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Preliminary communication

Oxidation of organometallic compounds with polychalcogenides: preparation and structure of $[(Me_5C_5)Mo(S_4)(S_2CO)]^-$ containing a dithiocarbonate ligand

Samantha L. Gales, William T. Pennington, Joseph W. Kolis *
Department of Chemistry, Clemson University, Clemson, SC 29634 (USA)

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Abstract

The reaction of polysulfide solution with $(Me_5C_5)Mo(CO)_3(CH_3)$ results in oxidation of the metal center to Mo^{IV}, with elimination of the carbonyl groups as well as the alkyl group. The final product $[(Me_5C_5)Mo(S_4)(S_2CO)]^-$, was isolated and structurally characterized. It contains a tetrasulfide chelating group as well a dithiocarbonate ligand.

The chemistry of molecular transition metal sulfide clusters [1], as well as organometallic transition metal sulfides [2] has been extensively investigated. This is due in part to the occurence of metal sulfides in electron transfer enzymes [3], as well as hydrodesulfurization catalysts [4]. We have recently discovered a new entry to metal sulfides and selenides, namely oxidative decarbonylation [5]. The reaction exploits the fact that soluble polychalcogenides will coordinate to low valent metal carbonyls, and then oxidize the metal to a higher valent state with concommitent loss of carbonyls (eq. 1).

$$M(CO)_6 + S_x^{2-} \longrightarrow MS_4^{2-}\ (M = Mo, W) \qquad (1)$$

This approach is useful in that entry to systems containing high valent metal sulfides can be obtained via the well developed chemistry of low valent metal carbonyls. For example, we have previously reported that $Cp_2Mo_2(CO)_6$ generates an unusual anionic organometallic metal sulfide, $[CpMo(S_4)_2]^-$, in reasonable yield, via a disulfide intermediate [6].

$$Cp_2Mo_2(CO)_6 + S_x^{2-} \longrightarrow [CpMo(S_2)(CO)_2]^- \qquad (2)$$

$$[CpMo(S_2)(CO)_2]^- + S_8 \longrightarrow [CpMo(S_4)_2]^- \qquad (3)$$

We have been hindered in developing its chemistry because it readily decomposes upon heating, or reaction with PPh_3 or reducing agents, with resulting formation of MoS_4^{2-}. It was felt that the better electron donor, $(CH_3)_5C_5^-$ would be less likely to dissociate from the high valent metal center. The difficulty in preparing $Cp^*_2Mo_2(CO)_6$ compared to the easy preparation of $Cp^*Mo(CO)_3(CH_3)$ [7], led us to explore this as a starting material.

We were surprised to find that we can isolate a molecule containing only one S_4 ring, in addition to the somewhat rare dithiocarbonate group, which apparently results from oxidation of a coordinated carbon monoxide by polysulfide. In this communication we report the preliminary preparation and structural characterization of this compound.

The molybdenum alkyl compound $(Me_5C_5)Mo(CO)_3(CH_3)$ reacts with one equivalent of polysulfide solution generated from a solid of nominal composition K_2S_3 [8*]. It generates an intermediate postulated to be I because of the similarity of the IR spectrum to that of the $C_5H_5^-$ analog. The IR spectrum contains two strong bands in the CO region at 1887 and 1791 cm^{-1} which are very nearly identical to the $C_5H_5^-$ analog (1885 and 1786 cm^{-1} [6]). The intermediate I reacts readily with elemental sulfur to form the salt of anion II in reasonable yield (eqs. 4 and 5) [9*].

$$(Me_5C_5)Mo(CO)_3(CH_3) + S_x^{2-} \longrightarrow \underset{(I)}{[(Me_5C_5)Mo(CO)_2(S_2)]^-} \qquad (4)$$

$$[(Me_5C_5)Mo(CO)_2(S_2)]^- + S_8 \longrightarrow \underset{(II)}{[(Me_5C_5)Mo(S_2CO)(S_4)]^-} \qquad (5)$$

The title molecule was characterized by IR, ^1H NMR, elemental analysis and single crystal X-ray diffraction [10*]. The $(Me_5C_5)^-$ group is symmetrically bound to the Mo center and the distances are normal (Mo–C average = 2.37(2) Å) (see Fig. 1). The Mo–S distances in the MoS_4 ring average 2.32(4) Å, which is comparable to many other systems [1]. The S_4 chain is slightly disordered but this is easily modeled and has no effect on the overall structure. The dithiocarbonate ligand has somewhat longer Mo–S distances (2.43(2) Å average), while the S–C–S angle is considerably constrained at 71.3(1)°.

The overall coordination environment around the Mo center is pseudo-square pyramidal with four sulfur atoms in the base and the (Me_5C_5) group apical. It is comparable to the coordination environment of $[CpMo(S_4)_2]^-$. Since the dithiocarbonate group is a dianion, the formal charge on the molybdenum is 4+, again similar to the $C_5H_5^-$ analog [6]. The IR spectrum displays two absorptions at 1585 and 833 cm^{-1}, which are typical for these compounds. They can be assigned as CO and CS stretches respectively [11]. The ^1H NMR spectrum displays a singlet at 2.17 ppm as expected.

Coordinated dithiocarbonate groups are somewhat unusual, however several coordination complexes of this ligand have been reported [12], as well as some extensive chemistry [13]. We have previously observed the formation of dithiocarbonates via the oxidative decarbonylation of $Cr(CO)_6$ with polysulfides [14].

$$Cr(CO)_6 + S_x^{2-} \longrightarrow [Cr(S_2CO)_3]^{3-} \qquad (6)$$

We presume that the ligand is formed via insertion of a disulfide fragment into a

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* Reference number with asterisk indicates a note in the list of references.

