now, no transition-metal-catalyzed version of this process has been discovered or developed such that it can be conducted in high yield and under more energy efficient conditions.<sup>[6]</sup> Herein, we now report that the group 6 molybdenum(II) cyclopentadienyl amidinate (CPAM) bis(carbonyl) complex,  $[\text{Cp}^*\text{Mo}\{\text{N}(\text{iPr})\text{C}(\text{Ph})\text{N}(\text{iPr})\}(\text{CO})_2]$  (**1**;  $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$ ), can serve as a precatalyst for the high-yielding photocatalytic production of COS from CO and  $\text{S}_8$  under near ambient conditions (e.g., 10 psi, 25 °C). We further demonstrate that this catalytic system can be used for the “on-demand” in situ generation and utilization of COS as a chemical reagent for the synthesis of 1,3-disubstituted ureas from primary amines, CO, and  $\text{S}_8$ .

Finally, we document the isolation and structural characterization of several transition-metal complexes which collectively provide key insights regarding the mechanism by which this novel molybdenum-based catalytic cycle might operate.

Recently, we reported that group 6 molybdenum(IV) terminal oxo and imido complexes which are supported by the CPAM ligand set, and more specifically,  $[\text{Cp}^*\text{Mo}\{\text{N}(\text{iPr})\text{C}(\text{Me})\text{N}(\text{iPr})\}(\text{E})]$ , where  $\text{E} = \text{O}$  (**I**) and  $\text{NR}$  (**II**), can function as competent catalysts for the production of isocyanates (RNCO) through either oxygen-atom transfer (OAT) from nitrous oxide ( $\text{N}_2\text{O}$ ) to isonitriles (RNC), or through nitrene-group transfer (NGT) from organoazides ( $\text{RN}_3$ ) to CO.<sup>[7,8]</sup> A third reported catalytic system involves the degenerative OAT between CO and carbon dioxide ( $\text{CO}_2$ ), a process which occurs upon photolysis of a solution containing the molybdenum bis(carbonyl) complex  $[\text{Cp}^*\text{Mo}\{\text{N}(\text{iPr})\text{C}(\text{Me})\text{N}(\text{iPr})\}(\text{CO})_2]$  (**III**).<sup>[7a]</sup> Importantly, all three of these catalytic processes proceed by a formal  $\text{Mo}^{\text{II}}/\text{Mo}^{\text{IV}}$  oxidation state couple, whereas all biological molybdenum-dependent oxotransferase enzymes favor thermal OAT mechanisms based on a more oxidized  $\text{Mo}^{\text{IV}}/\text{Mo}^{\text{VI}}$  couple.<sup>[9]</sup> With the success of these CPAM-based catalytic OAT and NGT processes firmly established, we next focused attention on developing comparable sulfur-atom transfer (SAT) chemistry.

As Scheme 1 reveals, compound **1** was conveniently prepared in high yield through the addition of CO (10 psi) to a toluene solution of the dinuclear “end-on-bridged” dinitrogen complex  $[\{\text{Cp}^*\text{Mo}\{\text{N}(\text{iPr})\text{C}(\text{Ph})\text{N}(\text{iPr})\}(\mu\text{-}\eta^1\text{-N}_2)\}_2]$  (**2**), which was itself obtained in a 44 % yield from sodium amalgam (NaHg) reduction of the molybdenum(IV) dichloride  $[\text{Cp}^*\text{Mo}\{\text{N}(\text{iPr})\text{C}(\text{Ph})\text{N}(\text{iPr})\}(\text{Cl})_2]$  (**3**) in tetrahydrofuran (THF) solution under a dinitrogen atmosphere according to our previously published procedures.<sup>[10,11]</sup> Photolysis of a mixture consisting of a solution of **1** in  $[\text{D}_6]$ benzene, an excess of  $\text{S}_8$  (ca. 10 equiv as a suspension), and  $^{13}\text{C}$ -labeled (98 %) CO (initial pressure: 10 psi), within a sealed Pyrex NMR tube, was conducted using a Rayonet carousel of medium pressure Hg lamps at 25 °C, and as the series of  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz)

