Ligand Exchange and Hydrogen Shift Reactions in the Cyclohexadienyltricarbonylmanganese Series

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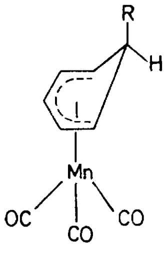
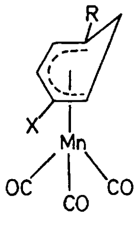
Summary On heating, cyclohexadienyltricarbonylmanganese derivatives can undergo hydrogen migration from the 6-*endo* position; the 6-*exo*-methyl derivative is thus converted into the 1- and 2-methyl isomers, but with arenes as solvents the principal reaction is exchange in which the original 6-*endo*-H becomes attached to the newly introduced arene so that both reactions can be visualised as proceeding *via* hydrido-manganese diene complexes.

Hydrogen migration has been found to occur in cycloheptatriene complexes of chromium,[1] molybdenum,[2] rhodium[3] and iron[3,4] and shown to be significantly influenced by the metal although the mechanistic details remain uncertain. Similar migration has been demonstrated[5] for the diene ligand of cyclopentadienecyclopentadienylcobalt derivatives and also occurs, although less readily, in cyclohexadienetricarbonyliron derivatives.[6] In all cases the migrating atom is the *endo*-H of the methylene group. We report now the first examples of such migration in dienyl complexes, those of the cyclohexadienyltricarbonylmanganese series (I).



(I)



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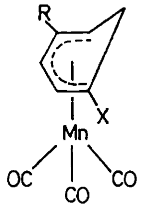

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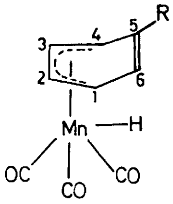

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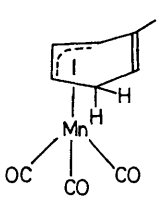

(V)

The 6-*exo*-methyl derivative (I; R = Me) undergoes rearrangement in solution at *ca.* 135 °C giving (initially) apparently equal proportions of the 1-(II; R = Me; X = H) and 2-(III; R = Me; X = H) isomers while at *ca.* 150 °C the *exo*-phenyl complex (I; R = Ph) gives a product in which the 1-isomer (II; R = Ph; X = H) predominates. In arene solvents it was found that all or part of the original ligand was displaced by the solvent so that *e.g.* cyclohexadienyltricarbonylmanganese with *p*-chlorotoluene gave benzene and the chloro(methyl)cyclohexadienyl complexes (II and III; R = Me; X = Cl).[7] The 6-*exo*-phenyl derivative (I; R = Ph) undergoes this exchange even more readily suggesting that the 6-*endo*-hydrogen is again involved and this is confirmed by the reaction using 6-*exo*-protio-hexadeuteriocyclohexadienyltricarbonylmanganese which gave a mixture whose principal component was shown to be the 6-*endo*-deuterio-derivative of the isomer (III; R = Me; X = Cl) together with C_6D_5H. All the above observations can be interpreted on the assumption that a metal hydride intermediate, possibly of the type (IV) is involved both in the hydrogen migration and in the ligand displacement reactions.

$$(C_6H_7)Mn(CO)_3 + MeC_6H_4Cl \rightarrow (MeC_6H_5Cl)Mn(CO)_3 + C_6H_6$$

Similar intermediates have previously been postulated for hydrogen migration;[1,2,3,6] migration of the hydrogen atom from the metal to a terminus [C(1) or C(4)] of the metal-bonded fragment would lead to a co-ordinatively unsaturated complex [*e.g.* (V), (*cf.* ref. 6)] which could rapidly stabilise itself by co-ordination of the metal with the free double bond, leading specifically to the 1- and 2-substituted isomers (II and III; X = H) and not the 3-substituted derivatives (if intermediate IV is not fluxional).

Displacement of one neutral organic ligand by another has been observed in a variety of related π-complexes, but we are not aware of previous examples where such exchange is accompanied by hydrogen transfer. We have shown that other arenes can be used in the present exchange reactions including some whose manganese derivatives were unavailable by other routes. Moreover the reaction proceeds, if somewhat less smoothly, with cycloheptatriene yielding the known[8] cycloheptadienyltricarbonylmanganese and may well be capable of further extension.

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