Tetrahedron Letters No.39, 3533-3535, 1965. Pergamon Press Ltd.
Printed in Great Britain.

THE ISOMERISATION OF CYCLO-OCTADIENES CATALYSED BY RHODIUM, IRIDIUM AND PLATINUM COMPLEXES

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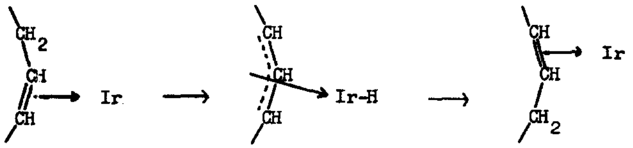
(Received 7 August 1965)

Chatt and Venanzi (1) showed that rhodium trichloride reacted with cyclo-octa-1,5-diene in ethanol to give the bridged chloro cyclo-octa-1,5-diene rhodium(I) complex $[RhCl(C_8H_{12})]_2$, the structure of which has been confirmed by X-rays (2). Rinehart and Lasky (3) have since shown that cyclo-octa-1,3-diene reacts with rhodium trichloride in ethanol to give the same cyclo-octa-1,5-diene complex $[RhCl(C_8H_{12})]_2$ but could detect no cyclo-octa-1,4-diene and postulated a slightly obscure mechanism not involving cyclo-octa-1,4-diene or its complex as intermediate. We now find that using the conditions given by Chatt and Venanzi (1) for the preparation of $[RhCl(C_8H_{12})]_2$ from cyclo-octa-1,5-diene and rhodium trichloride all the uncomplexed olefin is converted to the 1,3-isomer and much cyclo-octa-1,4-diene is formed as an intermediate (up to ca. 35% of total diene present). The isomerisation of 1,5-C_8H_{12} to 1,3-C_8H_{12} must occur before the conversion of all the rhodium to the complex $[RhCl(C_8H_{12})]_2$, which we have found to be a very poor catalyst e.g. a 10^{-2}M solution in boiling ethanol containing 40% $^v/v$ 1,5-C_8H_{12} caused negligible isomerisation after 90 min. We have found that in the reaction of chloroiridic acid with 1,5-C_8H_{12} to give $[IrHCl_2(C_8H_{12})]_2$ (4) all the uncomplexed olefin is converted into 1,3-C_8H_{12}.

We have also found that tertiary phosphine complexes are very good catalysts for the isomerisation of 1,5-$C_8H_{12} \longrightarrow$ 1,3-C_8H_{12} e.g. a 10^{-2}M solution of the yellow hydro complex $[IrHCl_2(PEt_2Ph)_3]$ in cyclo-octa-1,5-diene at 130° gives 50% conversion to the 1,3-isomer and ca. 30% to the 1,4- isomer after 22 min. and 90% conversion to the 1,3-isomer after 120 min. The corresponding trichloro complex $[IrCl_3(PEt_2Ph)_3]$ is approximately five times less efficient. Both isomerisations are completely inhibited by the presence of the free diethylphenylphosphine, at 5 x 10^{-2}M concentration, suggesting that olefin (1,5-C_8H_{12}) coordinates to the metal with displacement of free phosphine to set up the following equilibrium.

$$[IrCl_3(PEt_2Ph)_3] + C_8H_{12} \rightleftharpoons [IrCl_3(PEt_2Ph)_2C_8H_{12}] + PEt_2Ph$$

Isomerisation then proceeds and for this we favour a step-wise π-allylic hydro mechanism



Catalyst efficiency is in the order $[IrHCl_2(PEt_2Ph)_3] > [IrCl_3(PEt_3)_3] > [IrCl_3(PEt_2Ph)_3] > [IrCl_3(PMe_2Ph)_3]$ opposite to the probable order of increasing affinity of the phosphine ligands (5). $[RhCl_3(PEt_2Ph)_3]$ is also a very good catalyst but trans-$[PtHCl(PEt_3)_2]$ and trans-$[PdI_2(PMe_2Ph)_2]$ are relatively poor catalysts. The catalysts can be recovered from the product (1,3-C_8H_{12}) in high yield. Dr. R.S. Coffey first observed the isomerisation of olefins by tertiary phosphine-metal complexes and we are grateful to him for valuable discussion. We are also very grateful to I.C.I. Ltd. (H.O.C. Division) for financial support.

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