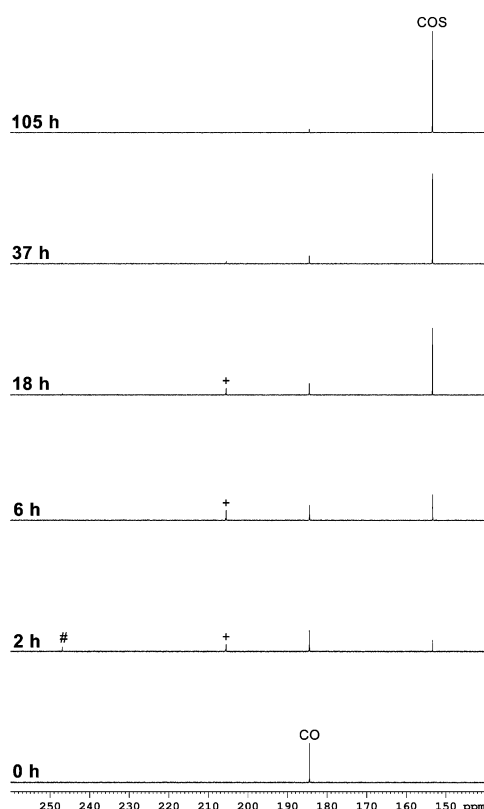


Scheme 1. Synthesis of compound **1**.

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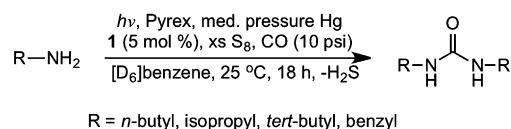
Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/ange.201410353>.



**Figure 1.** Partial  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra (125 MHz,  $[\text{D}_6]\text{benzene}$ , 25 °C) for the photolysis of **1** in the presence of  $^{13}\text{C}$ -labeled CO and excess  $\text{S}_8$  after different timed intervals. Labeled resonances are  $^{13}\text{C}$ -labeled **6** (#) and  $^{13}\text{C}$ -labeled **7** (+).

spectra in Figure 1 reveal, steady production of  $^{13}\text{C}$ -labeled COS was observed to occur over time at the expense of free  $^{13}\text{C}$ CO. During this same period of time, the appearance of two additional  $^{13}\text{C}$  resonances at  $\delta = 249$  ppm and 208 ppm in the  $^{13}\text{C}$  NMR spectra (see resonances labeled with a # and +, respectively, in Figure 1 for photolysis between 2 h and 18 h), were also shown by  $^1\text{H}$  NMR spectroscopy to correlate with the rapid disappearance of  $^1\text{H}$  resonances for **1** and the appearance of those corresponding to two new CPAM complexes. One is a complex of  $C_1$  symmetry and the other is of  $C_s$  symmetry.<sup>[11]</sup> Importantly, the role of **1** as a precatalyst in this catalytic production of COS from CO and  $\text{S}_8$  is strongly supported by both the  $^1\text{H}$  NMR spectra and the fact that the  $^{13}\text{C}$  resonance for  $^{13}\text{C}$ -labeled  $\text{1}_{(^{13}\text{C})_2}$ , which occurs at  $\delta = 270$  ppm, never appears over the time course of photolysis.

The ease with which COS is photolytically generated from CO and  $\text{S}_8$  using **1** as a precatalyst prompted us to explore the synthetic utility of this chemistry for the on-demand and in situ generated delivery of COS as a chemical reagent. In this regard, direct reaction of COS with amines has previously been used to prepare substituted ureas in a process which generates  $\text{H}_2\text{S}$  as the only by-product.<sup>[5a]</sup> The production of substituted ureas from mixtures containing a starting amine, CO, and  $\text{S}_8$  has also been reported to occur at high temperatures and pressure.<sup>[12]</sup> As presented in Scheme 2, photolysis of a  $[\text{D}_6]\text{benzene}$  solution containing a primary amine,  $\text{RNH}_2$  ( $\text{R} = \text{tert-butyl}$ , isopropyl,  $n$ -butyl, benzyl), CO (10 psi),  $\text{S}_8$



