

ether at 25°C to afford 1-phenylarsole **7** (25% yield).<sup>[8]</sup> The reaction is not stereospecific, since either pure (*Z,Z*)- or (*E,Z*)-1,4-dichloro-1,3-butadiene **6** gives 1-phenylarsole **7** in the same yield. Similarly, dithiophenylphosphane reacts with the mixed 1,4-dichlorobutadienes **6** to give 1-phenylphosphole in 25% yield, a procedure that offers an alternative to available literature preparations of C-unsubstituted phospholes.<sup>[9]</sup> The reaction of 1-phenylarsole **7** with lithium in tetrahydrofuran (THF) followed by treatment with FeCl<sub>2</sub> affords 1,1'-diarsaferrocene **1** in 50% yield as deep red, air-stable, monoclinic crystals (m.p. = 195°C).<sup>[8,10]</sup> NMR, UV, and mass spectra are similar to those of 1,1-diphosphaferrocene **4** (for NMR data see Table 1).

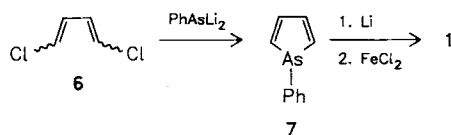


Table 1. <sup>1</sup>H- and <sup>13</sup>C-NMR chemical shift values (δ values) of **1** and **4** [a].

		<b>1</b>	<b>4</b>
<sup>1</sup> H-NMR	H <sub>α</sub>	4.38 [b]	3.79 [c]
	H <sub>β</sub>	5.14 [b]	4.88 [c]
<sup>13</sup> C-NMR	C <sub>α</sub>	88.0	79.3 [d]
	C <sub>β</sub>	84.0	82.0 [d]

[a] In [D<sub>6</sub>]benzene at 300 MHz, δ values relative to TMS. [b] Satisfactory spectral simulation using the Bruker PANIC program is achieved for J<sub>2,3</sub> = 4.5 Hz, J<sub>2,4</sub> = J<sub>2,5</sub> = 0.9 Hz, and J<sub>3,4</sub> = 3.2 Hz. [c] Satisfactory spectral simulation for J<sub>1,2</sub> = 37.5 Hz, J<sub>1,3</sub> = 5.6 Hz, J<sub>2,3</sub> = 4.15 Hz, J<sub>2,4</sub> = J<sub>2,5</sub> = 0.9 Hz, and J<sub>3,4</sub> = 2.5 Hz. [d] See [1a].

Like the parent complex ferrocene **5** and the heteroarene analogue bis(arsabenzene)chromium **2**, **1** may be electrochemically oxidized as well as reduced. Cyclovoltammetry yields the redox potentials  $E_{1/2}(1/1^{\oplus}) = 0.730 \pm 0.015$  V [−38°C in 1,2-dimethoxyethane (DME)/tetra-*n*-butylammonium perchlorate (TBAP) versus the saturated calomel electrode (SCE),  $v \geq 20$  mV s<sup>−1</sup>,  $I_{pa}/I_{pc} = 1.0$ ] and  $E_{1/2}(1/1^{\ominus}) = -2.190 \pm 0.01$  V [−40°C in DME/TBAP vs: SCE,  $v \geq 1$  V s<sup>−1</sup>,  $I_{pa}/I_{pc} = 0.98$ ]. As observed for the couple  $[\eta^6\text{-C}_6\text{H}_6)_2\text{Cr}]/[\eta^6\text{-C}_5\text{H}_5\text{As})_2\text{Cr}$  **2**,<sup>[4]</sup> replacement of two CH units of **5** by two As atoms leads to anodic shifts of the redox potentials (+0.24 V for the oxidation, +0.74 V for the reduction).<sup>[11]</sup> Obviously, compared with the cyclopentadienyl ring, the arsacyclopentadienyl ring is more effective in withdrawing electron density from the central metal, thereby stabilizing the HOMO of **1**, and in accommodating additional charge into the LUMO. Similar trends are observed in the case of **4**.<sup>[12]</sup>

