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Synthesis and Stereochemistry of the $C_6H_5(CO)_2Mo$ Complex with Cysteine Methylester*

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Amino acids and amino acid derivatives, well known ligands in Werner type transition metal complexes [1, 2], have recently also been used as ligands in organometallic compounds like $C_5H_5(CO)_2MoOCOCH(R)NH_2$ [3], in which the amino acid anion acts as a bidentate ligand coordinated via O of the carboxylic group and N of the NH_2 group. For cysteine methylester with its carboxylic group prevented from coordination by ester formation, S/N chelation is expected similar to $[(C_5H_5)_2MoSCH_2CH(COO)NH_2]X$ [4]. The synthesis, spectroscopic and stereochemical properties of the corresponding compound $C_5H_5(CO)_2MoNH_2CH(COOCH_3)CH_2S$, I, are reported here.

Experimental

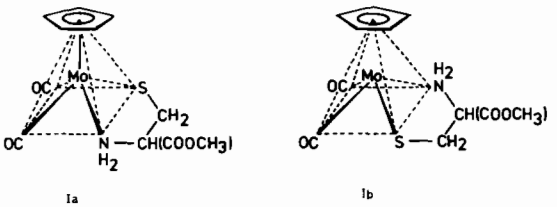
All operations were carried out under nitrogen atmosphere. Absolute solvents saturated with nitrogen were used. Cystein– methylester hydrochloride was converted into the free ester base by the literature method [5].

Synthesis of $C_5H_5(CO)_2MoNH_2CH(COOCH_3)CH_2S$, I

A solution of 1.0 g (3.6 mmol) $C_5H_5Mo(CO)_3Cl$ and 0.55 g (4.0 mmol) cysteine methylester in a mixture of 50 ml benzene and 2 ml pyridine was heated at 50 °C from 60 to 90 minutes until the theoretical quantity of CO is liberated. The reaction mixture was filtered and the filtrate was evaporated to dryness. The product so obtained was dissolved in benzene/acetone 1:1 and purified by chromatography on a SiO_2 column. Elution with pentane gives a purple red first band containing $[C_5H_5Mo(CO)_3]_2$. With benzene/ether 1:1 a second orange band containing $[C_5H_5Mo(CO)_3Cl]$ and with ether/acetone 1:1 a third dark red band of complex I is eluted. As the second and third bands usually overlap, another chromatography on SiO_2 at –40 °C with the material contained in the overlap area and band three is needed for complete separation. Elution first with ether and then ether/acetone 1:1 leads to a 30% yield of the pure compound I. *Anal.* Calcd. for $C_{11}H_{13}NO_4SMo$: C, 37.62; H, 3.73; N, 3.98. Found: C, 37.65; H, 3.77; N, 3.96. Compound I decomposes at about 55 °C. It is readily soluble in acetone, alcohols, CH_2Cl_2 and THF, sparingly soluble in benzene, ether, and almost insoluble in pentane. In solution it is very air sensitive.

Results and Discussion

The i.r. spectrum of complex I (CH_2Cl_2 solution) shows two characteristic strong absorptions due to $\nu(C{\equiv}O)$ stretching vibrations at 1955 and 1852 cm^{-1} as well as a band of medium intensity due to the $\nu(C{=}O)$ stretching vibration of the ester group at 1740 cm^{-1}. In the mass spectrum of complex I the molecular ion successively loses two CO groups as shown by the following m/e values (rel. int.): M^+ 353 (35), $(M-CO)^+$ 325 (17), $(M-2CO)^+$ 297 (30), $(M-2CO-NH_3)^+$ 280 (27), $(M-2CO-NH_3-S)^+$ 248 (100).



Complex I should form two diastereoisomers Ia and Ib differing in the configuration at the metal atom [6–8]. In most cases these diastereoisomers can be differentiated on the basis of their different chemical shifts in the ^1H nmr spectra.

However, the ^1H nmr spectrum of complex I in CD_3OD at 33 °C shows only sharp singlets at τ 4.58 ppm due to the C_5H_5 protons and at τ 6.27 ppm due to the $COOCH_3$ protons. The methine, methylene and amino protons at room temperature do not give rise to sharp signals; however, integration shows that they are present as broad peaks between τ = 6.0 and 8.5 ppm. As the temperature is decreased to +10 °C, the C_5H_5 and the $COOCH_3$ signals split into two. Further, the methine, methylene and the amino multiplets emerge as sharp signals. All these ^1H nmr changes as a function of temperature are completely reversible. From this D-NMR study the following approximate activation energies for the interconversion of the two isomers A and B observable in the low temperature NMR spectrum can be calculated: $\Delta G^{\ddagger}$ = 16.8 ± 0.3 and 17.3 ± 0.3 [Kcal/mol] using the

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following parameters: critical temperature $T_c = 289 \pm 2$ °K, half width $b_E = 0.44$ Hz, chemical shift difference (extrapolated to T_c) $\Delta\nu = 1.56$ Hz, equilibrium constant K = 2.21, rate constants $k = 2.27 \pm 1$ [sec^{-1}] for A → B and $k = 1.03 \pm 1$ [sec^{-1}] for B → A.

After chromatography the diastereoisomer mixture Ia/Ib shows the following high optical rotations: $[\alpha]^{20}_{365}$ + 1570°, $[\alpha]^{20}_{436}$ −640°, $[\alpha]^{20}_{546}$ +35° and $[\alpha]^{20}_{578}$ +370° (1.1 mg/ml, toluene). By one fractional crystallisation either from acetone/pentane 2:3 or from benzene/pentane 2:1 the following optical rotations of the less soluble fraction were measured: $[\alpha]^{20}_{365}$ +2295°, $[\alpha]^{20}_{436}$ −1180°, $[\alpha]^{20}_{546}$ +50° and $[\alpha]^{20}_{578}$ +500°. Repeated fractional crystallisations do not lead to an improvement of the values. These optical rotations do not change on heating the solutions until decomposition occurs. This can best be interpreted by a high configurational stability at the Mo center in I similar to that observed in closely related systems [8–10], whereas the dynamic process observed by temperature dependent ^{1}H nmr spectroscopy could be due to a conformational change, possibly a ring inversion, of the Mo cysteinato chelate system [1, 11, 12].

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