

Manganese Pentacarbonyl σ -Phenacyl Complex

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(Received 22nd June, 1983)

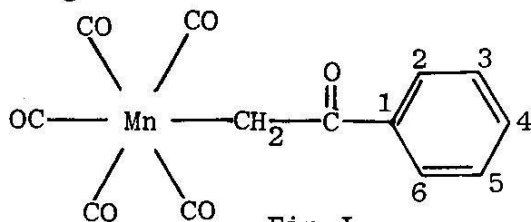
Introduction

Transition metal carbonyls are known to form bonded complexes with a variety of organic ligands [1-5] phenacyl complexes of Mo and Fe carbonyls forming bond with the metal have also been reported [6]. Here we describe the complex $(CO)_5Mn-CH_2COC_6H_5$ which was prepared by treatment of $[Mn(CO)_5]^-$ anion with α -chloroacetophenon (phenacylchloride) in tetrahydrofuran.

Results and Discussion

The complex $(CO)_5Mn-\sigma-CH_2COC_6H_5$ is a pale yellow oil soluble in common organic solvents. It is stable at room temperature and can be handled in air for a few minutes. Petroleum solution of the complex decomposes to the extent of 50% in 24 hours.

The complex $(CO)_5Mn-\sigma-CH_2COCH_6H_5$ was characterized by its infrared, nmr spectra and elemental analysis. The structure of the complex shown in Fig.1. is consistent with the data given in Table 1.



Infrared Spectrum

The metal terminal carbonyl (Mn-CO) stretching frequencies and that of the keto (C=O) stretching frequency in the free ligand was at 1712 cm^{-1} while on coordination with the metal it was observed at 1678 cm^{-1} thus lowering 35 cm^{-1} was observed.

A similar trend of lowering of the C=O stretch of the keto group has been observed in Mo and Fe complexes [6]. This lowering of the frequency may be attributed due to a direct interaction of the metal and the keto group of the ligand which is in the β -position with respect to the metal. This direct interaction of the metal with the β -carbon atom of the ligand has been suggested by Green and workers. They have shown anomalous chemical properties of protonation in complexes such as $\eta^5-C_5H_5Fe(CO)_2-\sigma-CH_2COR$ [7], $\eta^5-C_5H_5M(CO)_3-\sigma-CH_2CH=CH_2$ [8], $\eta^5-C_5H_5Fe(CO)_2-\sigma-CH_2-CH=CH_2$ [9].

N.M.R. Spectrum

The proton magnetic resonance spectrum of the complex is consistent with the proposed structure as shown in Fig.1. The methylene protons Mn-CH₂ are observed at $\tau 7.55$ as compared to the free ligand which is observed at 5.5τ . The 2,6 protons

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Table-1:

Compound	IR spectrum		NMR spectrum		
	Mn-CO ^(a) Freq.cm ⁻¹	Keto freq. cm ⁻¹	(ppm) ^b in CCl ₄	Relation intensity	Assignment
(CO) ₅ Mn-CH ₂ -C-C ₆ H ₅	2048(m)	1678(s)	2.25	2	2,6-protons of C ₆ H ₅
	2026 (s)				
	1978(m)		2.65	3	3,4,5,protons
	1918 (s)		7.55	2	Mn-CH ₂

a = as neat no NaCl plates b = Relative to TMS as an internal reference = 10 s, strong m, medium of the phenyl group are observed at lower field than the 3,4,5 protons and do not show any appreciable effect on coordination.

Experimental

The complex was prepared under an atmosphere of dry nitrogen using THF as a solvent. The elemental analysis was carried out in the departmental microanalysis laboratory. The infrared spectrum was recorded on Pye Unicam infrared spectrophotometer model SP 110 Cambridge, England.

Pentacarbonyl σ -Phenacylmanganese

A solution of the sodium salt of Na⁺ [(Mn(CO)₅]⁻ was prepared in tetrahydrofuran (25 ml) using 1.g of Mn₂(CO)₁₀ as described in the literature (2). This solution was slowly transferred to a stirred and cooled (-10°C) solution of α -chloroacetophenone (0.7 g) in tetrahydrofuran (8 ml). After addition the reaction mixture was allowed to come to room temperature and was stirred for another 1 hr. The solvent was removed under reduced pressure. The reaction product was extracted with petroleum ether and chromatographed on an alumina column packed in pet.ether. Elution with petroleum ether afforded a pale yellow band. This was collected and the solvent was removed under reduced

pressure giving a pale yellow oil of (CO)₅Mn σ CH₂COC₆H₅ yield 20%. The second yellow band was collected and was not identified. (Found: C, 50.1; H, 1.2 C₁₃H₇MnO₆, Calcd: C, 49.6; H, 2.2%).

Acknowledgement

N.S.Ganji thanks King Abdul Aziz University for the scholarship.

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