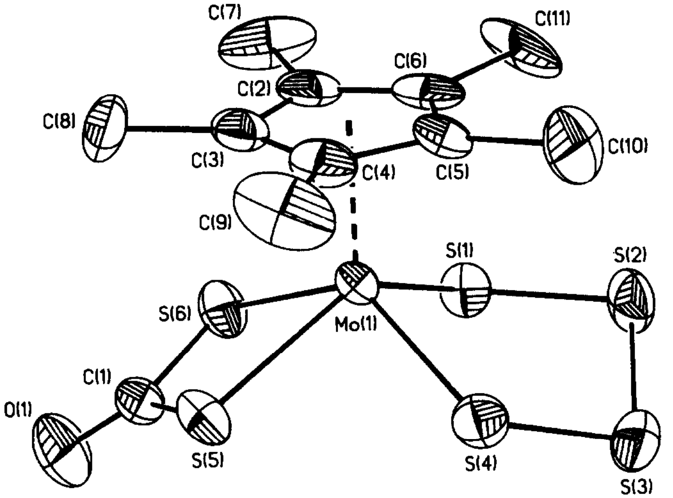
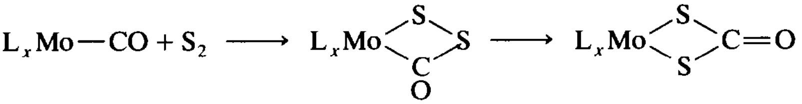


Fig. 1. Thermal ellipsoid plot (35% probability) of $[((CH_3)_5C_5)Mo(S_4)(S_2CO)]^-$. Some significant distances (Å) are Mo1–S1 2.351(3), Mo1–S4 2.296(3), Mo1–S5 2.449(3), Mo1–S6 2.418(3), Mo1–C2 2.378(11), Mo1–C3 2.359(10), Mo1–C4 2.345(10), Mo1–C5 2.370(9), Mo1–C6 2.387(10), S1–S2 2.131(6), S2–S3 1.990(19), S3–S4 2.131(17) S5–C1 1.784(12), s6–C1 1.761(12), C1–O1 1.184(14). Some significant angles (°) are: S1–Mo1–S4 88.9(1), S1–S2–S3 102.0(5), S2–S3–S4 101.6(7), Mo1–S5–C1 90.4(4), Mo1–S6–C1 92.0(4), S5–C1–O1 126.0(1), S6–C1–O1 127.5(9).

metal carbon bond followed by rearrangement, as proposed by Roper for reactions of CO and O_2 to form coordinated carbonate [15]. However we have no direct evidence for this mechanism.



$$\mathrm{L_xMo{-}CO + S_2} \longrightarrow \mathrm{L_xMo}\begin{array}{c}\mathrm{S}\\ \\ \mathrm{C}\\ \mathrm{O}\end{array}\mathrm{S} \longrightarrow \mathrm{L_xMo}\begin{array}{c}\mathrm{S}\\ \\ \mathrm{S}\end{array}\mathrm{C{=}O}$$

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Supplementary material available. Complete structural data, complete distances and angles, atomic coordinates, anisotropic thermal parameters, hydrogen coordinates, description of the disorder or the S_4 chain, and calculated and observed structure factors are available from the authors.

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8 The starting polysulfide was prepared by stirring appropriate ratios of the elements in liquid NH_3 at $-78\,^\circ C$ for 4 h followed by removal of the NH_3 under vacuum. The yellow orange powder was stored under argon and used without further purification.

9 Under an atmosphere of argon, a mixture of 0.125 g of $((CH_3)_5C_5)Mo(CO)_3(CH_3)$ (0.377 mmol), 0.066 g of K_2S_3 (0.377 mmol) and 0.157 g of $(C_6H_5)_4PBr$ (0.377 mmol) were dissolved in a 6 mL solvent mixture of 5:1 CH_3CN and DMF, and stirred for 2 h at 25 °C. The dark brown solution was filtered and excess elemental sulfur (0.289 g, 1.13 mmol) was added and the solution stirred for an additional hour. The resultant dark red solution was filtered, layered with 4 mL diethyl ether and stored at 4 °C overnight. This produced 0.123 g of lustrous red crystals (yield 44%). Elemental analysis: Found: C, 53.02; H, 4.44. $C_{35}H_{35}MoOPS_6$ calcd.: C, 53.14; H, 4.47%. ^1H NMR ($CDCl_3$): δ 2.17 $((CH_3)_5C_5)^-$. IR (Nujol mull); 1585s (C=O), 833m (S–C–S) cm^{-1}.

10 Crystal structure data for $[(C_6H_5)_4P][((CH_3)_5C_5)Mo(S_4)(S_2CO)]$: space group monoclinic, $P2_1/c$, $a = 15.472(5)$, $b = 16.108(4)$, $c = 14.116(5)$ Å, $\beta = 93.59(3)^\circ$, $V = 3511(2)$ Å^3, $Z = 4$, $D_{calc} = 1.50$ g cm^{-3}, $\mu(Mo\text{-}K_\alpha) = 7.8$ cm^{-1}, (transmission factors: 0.93–1.00), $T = 21\,^\circ C$. Measured 5327 reflections ($3.5 \leqslant 2\theta \leqslant 45^\circ$), of which 3796 were unique ($R_{int} = 0.015$); data were corrected for absorption using the ψ scan technique; refinement used 2362 reflections with $F_o^2 > 3\sigma(F_o^2)$ and resulted in residuals of $R = 0.0440$ and R_w 0.0509 (417 parameters) with all non hydrogen atoms anisotropic and phenyl hydrogens idealized.

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