Conversion of Arenes into Cyano-arenes *via* Co-ordination to Manganese(I)

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Summary Oxidation of cyanocyclohexadienyl complexes $[(C_6H_{6-n}Me_nCN)Mn(CO)_3]$, obtained by reaction of cyanide ion with complexes $[(C_6H_{6-n}Me_n)Mn(CO)_3]^+$, yields free cyano-arene $C_6H_{5-n}Me_nCN$ uncontaminated by $C_6H_{6-n}Me_n$.

In a recent paper,[1] we reported the attack—under extremely mild conditions—by cyanide ion on co-ordinated arenes in complexes $[(C_6H_{6-n}Me_n)Mn(CO)_3]^+$ to give *exo*-cyanocyclohexadienyl complexes of the type $(C_6H_{6-n}Me_nCN)Mn(CO)_3$. Prior to this report, the only nucleophiles known[2] to add to arenes in complexes of this and similar types were hydride, alkyl, and aryl, but we have now found that several other types of nucleophile, for example, $CH(COMe)_2^-$, $CH(CO_2Et)_2^-$, N_3^-, OMe^-, PPh_2^-, NCS^-, react in a similar manner, although the stability of many of the adducts obtained is low.

The prospect of nucleophilic addition to co-ordinated arenes by a wider range of reagents raises the possibility of synthesising useful substituted arenes by following this attack by abstraction of the *endo*-hydrogen atom from the carbon atom bearing the added substituent.

Whereas conventional abstracting reagents such as Ph_3C^+, Et_3O^+, and HBF_4 removed the cyano-group from *exo*-cyanocyclohexadienyl complexes to regenerate the original compounds $[(C_6H_{6-n}Me_n)Mn(CO)_3)^+$, we have found that reaction with cerium(IV) sulphate in sulphuric acid at room temperature breaks down the complexes to yield free cyano-arene uncontaminated by the unsubstituted arene $C_6H_{6-n}Me_n$. Thus, for example, the complex $(C_6H_6CN)Mn(CO)_3$, obtained from $[(C_6H_6)Mn(CO)_3]^+$ and cyanide ion, reacted with cerium(IV) sulphate to yield 80% of benzonitrile, C_6H_5CN, but *no* benzene. Similarly $(C_6H_3Me_3CN)Mn(CO)_3$, obtained from the mesitylene complex $[(C_6H_3Me_3)Mn(CO)_3]^+$, yielded over 70% of mesitonitrile, $C_6H_2Me_3CN$, and no mesitylene.

A similar degradation of cyclohexadienyl complexes of iron(II) by permanganate oxidation has recently been reported by Helling and Braitsch,[3] but our own investigations have shown that arene complexes of iron(II) do not undergo the *range* of nucleophilic addition reactions characteristic of the complexes [(arene)Mn$(CO)_3$]$^+$ (being attacked only by hydride, alkyl, and aryl anions) and hence are much less useful as starting materials for the synthesis of substituted arenes.[4]

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