Like arsabenzene,<sup>[13]</sup> 1,1'-diarsaferrocene **1** undergoes rapid acid-catalyzed deuterium exchange. At −20°C in CF<sub>3</sub>CO<sub>2</sub>D/CH<sub>2</sub>Cl<sub>2</sub>, **1** exchanges its four α-protons in 1 min, although heating to 70°C for 7 h allows only partial exchange at the β-position. In competition experiments, an α-hydrogen undergoes exchange 165 times faster than a hydrogen of ferrocene, while a β-hydrogen exchanges 4 times more slowly than the hydrogen at the 4-position of toluene. Although the scale is only semiquantitative, the relative reactivity of α/β positions must exceed 10<sup>6</sup>.<sup>[14,15]</sup> Similarly, acetylation with acetyl chloride/AlCl<sub>3</sub> in CH<sub>2</sub>Cl<sub>2</sub> at 25°C gives exclusively the α-acetyl derivative of **1**.<sup>[16]</sup> This large directive effect is much greater than that reported for substituted ferrocenes<sup>[17]</sup> but is similar to that

found for arsabenzene **3**<sup>[13]</sup> and for metal-complexed heterocycles.<sup>[18]</sup>

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## Synthesis and Structure of [(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Mo<sub>2</sub>S<sub>4</sub>·SO<sub>3</sub>]: Concerning the Oxidation of Sulfur Ligands in Transition-Metal Complexes

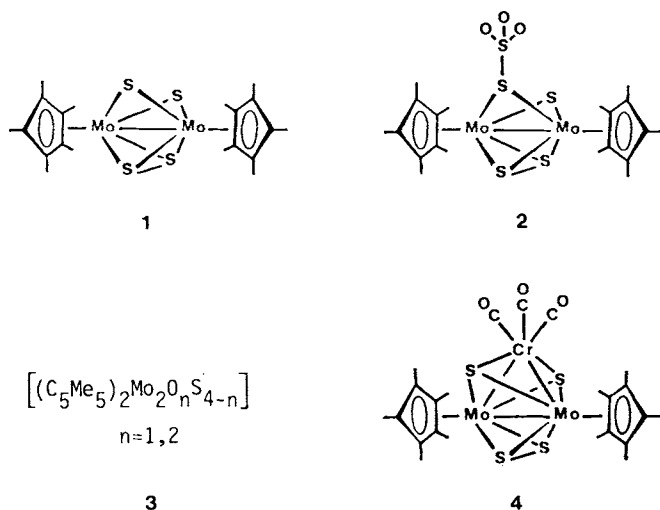
By Henri Brunner, Ulrich Klement, Joachim Pfauntsch, and Joachim Wachter\*

The oxidation of coordinated sulfur in transition-metal complexes can result not only in the formation of sulfur

\* Dr. J. Wachter, Prof. Dr. H. Brunner, Dr. U. Klement, J. Pfauntsch  
Institut für Anorganische Chemie der Universität  
Universitätsstrasse 31, D-8400 Regensburg (FRG)

oxides,<sup>[1]</sup> which would be highly reactive as free species, but also of sulfur-rich anions such as  $S_2O_3^{2-}$  and  $S_3O_3^{2-}$ .<sup>[2]</sup> Such reactions are of interest as model systems for the microbiological oxidation of  $S^{2-}$  and  $S^0$  in nature.<sup>[2a]</sup> We report here on the unusual oxidation of an  $S^{2-}$  ligand to an  $S_2O_3^{2-}$  ligand that is coordinated in a novel fashion.

When a dark blue solution of complex **1** is stirred in toluene while being exposed to air (50°C, 18 h), **2** precipitates in 17% yield as red-violet crystals. Other sulfur-containing complexes, **3**, which can only be separated with difficulty by column chromatography, remain in solution.<sup>[3]</sup>

