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Preliminary communication

DIMETHYLSULFONIUMCYCLOPENTADIENYLIDEMOLYBDENUM TRICARBONYL

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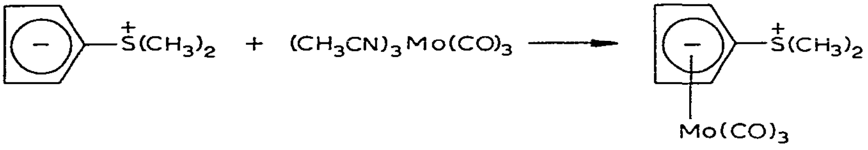
Summary

Dimethylsulfoniumcyclopentadienylidemolybdenum tricarbonyl has been prepared, and PMR, IR and mass spectra are reported.

Quantum-mechanical calculations indicate 83% ylide structure in the ground state of dimethylsulfoniumcyclopentadienylide [1].

Therefore, the cyclopentadienyl ring in this compound is expected to behave as a six-electron ligand in complexing with transition metals.

Indeed, we found that in the reaction of dimethylsulfoniumcyclopentadienylide with $(CH_3CN)_3Mo(CO)_3$ in diglyme at room temperature a complex had been formed with the structure corresponding to formula I*.



(I)

Similar complexes were reported earlier for triphenylphosphonium- and triphenylarsonium-cyclopentadienylides and the Group VIB metals [2,3].

Dimethylsulfoniumcyclopentadienylidemolybdenum tricarbonyl is a light-yellow substance, stable in the air in solid state, m.p. 173—175°C (decomp.). It is poorly soluble in benzene, ether, ethyl alcohol, chloroform, and much more soluble in acetone and dimethyl sulfoxide. The solutions are unstable in the air.

In the NMR spectrum of complex I resonance signals of the methyl protons appear as a singlet at δ 3.16 ppm, and those of the C_5H_4-ring protons appear as two triplets at δ 5.47 and 6.09 ppm. To compare, non-complexed dimethylsulfoniumcyclopentadienylide in the same solvent gives a singlet at

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* The X-ray analysis of this complex is now under way.

δ 2.78 ppm (methyl protons) and triplets at δ 5.92 and 6.23 ppm (C_5H_4-ring protons). It should be noted that complexing with $Mo(CO)_3$ results but in a slight upfield shift of the C_5H_4-ring proton signals ($\Delta\delta$ 0.29 ppm, measured between the centers of the doublets of triplets.

The C=O stretching frequencies observed in the IR spectrum of complex I are characteristic of carbonyl complexes, i.e.: ν(CO) 1825 and 1925 cm^{-1} (in acetone). Other frequencies observed in the IR spectrum (KBr) are as follows: 465 m, 490 w, 510 s, 520 s, 610 s, 635 s, 790 s, 800 s, 835 m, 885 m, 900 w, 925 w, 970 m, 990 s, 1020 m, 1040 s, 1060 w, 1170 s, 1310 w, 1330 m, 1345 w, 1410 s, 1425 w, 2920 m, 3000 w, 3020 w, 3030 w, 3100 m, 3120 w cm^{-1}.

The structure corresponding to formula I was also confirmed by analysis of the mass spectrum. Along with the molecular ion (*m/e* 310—302) the following fragments were observed: $[C_5H_4S(CH_3)_2Mo(CO)_n]^+$ (n = 0—3); $[C_5H_4S(CH_3)Mo(CO)_n]^+$ (n = 0—3); $[MoC_5H_4SCH_2]^+$; MoS^+; $[C_5H_4S(CH_3)_2]^+$; $[C_5H_4SCH_3]^+$

Experimental

$(CH_3CN)_3Mo(CO)_3$ was prepared from 2.4g (9 mmol) of $Mo(CO)_6$ and 75 ml of acetonitrile in argon, according to the method in ref. 4. The excess of acetonitrile was distilled off, and 1.08g (9 mmol) of dimethylsulfoniumcyclopentadienylide [5] and 75 ml of diglyme were added to the flask. Upon shaking the reaction mixture immediately produced light-yellow crystals which were filtered off, washed with benzene and dried. The yield of dimethylsulfoniumcyclopentadienylidemolybdenum tricarbonyl was 1.05g (38%). Found: C, 39.03; H, 3.66; Mo, 32.73; S, 10.28. $C_{10}H_{10}MoSO_3$) calcd.: C, 39.21; H, 3.27, Mo, 31.37 S, 10.46%.

The mass spectrum was measured on a MX-1303 spectrometer with direct inlet, at the temperature of 160° C and the voltage of ionization 30 V.

The IR spectra were measured on a UR-20 spectrophotometer, and the NMR spectra on a Perkin—Elmer R-12 instrument, at 60 MHz (with TMS as an internal standard).

Acknowledgment

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