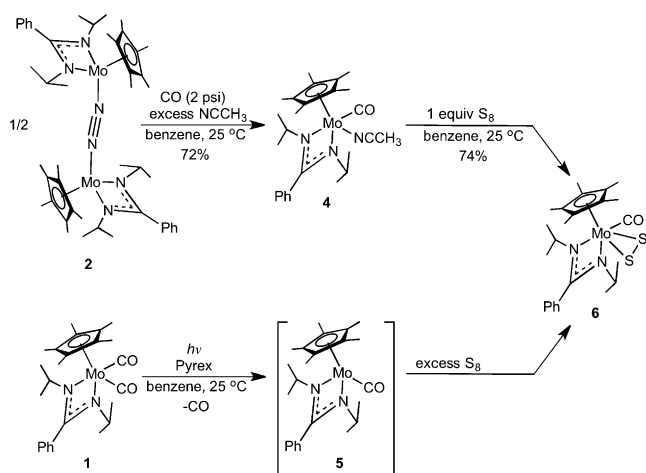
**Scheme 2.** Coupling of primary amines to 1,3-disubstituted ureas using in situ generated COS.

(one equivalent relative to the amine), and **1** (5 mol % relative to the amine) for 18 hours resulted in a near quantitative conversion into the 1,3-disubstituted urea in each case, as determined by isolation and spectroscopic comparison of each product against literature data.<sup>[11]</sup> When conducted on a preparative scale, the amount of **1** could be reduced to as little as 0.5 mol %.

Control experiments were conducted to substantiate that the coupling of primary amines to 1,3-disubstituted ureas was occurring through the intermediacy of in situ generated COS. To begin, no urea product was formed when photolysis was conducted in the absence of either **1** or  $\text{S}_8$ . Second, when isotopically labeled  $^{13}\text{CO}$  (98 %) was used for the coupling of *tert*-butylamine,  $t\text{BuNH}_2$ , the  $^{13}\text{C}$  NMR spectra obtained at different time intervals of photolysis clearly showed the coexistence of  $^{13}\text{C}$ -labeled COS and  $^{13}\text{CO}$ -labeled  $(t\text{BuNH})_2\text{CO}$ .

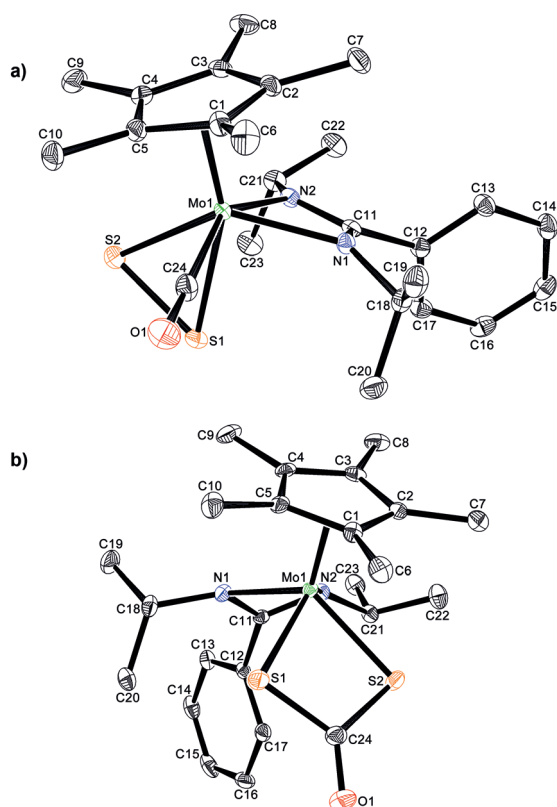
While many reports of transition-metal-catalyzed oxidative coupling of amines with CO to produce ureas have appeared in the literature,<sup>[13]</sup> virtually all of these methods require elevated temperatures and pressures, as well as the use of co-reagents which are more exotic than  $\text{S}_8$  and which serve as sacrificial oxidants that return the transition metal to the starting formal oxidation state within the catalytic cycle. These catalytic processes are also thought to involve intimate bonding interactions between the transition metal and amine and CO substrates within the urea-product-forming steps. In contrast, the chemical process presented in Scheme 2 proceeds through the far simpler mechanism of transition-metal-catalyzed in situ generation of COS which is then responsible for production of the final urea product. It is also important to note that the success of the chemistry of Scheme 2 requires that all the transition-metal complexes, which are intermediates in the photocatalytic generation of COS, must be chemically tolerant of the protic and Brønsted basic nature of both the primary amine starting materials and of the urea products. It can also be noted that primary amines of Scheme 2 were degassed but not distilled from a drying agent before use.