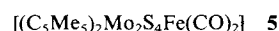


Single crystals of **2** suitable for an X-ray structure analysis can be prepared by slow evaporation of a solution of **2** in acetone/ $CH_2Cl_2$  (5 : 8) exposed to air. The structure of **2** (Fig. 1) is characterized by one each of the following ligands:  $S^{2-}$ ,  $S_2^{2-}$ , and  $S_2O_3^{2-}$ , the S atoms of which lie roughly in a plane that is perpendicular to the Mo–Mo axis.<sup>[4]</sup> The methyl groups of the nearly parallel  $C_5Me_5$  rings are oriented in an eclipsed fashion. This reveals a close structural relationship between **1** and **2**, which is also reflected in their largely similar bonding parameters.<sup>[5]</sup> A further structural feature, however, is the pseudotetrahedral  $SO_3$  unit fixed at one of the  $S^{2-}$  ligands. To the best of our knowledge, thiosulfate ligands bridging two metal centers were previously unknown. Noteworthy, in contrast to

the distances in mononuclear, S-coordinated thiosulfate complexes, is the very long S4–S5 distance (2.168(2) Å).<sup>[6]</sup>

Significant thermal instability of **2** is indicated by the mass spectra, which only show the molecular ion of **1**, even when the field desorption technique is used. In contrast, the elemental analyses confirm the calculated S/O ratio. The  $S_2O_3^{2-}$  ligand is revealed in the IR spectrum (KBr) by the strong  $\tilde{\nu}_{SO}$  absorptions at 1246, 1217 (sh), 1207, 1010, and 600  $cm^{-1}$ . A similar pattern is observed for monodentate-bonded sulfate ligands, which is interpreted as being a consequence of local  $C_{3v}$  symmetry.<sup>[7]</sup>

The long S–S distance in the thiosulfate ligand suggests a certain lability of this bond. Indeed, **2** reacts with  $[Cr(CO)_5(thf)]$  ( $CH_2Cl_2$ /tetrahydrofuran (THF) mixtures, 20°C) under mild conditions with loss of the  $SO_3$  unit to give the trinuclear cluster **4**,<sup>[8]</sup> whose structure corresponds to that of the isoelectronic complex **5**<sup>[9]</sup>.



The formation of **2** may be explained in terms of several steps. Under the reaction conditions, isomerization of **1** to give complexes containing terminal M=S groups<sup>[5]</sup> precedes the substitution of sulfur by oxygen. The  $SO_2$  thereby formed requires an additional catalytic oxidation, however, by an as yet unidentified complex component. In this way, approximately 37% of the sulfur released from **1** is converted into  $SO_3$ , which then adds to **1**.<sup>[3]</sup> In this connection, it is interesting that the nucleophilic character of the  $\mu$ -S ligand can already be used to bind  $SO_2$ .<sup>[10]</sup> The simultaneous formation of an  $SO_2$  and an  $S_2$  ligand from an initially sulfur-poor complex by oxidation with air has also been described already.<sup>[11]</sup> Further experiments are required, however, to elucidate the details of the oxidation mechanism.

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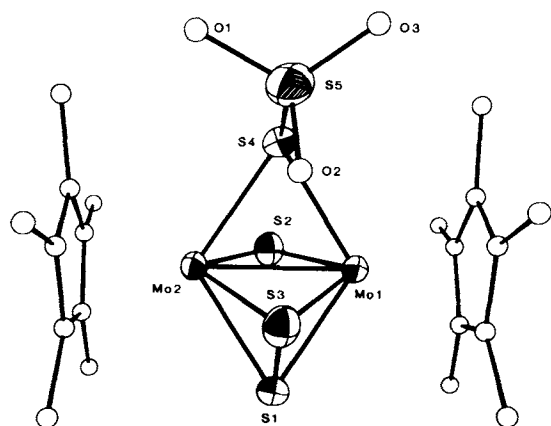


Fig. 1. Structure of **2** in the crystal (ORTEP plot). Selected bond lengths [Å] and angles [°]: Mo1–Mo2 2.628(0), Mo1–S1 2.426(1), Mo1–S2 2.308(1), Mo1–S3 2.432(1), Mo1–S4 2.449(1), S1–S3 2.066(2), S4–S5 2.168(2); Mo1–S1–Mo2 65.50(3), Mo1–S2–Mo2 69.32(3), Mo1–S3–Mo2 65.42(3), Mo1–S4–Mo2 64.91(3), Mo1–S4–S5 113.22(5), Mo2–S4–S5 112.82(5), S4–S5–O 104.4(3) (average).

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