π-Cyclo-octenyl-rhodium and -iridium Complexes as Intermediates in the Isomerisations of Cyclo-octadienes

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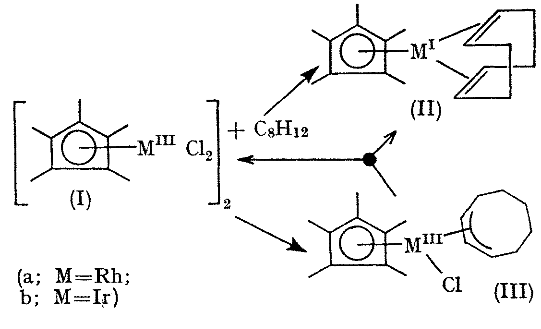
Summary Cyclo-octa-1,3-, -1,4-, and -1,5-dienes react with $(C_5Me_5MCl_2)_2$ to give $C_5Me_5M(1,5\text{-}C_8H_{12})$ *via* a π-cyclo-octenyl complex, $C_5Me_5M(C_8H_{13})Cl$, isomerisation of uncomplexed diene occurring concurrently with the second step.

THE metal complex-catalysed isomerisations of cyclo-octadienes have been the subjects of considerable work and speculation over the last eight years.[1–5] A stepwise mechanism by which the 1,3- is isomerised to the 1,5-isomer (or *vice-versa*) *via* the cyclo-octa-1,4-diene appears popular.[3,5]

We have been investigating the reactions of pentamethylcyclopentadienyl-rhodium and -iridium dichloride complexes, (I), with a number of olefins and dienes.[6–9] These systems often allow the isolation of intermediates, and have a very simple stereochemistry which makes them amenable to more detailed study. The complexes (I) are also well characterised crystalline solids, which makes them more attractive starting materials than the metal "trihalides" which have been so widely used in these types of reactions. Preliminary results on the reactions with cyclo-octadienes, which we present here, show that a π-cyclo-octenyl complex is an intermediate, and that cyclo-octa-1,4-diene (except when used as starting material) is not involved in most of these isomerisation and complexation reactions.

The complexes (I) reacted ($EtOH–Na_2CO_3$; 50—70°; 3—6 hr.) with cyclo-octa-1,3-, -1,4-, and -1,5-dienes to give the (cyclo-octa-1,5-diene)(pentamethylcyclopentadienyl)-rhodium and -iridium complexes (II).† Acetaldehyde (and/or diethylacetal) was always found; in addition, in the rhodium reactions, some isomerisation, 1,5- and 1,4- to 1,3- (but not otherwise) of the diene remaining in solution occurred. A small amount of cyclo-octene was also usually detected. Little isomerisation was detected in any of the iridium reactions.

Under milder conditions ($EtOH–Na_2CO_3$; 20—40°; 1—2 hr.), however, *all three* dienes‡ reacted with (Ia) and (Ib) to give the identical complexes, identified as chloro-(π-cyclo-octen-3-yl)-(pentamethylcyclopentadienyl)-rhodium (IIIa), and -iridium (IIIb),† respectively. Even with the 1,4-diene, there was virtually no isomerisation of the excess of diene but acetaldehyde (and/or diethylacetal) was invariably found.



We therefore conclude that the cyclo-octenyl complexes (III) are intermediates in the formation of (II). The process by which this latter transformation occurs is surprisingly complex; the obvious route, involving an

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† All new complexes described were completely characterised by analysis and spectroscopically. Yields were virtually quantitative.

‡ The reaction of $1,4\text{-}C_8H_{12}$ with (Ib) was, however, not studied.

isomerisation and loss of HCl, only occurs to a very small extent (if at all, under our conditions) for the rhodium complex (IIIa). It is probably more significant for the iridium complex (IIIb) in some cases.

The complex (IIIb) decomposed smoothly *in vacuo* at 95° to give approximately equal amounts of starting material, (Ib), and (IIb), together with some cyclo-octene. In solution, in the presence of base, more (IIb) [and less (Ib)], was obtained and in EtOH–Na_2CO_3 (IIb) was the only product.

The rhodium complex (IIIa) decomposed *in vacuo* to give (Ia), (IIa), cyclo-octene, and also some cyclo-octa-1,3-diene. In the absence of added diene, very similar results were obtained in solution, except that the organic products frequently contained more 1,3-C_8H_{12} than cyclo-octene [*e.g.*, in benzene at 80°, with or without Et_3N, approximately equal amounts of (Ia), (IIa), and *ca.* 30% 1,3-C_8H_{12} and 17% C_8H_{14} were found].

In ethanol, in the presence of 1,5-C_8H_{12}, (IIIa) decomposed in the same way. However, on addition of Na_2CO_3, quantitative conversion into (IIa), accompanied by substantial isomerisation of 1,5- to 1,3-C_8H_{12}, was observed.

The cyclo-octadiene complex (IIa) did itself catalyse the decomposition of 1,5-C_8H_{12} (to cyclo-octene, 1,3- and 1,4-C_8H_{12}), but this catalysis was very slow and we conclude that this complex was not responsible for the reactions described above.

It is evident that a possible path for the formation of (II) from (I) in the presence of an excess of diene is the cyclic one:

$$\text{(I)} + C_8H_{12} \rightarrow \text{(III)}$$
$$2\,\text{(III)} \rightarrow \text{(I)} + \text{(II)}$$

These results (i) suggest that olefin isomerisation reactions are extremely complex and that several reaction paths can coexist under a given set of conditions, and (ii) show that, in some cases at least, π-allylic complexes are intermediates.

Full details of this work and some mechanistic suggestions will be reported shortly.

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