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CYCLOPENTADIENYLIDES AS LIGANDS IN MANGANESE COMPLEXES

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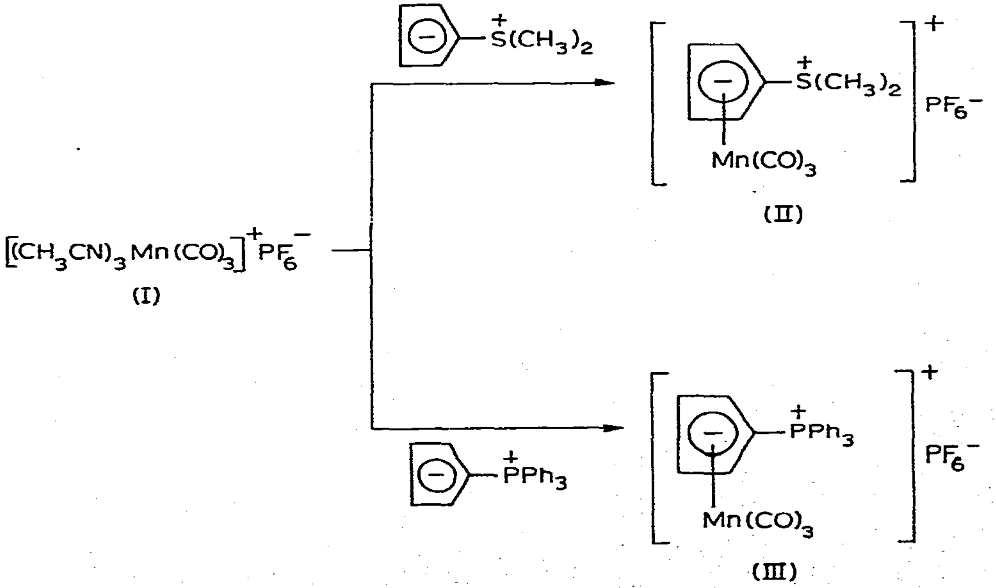
Summary

Dimethylsulfonium- and triphenylphosphonium-cyclopentadienylide-manganese tricarbonyl hexafluorophosphate have been prepared and their PMR, IR and mass spectra are reported.

In earlier papers [1,2] we described the synthesis of π-$M(CO)_3C_5H_4S(CH_3)_2$ (M = Cr, Mo, W) from dimethylsulfoniumcyclopentadienylide and $(CH_3CN)_3$-$M(CO)_3$. We have continued these investigations by substituting three acetonitrile groups in the manganese charged complex (I) with cyclopentadienylides:



These reactions occur in diglyme or tetrahydrofuran even at room temperature. The complexes II and III are yellow or orange crystalline solids. They are stable in air when solid, soluble in the polar solvents (acetone, THF, methanol and ethanol) and insoluble in the nonpolar solvents (benzene and hexane). The IR spectra of complexes II and III show an intensive absorption at 833 cm^{-1} characteristic of the PF_6^- anion and also the absorptions at 1960 and 2040 cm^{-1} due to the stretching modes of terminal carbonyls. The PMR spectrum of II contains a singlet at δ 3.55 ppm ($S(CH_3)_2$ protons) and two triplets at δ 5.47 and 6.23 ppm, assigned in turn to the α- and β-protons in the cyclopentadienyl ring. The relative signal intensities are 3 : 1 : 1 respectively. The PMR spectrum of III has a signal at δ 5.83 ppm (C_5H_4 ring protons) and a signal at δ 8.11 ppm (m, PPh_3 protons). The relative signal intensities are 4 : 14.6 respectively. The mass spectrum of complex II exhibits a molecular ion at *m/e* 410. The mass spectrum of III shows no peak due to the molecular ion but signals due to $[C_5H_4PPh_3]^+$ (*m/e* 326) and an ion of *m/e* 325 are observed.

Thus the IR, PMR and mass spectra, together with elemental analysis of the obtained compounds, suggest they are of formulae II and III. To determine the structures of the complexes a complete X-ray analysis is under way.

Experimental

The IR spectra were run on a UR-20 spectrometer and the PMR spectra on a Perkin—Elmer R12 instrument at 60 MHz. In the latter case acetone-d_6 was used as solvent, and HMDS as an internal standard. The mass spectra were measured on an MX-1303 spectrometer with direct sample inlet into the ion source at a temperature of 150°C and an ionizing voltage of 30 eV.

All the reactions were carried out under argon. Acetonitrile was purified by multiple refluxing over P_2O_5 and subsequent distillation over K_2CO_3. THF was distilled under argon over $LiAlH_4$ immediately before reaction. $[(CH_3CN)_3Mn(CO)_3]^+PF_6^-$ was prepared by a literature method [3], m.p. 129—131°C (lit. 131—133°C).

Preparation of $[(CH_3)_2SC_5H_4Mn(CO)_3]^+PF_6^-$

(a). 0.42 g (1 mmol) of $[(CH_3CN)_3Mn(CO)_3]^+PF_6^-$ was added to a solution of 0.14 g (1 mmol) of dimethylsulfoniumcyclopentadienylide [4] in 50 ml of THF. The resulting yellow solution was allowed to stand for 24 h at 20°C. A small quantity of precipitate was filtered off and the solution was evaporated to dryness. The residue was crystallized from ethanol. Yield 0.39 g (92%) m.p. 150—153°C (dec.).

(b). The solution of 0.14 g (1 mmol) of $C_5H_4S(CH_3)_2$ and 0.42 g (1 mmol) of $[(CH_3CN)_3Mn(CO)_3]^+PF_6^-$ in 20 ml of diglyme was heated at 50—60°C for 3 h. The diglyme was evaporated and the residue crystallized from ethanol. Yield 0.19 g (45%), m.p. 146—148°C (dec.). (Found: C, 29.77; H, 2.38; F, 27.61; S, 7.70. $C_{10}H_{10}F_6MnO_3PS$ calcd.: C, 29.27; H, 2.44; F, 27.80; S, 7.80%.)

Preparation of $[Ph_3PC_5H_4Mn(CO)_3]^+PF_6^-$

0.42 g (1 mmol) of $[(CH_3CN)_3Mn(CO)_3]^+PF_6^-$ was added to a solution of 0.36 g (1 mmol) of triphenylphosphoniumcyclopentadienylide [5] in 50 ml of THF. The yellow solution was allowed to stand for a day at 20°C. THF was evaporated under vacuo and the solid crystallized from ethanol. Yield 0.46 g (68%), m.p. 196—197°C (dec.). (Found: C, 51.42; H, 3.13; F, 19.18; P, 9.92. $C_{26}H_{19}F_6MnO_3P_2$ calcd.: C, 51.15; H, 3.11; F, 18.70; P, 10.16%.)

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