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Preliminary communication

ARENE—MANGANESE COMPLEXES

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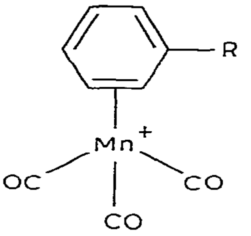
Summary

Direct reaction between arene and the perchlorate $Mn(CO)_5OClO_3$ provides a simple, rapid and uncatalysed route to the salts $[(arene)Mn(CO)_3]^+$. Hydrolysis of $[(C_6H_5F)Mn(CO)_3]^+$ yields the corresponding phenol complex which is readily deprotonated to the weakly basic oxocyclohexadienyl complex, $(C_6H_5O)Mn(CO)_3$.

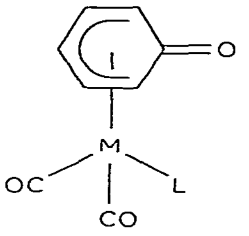
Arenetricarbonylmanganese salts of the type I were first obtained by Coffield, Sandel and Closson [1] from the arene, manganese pentacarbonyl halide and aluminium halide and have always been prepared by this route or via the related cyclohexadienyl complexes. The need to use aluminium chloride severely limits the possible arene substituents. Although the facile nucleophilic substitution [2] of e.g. the chlorobenzene complex II provides access to certain functional derivatives a milder direct method of preparation is clearly desirable. We have found that both the cation $[Mn(CO)_3(CH_3COCH_3)_3]^+$ and the perchlorate $Mn(CO)_5OClO_3$ [3] react without catalyst to form arene complexes.

In the simplest procedure pentacarbonylmanganese perchlorate reacts with e.g. benzene in refluxing dichloromethane; precipitation of the perchlorate of the benzene cation (I) begins within 15 min and is apparently complete after approx. 2 h. The same cation is the major product when 1,3-cyclohexadiene replaces benzene and the reaction is conducted at room temperature overnight.

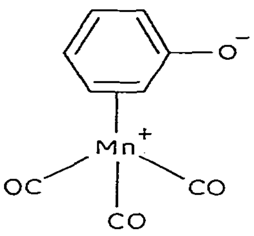
The extreme reactivity of the fluorobenzene complex (III) has prevented its isolation in a pure state although we have demonstrated its formation (by the $AlCl_3$ route) by conversion to the piperidino (IV) and ethoxybenzene complex (V) [2]. Analogous to formation of the latter by ethanolysis, the phenol complex (VI) should arise by hydrolysis. It should be a stronger acid than the previously reported [2] anilino complex (VII) and hence readily deprotonate



(I, R = H;
II, R = Cl;
III, R = F;
IV, R = $N(CH_2)_5$;
V, R = OEt;
VI, R = OH;
VII, R = NHPh)



(VIII, M = Mn; L = CO
IX, M = Cr; L = η^3-C_3H_5)



(X)

to the oxocyclohexadienyl complex (VIII). Cole-Hamilton, Young and Wilkinson [4] isolated the first complex of the oxocyclohexadienyl ligand, the ruthenium compound $Ru(H)(C_6H_5O)(PPh_3)_2$ and cationic rhodium and iridium complexes [5] of this ligand and a related cobalt compound [6] have been described. But it was Trahanovsky and Hall's description [7] of the more closely related chromium complex (IX) which guided us in the isolation of the manganese compound (VIII). The water solubility of the former is so far enhanced in our product VIII, presumably due to increased contribution of the dipolar from X, that it can only be extracted into organic solvents after complete removal of water from the crude reaction products (after neutralisation). It is a relatively weak base which affords the cationic phenol complex (VI) in aqueous solutions only in the presence of excess of strong acid. It crystallises from a mixture of dichloromethane and hexane and its structure has been confirmed by an X-ray crystallographic study which will be published elsewhere [8].

We are continuing to explore the scope of the new route to arenemanganese complexes and the chemical properties of the oxocyclohexadienyl derivative VIII.

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