To further establish the structural identity of the intermediates arising from photolysis of **1** with  $\text{S}_8$  and CO, the CPAM  $\text{Mo}^{\text{II}}$  mono(carbonyl), mono(acetonitrile) complex,  $[\text{Cp}^*\text{Mo}\{\text{N}(\text{iPr})\text{C}(\text{Ph})\text{N}(\text{iPr})\}(\text{CO})(\text{NCMe})]$  (**4**) [ $\text{IR}$  (KBr)  $\nu_{\text{CO}} = 1767 \text{ cm}^{-1}$ ], was prepared in high yield (Scheme 3).<sup>[11]</sup> As we have previously documented,<sup>[7,8]</sup> **4** should function as a viable synthetic model for the reactive transient species **5**, which is presumed to be generated in situ through initial photodissociation of CO from **1**. In the present work, reaction of **4** with an excess of  $\text{S}_8$  in benzene rapidly generated the molybdenum(IV) mono(carbonyl),  $\eta^2$ -persulfido complex



**Scheme 3.** Synthesis of compounds **4** and **6**.

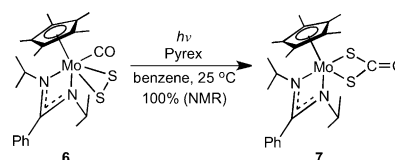
[Cp\*Mo{N(*i*Pr)C(Ph)N(*i*Pr)}(CO)( $\eta^2$ -S<sub>2</sub>)] (**6**) [IR (KBr)  $\nu_{\text{CO}}$  = 1921 cm<sup>-1</sup>] in high yield as an orange, crystalline solid.<sup>[11]</sup> Figure 2a provides the solid-state molecular structure of **6** as obtained from a single-crystal X-ray analysis, along with selected geometric parameters. Compound **6** represents



**Figure 2.** Molecular structures (30% thermal ellipsoids) of a) **6** and b) **7**. Hydrogen atoms have been removed for clarity. Selected bond lengths [Å] and angles [°] for **6**: Mo1–S1 2.4659(4), Mo1–S2 2.4665(4), S1–S2 2.0555(6), Mo1–C24 1.9901(17), C24–O1 1.149(2); S1–Mo1–S2 49.257(14), S1–Mo1–C24 70.90(5) and for **7**: Mo1–S1 2.3876(9), Mo1–S2 2.3954(9), S1–C24 1.784(4), S2–C24 1.786(4), C24–O1 1.198(4); S1–C24–S2 105.77(18).

a rare example of a neutral molybdenum(IV) persulfido complex, and the S1–S2 bond length of 2.0555(6) Å can be compared to the corresponding bond length value of 2.091(2) Å reported for [Cp\*<sub>2</sub>Mo( $\eta^2$ -S<sub>2</sub>)].<sup>[14,15]</sup> Finally, and most significantly, the <sup>1</sup>H and <sup>13</sup>C NMR spectra for **6** could now be used to confirm that this compound is indeed identical to the C<sub>1</sub>-symmetric complex (marked with a # in Figure 1) which is observed during photolysis of **1** with S<sub>8</sub> and CO.

As presented in Scheme 4, photolysis of a dilute solution of **6** in [D<sub>6</sub>]benzene, for a short period of time (i.e., 2.5 h), provided a quantitative yield of the isomeric molybde-

