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Preliminary communication

POLYMERIZATION OF TRICARBONYLCYCLOHEPTATRIENEIRON

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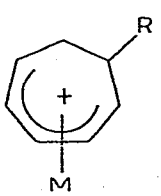
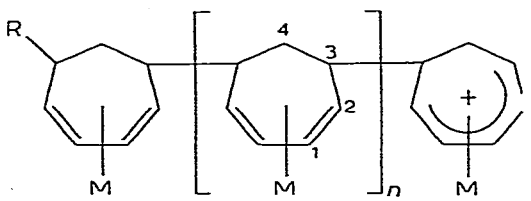
Summary

Addition of some cationic tricarbonyliron complexes to tricarbonylcycloheptatrieneiron can lead to polymerization.

Trityl and tropylium cations readily add to tricarbonylcycloheptatrieneiron(I) [1,2]. If excess I is added to $C_7H_7PF_6$ and if the reaction time is increased from 3 to 24 hours then the weight of ionic product (i.e. insoluble in ether) is greater than would be expected for IIb. The MC—O IR absorptions of the product also change with increasing time and excess of I. Together with the expected "cationic" MC—O absorptions (2120 and 2080 cm^{-1}) "neutral" MC—O peaks (2050 and 1980 cm^{-1}) gradually increase until the cationic absorptions are just visible. Attempts to follow this reaction by ^1H NMR were not successful. Addition of a fifteenfold excess of I tc IIc in

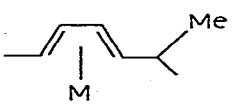


(II)



(III)

(a) R = H
(b) R = C_7H_7
(c) R = Me



M = $Fe(CO)_3$

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CH_2Cl_2 and observation of the ^{13}C NMR spectrum showed a decrease in the absorptions of I and new broad absorptions at 89.8, 63.4, 50.3 and 30.5 ppm from TMS (approximate intensity ratios 2:2:2:1). These broad absorptions suggest a polymeric structure of type III.

In another reaction IIa, a one hundred-fold excess of I and CH_2Cl_2 were sealed under vacuum. Work up after three weeks at room temperature gave an 80% yield of product, based on I. The ^{13}C NMR spectrum of this very soluble compound was obtained in $CDCl_3$ solution using 30° pulses and a 1.2 second delay. Broad absorptions at 88.8 [C(1)], 61.3 [C(2)], 48.5 [C(3)] and 29.4 [C(4)] ppm from TMS had intensity ratios very close to 2:2:2:1. The sharp $Fe(CO)_3$ resonance at 211.5 ppm had a signal/noise of 40/1 but the expected absorption for the cationic end at circa 200 ppm was not detectable. This suggests a value for n greater than 30.

The C and H analyses of this product were found to be: C, 50.8; H, 3.4, n = 33 calcd.: C, 50.85; H, 3.42%. Attempts were made to obtain molecular weight values however results were unreliable due to decomposition problems. Further studies on these systems are in progress.

References

1 H.J. Dauben and D.J. Bertelli, J. Amer. Chem. Soc., 85 (1961) 497.
2 P. McArdle, J. Chem. Soc. Chem. Commun., (1973) 482.