# The Mechanisms of the Reactions of Dewar Hexamethylbenzene with Rhodium and Iridium Chlorides

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WE have reported that Dewar hexamethylbenzene {hexamethylbicyclo[2,2,0]hexadiene (I)}[1] reacted with (a) $RhCl_3,3H_2O$ in methanol,[2] and (b) potassium chloroplatinate and HCl in methanol containing some stannous chloride,[3] to give cyclopentadienyl- and cyclopentadiene-metal complexes respectively, in high yields. In both cases the only other product (apart from hexamethylbenzene) was 1,1-dimethoxyethane, isolated by preparative v.p.c. and identified by its $^1H$ n.m.r. and mass spectra.

$RhCl_3,3H_2O$ also reacted with (I) under heterogeneous conditions in water at 90° to give pentamethylcyclopentadienylrhodium chloride dimer (II) (25%); acetaldehyde was the only other organic product. Methanol is therefore not acting as a reducing agent and it is unlikely that a lower valency state of rhodium or a rhodium hydride is involved in the reaction.

Iridium trichloride hydrate also reacted with (I) in methanol at 65°. In this case, however, the Dewar benzene was largely isomerized to hexamethylbenzene; only a small amount (*ca.* 10% based on iridium) of pentamethylcyclopentadienyliridium chloride dimer (III)† was obtained.

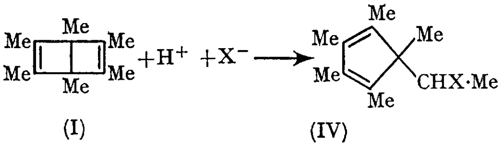
The considerations outlined in the previous Communication led us to conclude that all these reactions involved a common first step in which the Dewar benzene (I) was converted by acid into a substituted ethylpentamethylcyclopentadiene (IV; X = Cl or more probably, OMe or OH). This then reacted with the metal halide to give the pentamethylcyclopentadiene- or pentamethylcyclopentadienyl-metal complexes. The transformation of (I) to (IV; X = Cl or OMe) has recently been reported by Paquette and Krow.[3] We have repeated these preparations and found that (IV; X = Cl or OMe) reacted readily with $RhCl_3,3H_2O$ and $IrCl_3,5H_2O$ to give (II) and (III) in high yield.‡ In both cases 1,1-dimethoxyethane was the only other organic product.

The acid needed to convert (I) into (IV) in the reactions, which started from (I), presumably arises from ionisation of the metal chloride hydrates:

$$MCl_3,x(H_2O) \rightleftharpoons [MCl_3(x-1)H_2O,OH]^- + H^+$$

Aqueous solutions (0·01M) of the rhodium and iridium chlorides (Johnson, Matthey, and Mallory) had pH's of 2·7 and 2·9 respectively.

We therefore propose the following mechanism for the synthesis of (II) and (III) from (I) or (IV) in methanol:



(I) (IV)

$$(IV; X = Cl) + OMe^- \xrightarrow{M^{III}} (IV; X = OMe) + Cl^-$$

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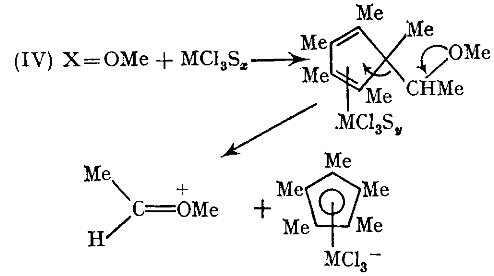
† Identified by analysis, $^1H$ n.m.r. spectrum, and its reactions.

‡ For example, an 85% yield of (III) was obtained from (IV; X = Cl) and $IrCl_3,5H_2O$ in methanol at 65°. $RhCl_3,3H_2O$ reacted significantly faster than $IrCl_3,5H_2O$, and the reaction with (IV; X = Cl) was faster than that with (I).



$$2\ C_5Me_5MCl_3^- \longrightarrow (C_5Me_5MCl_2)_2 + 2Cl^-$$

(II; M = Rh)
(III; M = Ir)

$$MeCH = \overset{+}{O}Me + MeOH \longrightarrow MeCH(OMe)_2 + H^+$$

The driving force for the reaction, *i.e.* for cleavage of the C–C bond, is presumably the great stability of the pentamethylcyclopentadienyl–metal complexes. The reactions in water and those of (I) or (IV) with potassium chloroplatinate can be explained analogously.

Not all metals which form stable cyclopentadienyl complexes react in this way however. For example, reaction of (IV; X = Cl) with $Fe(CO)_5$ in iso-octane yielded only hexamethylbenzene and ferrous chloride. This represents a hitherto unknown ring-expansion reaction.

We thank the National Research Council, the Petroleum Research Fund, and the Alfred P. Sloan Foundation for supporting this work.

(*Received, August 5th,* 1968; *Com.* 1070.)

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