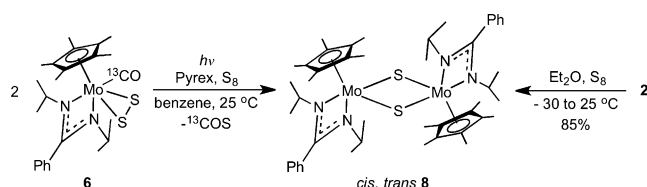


**Scheme 4.** Photolytic conversion of compound **6** into **7**.

num(IV) dithiocarbonate complex, [Cp\*Mo{N(*i*Pr)C(Ph)N(*i*Pr)}(κ-(S,S)-S<sub>2</sub>CO)] (**7**) [IR (KBr)  $\nu_{\text{CO}}$  = 1673 cm<sup>-1</sup>], as determined by <sup>1</sup>H NMR spectroscopy.<sup>[11,16]</sup> The identity of **7** was further established through single-crystal X-ray analysis which provided the solid-state molecular structure shown in Figure 2b. More importantly, with **7** in hand, it was then possible to unequivocally verify by NMR spectroscopy that this compound represents the other C<sub>s</sub>-symmetric species (marked with a + in Figure 1) which appears during photolytic generation of COS from CO and S<sub>8</sub> using **1** as a pre-catalyst. Finally, when photolysis of **6** was conducted under an atmosphere of <sup>13</sup>CO (10 psi), <sup>13</sup>C-labeled **7**(S<sub>2</sub>-<sup>13</sup>CO) was produced, presumably through an associative mechanism for initial ligand substitution of CO by <sup>13</sup>CO, followed by a formal intramolecular 1,2-insertion of <sup>13</sup>CO into the sulfur–sulfur bond of **6** to form **7**.<sup>[16,17]</sup>

In contrast to the quantitative photoconversion of **6** into **7** which occurs at short periods of time in the absence of any other chemical reagents, photolysis of a solution of **6** ([D<sub>6</sub>]benzene) in the presence of an excess of S<sub>8</sub> for a longer period of time (e.g., 6.5 h versus 2.5 h) generated a new C<sub>s</sub>-symmetric product at the expense of **7**, as monitored by <sup>1</sup>H NMR spectroscopy.<sup>[11]</sup> Furthermore, when this extended photolysis was repeated using <sup>13</sup>C-labeled **6**(<sup>13</sup>CO), the <sup>13</sup>C NMR spectrum confirmed that while <sup>13</sup>C-labeled COS had been produced, no <sup>13</sup>CO-enriched resonances, which could be tied to generation of the new C<sub>s</sub>-symmetric species, appeared. Finally, extended photolysis of a pure sample of <sup>13</sup>C-labeled **7**(S<sub>2</sub>-<sup>13</sup>CO) only led to photodegradation and with no evidence, by either <sup>1</sup>H or <sup>13</sup>C NMR spectroscopy, for the generation of either **6** or the new C<sub>s</sub>-symmetric species.

Working on the assumption that the new C<sub>s</sub>-symmetric product obtained from photolysis of **6** with S<sub>8</sub> might be a CPAM Mo<sup>IV</sup> sulfide (e.g., E = S in **1**), an effort was made to synthesize such a complex through an alternative route in a more controlled manner. Accordingly, as Scheme 5 presents, treatment of a solution of **2** in diethyl ether (Et<sub>2</sub>O) with S<sub>8</sub> yielded a red crystalline product which indeed proved to be



Scheme 5. Synthesis of compound **8**.

the dimer of the proposed molybdenum(IV) sulfide in the solid state, as confirmed by single-crystal X-ray analyses which were obtained for both the *cis*- and *trans*-isomers of  $[\text{Cp}^*\text{Mo}[\text{N}(\text{iPr})\text{C}(\text{Ph})\text{N}(\text{iPr})]]_2(\mu\text{-S})_2$  (**8**).<sup>[11,18,19]</sup> Figure 3

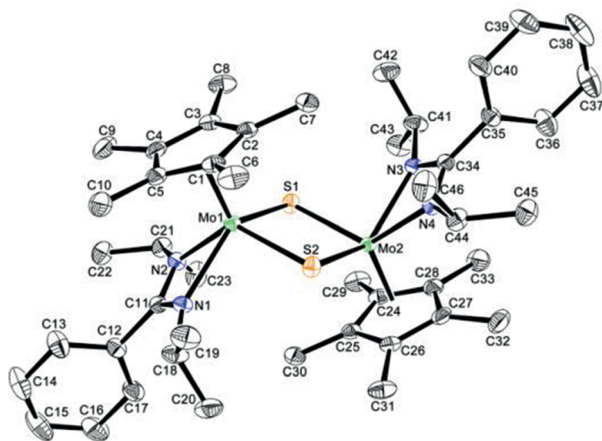
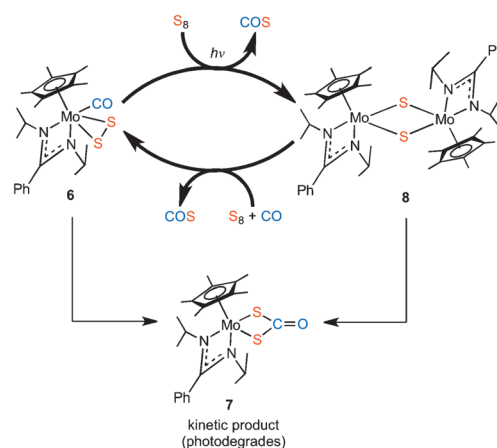


