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Preliminary communication

Complete photochemical carbonyl substitution in cyclopentadienyltricarbonylmanganese

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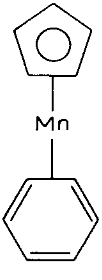
SUMMARY

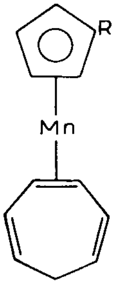
Cycloheptatriene and related trienes undergo efficient photochemical reaction with displacement of all three carbonyl groups from cyclopentadienyltricarbonylmanganese; the very air-sensitive cycloheptatriene complexes so formed undergo smooth hydride abstraction forming the stable cyclopentadienyltropyliummanganese salts.

Fischer and Herberhold[1] obtained cyclopentadienylbenzenemanganese (I) in ≈ 2% yield by photolysis of cyclopentadienyltricarbonylmanganese in benzene, but no other example of complete carbonyl displacement from the latter appears to have been reported. Even the displacement of two carbonyls by butadiene to give the complex $C_5H_5Mn(C_4H_6)CO$ is regarded as exceptional[1]; 1,3-cyclohexadiene gives only a trace of the corresponding product, acting chiefly as a monodentate or bridging ligand and all other dienes tried[1] (whether conjugated or potentially chelating) reacted only in these last two modes to give products of the types $C_5H_5Mn(CO)_2$(diene) and $[C_5H_5Mn(CO)_2]_2$(diene).

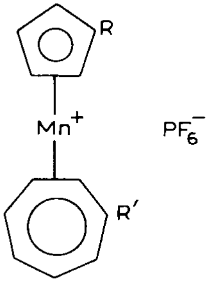
Following the observation[2] that complete photochemical displacement of carbonyl can occur with cyanide, we have now found a much more efficient displacement with cycloheptatriene.



(I)



(II)



(III)

The formation of the product* (II; R = H), an air sensitive, sublimable red crystalline compound like its analogue (I), occurs in 87% yield (8 h irradiation) and its methyl derivative* (II; R = Me) is formed similarly. 1,3,5-Cyclooctatriene and cyclooctatetraene also appear to react analogously, but give less stable products. Triphenylmethyl hexafluorophosphate converts the new cycloheptatriene complexes (II) almost quantitatively to the very stable pink tropylium salts* III; R = R′ = H) and (III; R = Me; R′ = H). An isomer (III; R = H; R′ = Me) of the latter has previously been obtained[3] by ring expansion of the benzene complex (I) using acetyl chloride-aluminium chloride. The present route to such compounds is not only more convenient, but also more flexible.

Related photochemical reactions as well as the chemical behaviour of the manganese complexes (II) and (III) are being investigated.

ACKNOWLEDGEMENT

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3 E.O. Fischer and S. Breitschaft, *Chem. Ber.*, 99 (1966) 2213.

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*These products have been characterised by NMR spectra, satisfactory elemental analyses, and in the cases of the neutral products (II) by mass spectra.