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Preliminary communication

Photolysis of cyclopentadienyltricarbonylmanganese; detection of $(\pi\text{-}C_5H_5)Mn(CO)_2$

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The species $(\pi\text{-}C_5H_5)Mn(CO)_2$ has been postulated as an intermediate in the photochemical substitution of $(\pi\text{-}C_5H_5)Mn(CO)_3$ [1] and, more recently, in the interconversion of $(\pi\text{-}C_5H_5)Mn(CO)_2PPh_3$ and $(\pi\text{-}C_5H_5)Mn(CO)_2(SiPh_3)H$ [2]. As an extension of our previous studies of photolytic fragmentation[3,4,5] we have investigated the behaviour of $(\pi\text{-}C_5H_5)Mn(CO)_3$ on irradiation in rigid and viscous media.

Attempts to study the photolysis of $(\pi\text{-}C_5H_5)Mn(CO)_3$ and $(\pi\text{-}C_5H_4CH_3)Mn(CO)_3$ in isopentane–methylcyclohexane glasses failed because of solubility problems. Accordingly, a 3/1 methylcyclohexane/nujol mixture which formed a glass at about 175 K was used as a matrix medium. The nujol was previously purified to remove aromatics and carefully dried. The glasses were photolysed at 80 K. It was found that light of frequency less than 22000 cm^{-1} was without effect, but unfiltered light from a medium pressure Hg discharge lamp caused extensive production of matrix trapped CO together with new species with two sharp bands in the CO stretching region. These, which we assign as $(\pi\text{-}C_5H_5)Mn(CO)_2$ and $(\pi\text{-}C_5H_4CH_3)Mn(CO)_2$ species, disappeared on allowing the glass to soften with regeneration of the parent tricarbonyls.

Carbonyl stretching frequencies and parameters are given in Table 1, as is the apparent C–M–C angle (θ) estimated from the approximate areas for the two peaks (derived from the product of absorbance and peak half-width) using the local oscillating dipole model[6]. Our data for the parent tricarbonyls are included for comparison.

The lowering of CO stretching parameters is not unexpected but serves to confirm that, even when attached to Mn^I, CO is a net remover of charge. The apparent angle is an inherently less reliable quantity[7], quite apart from experimental error. The value of θ found for $(\pi\text{-}C_5H_5)Mn(CO)_3$ is 94–96° compared with the values of 91, 91, and 94° found in the crystal[8]; agreement is good despite the limitations[7] of this type of calculation. The increase in apparent angle on loss of CO may thus be physically significant.

TABLE 1

Compound	*CO stretching symmetric*	*Frequency (cm^{-1}) [a] antisymmetric*	*K(md/Å)*	*k_i(md/Å)*	*θ (°)*
$(\pi\text{-}C_5H_5)Mn(CO)_3$	2026	1938	15.64	0.470	94, 96 [b]
$(\pi\text{-}C_5H_4CH_3)Mn(CO)_3$	2022	1936	15.59	0.460	98
$(\pi\text{-}C_5H_5)Mn(CO)_2$	1955	1886	14.90	0.535	100
$(\pi\text{-}C_5H_4CH_3)Mn(CO)_2$	1950	1881	14.82	0.530	110

[a] Frequencies ± 0.5 cm^{-1}. [b] 94° from 77 K spectrum; 96° from room temperature spectrum.

Photolyses of $(\pi\text{-}C_5H_5)Mn(CO)_3$ and $(\pi\text{-}C_5H_4CH_3)Mn(CO)_3$ dissolved in Apiezon N grease gave rise to a number of broad bands in the CO stretching region. This behaviour is unlike that of $Mo(CO)_6$ [5] and $Fe(CO)_5$, where the behaviour on irradiation was the same in room temperature Apiezon matrices as in 4/1 methylcyclohexane/isopentane glass at 80 K.

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