Figure 3. Molecular structure (30% thermal ellipsoids) of *trans*-**8**. Hydrogen atoms have been removed for clarity. Selected bond lengths [Å] and angles [°]: Mo1–S1 2.3408(7); S1–Mo1–S2 91.40(2), Mo1–S1–Mo2 88.60(2).

provides the solid-state molecular structure of *trans*-**8** along with selected geometric parameters. It is also important to note, however, that the solution structure of **8** is less clear. More specifically, despite extensive efforts, we have not been able to obtain an analytically pure sample of **8** which provides a satisfactory elemental analysis. Furthermore, with variable-temperature  $^1\text{H}$  NMR spectroscopy, only a single set of resonances for the mixture of *cis* and *trans* isomers for diamagnetic **8** are observed down to the limiting temperature of  $-90^\circ\text{C}$ , and this observation suggests the possibility that, in solution, **8** is engaged in a dynamic dimer–monomer exchange equilibrium at all temperatures. Finally,  $^1\text{H}$  NMR spectra for crystalline samples of **8** always present evidence for a varying amount of a paramagnetic impurity which can account for up to 20% by weight of the material, as based on the use of an internal standard (durene). When further interrogated by electrospray ionization mass spectrometry (ESI-MS), a solution of **8** provided additional molecular ion ( $M + H$ ) clusters which correspond to the dinuclear  $[\text{Mo}^V, \text{Mo}^V]$  tris(sulfide)  $[\{\text{Cp}^*\text{Mo}[\text{N}(\text{iPr})\text{C}(\text{Ph})\text{N}(\text{iPr})]\}_2(\text{S})_3]$  and the formal dinuclear  $[\text{Mo}^{IV}, \text{Mo}^V]$  tris(sulfide)  $[\text{Cp}^*\text{Mo}[\text{N}(\text{iPr})\text{C}(\text{Ph})\text{N}(\text{iPr})](\text{S})_3\text{Cp}^*\text{Mo}]$ .<sup>[11]</sup>

While additional efforts to quantify sample composition and the dynamic solution behavior displayed by **8** remain in

progress, a key finding regarding the possible role that this species plays in the photocatalytic generation of COS was that, upon introduction of  $^{13}\text{C}$ O into a solution of **8** in  $[\text{D}_6]$ benzene, non-photolytic production of **6**( $^{13}\text{C}$ O) (57%), **7**( $\text{S}_2\text{-}^{13}\text{C}$ O) (29%), and an unquantified amount of  $^{13}\text{C}$ -labeled COS was observed to occur at room temperature. Collectively, these experimental results conclusively establish that **6** and **8** are interconverted under the reaction conditions of Figure 1, and accordingly, these compounds are reasonable candidates as intermediates in the catalytic cycle which generates COS from CO and  $\text{S}_8$ . In contrast, **7** appears to be a kinetic product which can be produced from either **6** or **8**. However, simultaneous photodegradation of **7** under the reaction conditions fortuitously eliminates the buildup of this species over time. Scheme 6 summarizes these proposed relationships of **6–8** to photocatalytic production of COS.



Scheme 6. Proposed relationship of **6–8** to photocatalytic production of COS. Bold arrows represent catalytically-relevant pathways for COS generation.

In conclusion, the present report makes the case for the first example of metal-catalyzed synthesis of COS from CO and  $\text{S}_8$  that proceeds under near ambient conditions. The tolerance to protic substrates that is demonstrated by this catalytic process further supports the synthesis of more complex organic products through the on-demand production of COS. Finally, it is interesting to speculate that the prebiotic existence of a similar metal-catalyzed low-energy pathway could have effectively lowered the free energy threshold conditions required for the COS-facilitated genesis of life, and perhaps more importantly, under the highly reducing atmosphere which is proposed to have existed for archaic Earth, and presently, for Titan.<sup>[20]</sup>

**Keywords:** molybdenum · oxidation · structure elucidation · sulfur · synthetic methods

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