A Monomeric Methanedithiolate Complex of Molybdenum

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Dedicated to Prof. Dr. H. P. Fritz on the occasion of his 60th birthday
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Methanedithiolate Complex, Molybdenocene Dihydride, Carbon Disulfide Hydrogenation

Thermal reaction of molybdenocene dihydride \((\eta^5-C_5H_5)_2MoH_2\) with carbon disulfide affords a new molybdenocene complex \((\eta^5-C_5H_5)_2Mo(S_2CH_2)\) which according to analytical and spectroscopic data contains a methanedithiolate ligand.

The reactions of metalocene hyridro complexes of early transition metals such as molybdenocene dihydride \((\eta^5-C_5H_5)_2MoH_2\) (1) with unsaturated substrates can be regarded as models for steps in homogeneous and heterogeneous hydrogenation processes. For instance, 1 reacts with diphenylacetylene in carbon disulfide as a solvent, but apparently interacts with the heterocumulene itself. Here we wish to report on the unexpected product from the reaction of 1 with carbon disulfide.

When a THF solution of 1 is heated with excess carbon disulfide to 45 °C over a period of several hours, a dark-colored reaction mixture is formed from which, after chromatographic work-up, dark red needles of molybdenocene methanedithiolate \((\eta^5-C_5H_5)_2Mo(S_2CH_2)\) (2) is isolated as the sole tractable organometallic product. The \(^1H\) NMR spectrum of 2 consists of two sharp singlets at 5.44 and 5.63 ppm with an intensity ratio of 10:2, which can be assigned to the cyclopentadienyl and methylene protons, respectively. In the \(^13C\) NMR spectrum the carbon atom of the methanedithiolate ligand gives rise to a triplet at 61 ppm with \(J(CH) = 150\) Hz, while the ring carbon atoms resonate at 97 ppm. The temperature independence of the NMR spectra in the range of +60 to –80 °C supports either a structure of \(C_{\infty v}\) symmetry with a planar \(MoS_2CH_2\) ring or, more likely and in analogy to 1,3-dithietane \(C_2S_2\) [3], a puckered molecule of \(C_v\) symmetry which rapidly interconverts into a second conformer. The rather simple IR spectrum exhibits, in addition to bands of the molybdenocene fragments, \(v(CH_2)\) modes and a rather intense absorption at 1263 cm\(^{-1}\) that can be assigned to a deformation mode of the four-membered ring. The EI mass spectrum shows as the most prominent fragmentation the loss of thioformaldehyde from the molecular ion to give \([(\eta^5-C_5H_5)_2MoS^+]\) as the base peak.

While mechanistic features for the formation of 2 remain obscure, it is noteworthy that we failed to detect in the above reaction mixture the carbon disulfide complex of molybdenocene \((\eta^5-C_5H_5)_2Mo(\eta^2-CS_2)\) which is easily accessible by ligand substitution of 1 [4]. Normally carbon disulfide inserts into the metal-hydrogen bond of a dihydride to give an \(\eta^1\)-[5] or \(\eta^2\)-dithioformiate ligand system [6], and to our knowledge only in one case has a methanedithiolate complex resulting from direct interaction of carbon disulfide with a transition metal hydride been reported in the literature [7].

\[\begin{align*}
(\eta^5-C_5H_5)_2MoH_2 + CS_2 & \rightarrow \text{1} \\
(\eta^5-C_5H_5)_2Mo(S_2CH_2) + ... & \rightarrow \text{2}
\end{align*}\]
**Experimental Part**

All operations were performed under exclusion of air and moisture using standard Schlenk-techniques. NMR spectra were recorded by using a Bruker WP-80 SY spectrometer, IR spectra were measured on a Perkin-Elmer IR-spectrometer 580, and mass spectra were obtained on a Varian MAT CH-5-DF spectrometer.

\[(\eta^2-C_5H_5)_2Mo(S_2CH_2)\] (2)

A solution of \((\eta^2-C_5H_5)_2MoH_2\) (1.30 g, 5.7 mmol) in 20 ml of THF was treated with carbon disulfide (1.26 g, 16 mmol) and heated to 45 °C for 16 h. After removal of all volatiles the orange residue was chromatographed on florisoril (column 2 × 20 cm). Elution with pentane gave a brownish grey band containing an unidentified material and with CH_2Cl_2/ether (1:1) a yellow band which was collected as an orange red solution. The solvent was removed in vacuo and the residue crystallized from carbon disulfide as dark red needles which could be further purified by sublimation at 150 °C/10^{-7} bar. Yield 180 mg (10%), m.p. 207 °C (dec). \(^1\)H NMR (CDCl_3, -80 °C): \(\delta = 5.44\) (s, 5H, C_5H_5), 5.63 (s, 1H, CH_2). \(^13\)C NMR (CDCl_3, 25 °C): \(\delta = 60.96\) (t, \(^1J(C,H) = 150\) Hz, CH_2), 97.10 (d, \(^1J(C,H) = 180\) Hz, C_5H_5). IR (KBr): v = 3080m, 2965m, 2874w, 2808w, 1436w, 1421 w, 1386w, 1263s, 1090s, 1068 ms, 1021 s, 988m, 813s, 698w, 390w, 365w. EI MS (70 eV): \(m/z = 306\) (11%, M^+), 260 (100, C_10H_10MoS^+), 228 (31, C_10H_10Mo^+).

\(C_{11}H_{12}S_2Mo\) (304.3)

Calcd C 43.42 H 3.98,

Found C 43.25 H 4.01.

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