A Metal-assisted 1,5-Sigmatropic Shift

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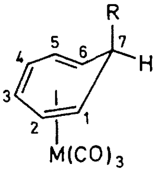
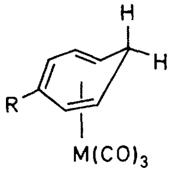
Summary The thermal rearrangement of tricarbonylmethylcycloheptatrienechromium is shown to follow a metal-assisted stereospecific pathway involving sequential 1,5-shifts of the 7-*endo*-hydrogen atom across the face of the ring adjacent to the metal atom.

THE rearrangement of cycloheptatrienes by hydrogen migration has been thoroughly studied. It was shown[1] by Büchi that the process involves a 1,5-shift and interpreted[2] by Woodward and Hoffmann as a suprafacial sigmatropic migration in terms of their rules of conservation of orbital symmetry. With such concerted rearrangements, it is known that a metal-complexed hydrocarbon may behave differently from the free ligand and it was of interest, therefore, to investigate the behaviour of cycloheptatriene–metal complexes.

Roth and Grimme had already established[3] that tricarbonylcycloheptatrienemolybdenum (I; R = H, M = Mo) does indeed undergo hydrogen migration on heating. Using a deuterium-labelled compound (I; R = D, M = Mo), they showed that it is the 7-*endo*-hydrogen (*i.e.* ψ-equatorial) which migrates in contrast with the behaviour[1] of the free ligand where migration almost certainly occurs from the 7-ψ- axial position across the concave face of the boat-shaped ring. The rearrangement of the metal complex was considered to involve initial migration of the hydrogen atom to the metal since, under their conditions, essentially complete scrambling of the deuterium label appeared to occur.



(I)



(II)

In the course of other work using complexes of this type, we have re-investigated this rearrangement. Our preliminary results confirm that only the 7-*endo*-hydrogen atom migrates. Thus the 7-*exo*-phenyl-chromium complex (I; R = Ph, M = Cr) undergoes ready thermal isomerisation whereas the 7-*endo*-phenyl isomer is unaffected up to its decomposition temperature. We have also found that the 7-*exo*-methyl-molybdenum (I; R = Me, M = Mo), the 7-*exo*-methyl-chromium (I; R = Me, M = Cr), and the 7-*exo*-phenyl-chromium (I; R = Ph, M = Cr) complexes rearrange significantly more readily than the free ligands and give cleanly, in the first instance, the corresponding 3-isomers (II; R = Me or Ph, M = Mo or Cr). In the case of the chromium complex (I; R = Me, M = Cr), kinetic studies using ^{1}H n.m.r. techniques show this rearrangement to be unimolecular, first-order, and apparently insensitive to solvent (at 91°; $k_{\mathrm{MeOH}} = 1{\cdot}2 \times 10^{-4}$ sec.$^{-1}$; $k_{\mathrm{benzene}} = 1{\cdot}3 \times 10^{-4}$ sec.$^{-1}$). The free energy of activation for the process ($\Delta G^{\ddagger} =$ *ca.* 100kJ mole^{-1}) is significantly lower than that found[4] for the free ligand.

The ease of this rearrangement must be taken as evidence of participation of the metal orbitals. The initial formation of a single isomer, however, indicates a concerted process which does not involve a discrete metal-hydride species since this intermediate would be expected to afford an equilibrium mixture of products. Such a mixture is indeed formed under more vigorous conditions which permit rapid and repeated rearrangement as was shown by further heating of the 3-methyl-chromium complex (II; R = Me, M = Cr) at 150°. No evidence was found for the presence of the 7-*endo*-methyl isomer in this equilibrium mixture. Since the corresponding 7-*exo*-methyl isomer (I; R = Me, M = Cr) was detected as a minor constituent, migration of the 7-*endo*-hydrogen atom across the side of the ring adjacent to the metal is the favoured process. In the free ligand, which is less flattened,[5] a similar migration of the 7-ψ-equatorial hydrogen atom can probably be excluded because of unfavourable geometry. The use of benzene as solvent in the last experiment did not result in formation of tricarbonylbenzenechromium, showing that a ligand-exchange mechanism is not involved.

We conclude that the rearrangements (I $\rightleftharpoons$ II) described are examples of a metal-assisted 1,5-sigmatropic shift. In these cases, involvement of the metal atom does not appear to alter the orbital symmetry requirements of the process relative to the uncomplexed ligand.

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