Rearrangement of Co-ordinated Cyclo-octadienes in Palladium(II) and Platinum(II) Complexes

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Summary Cyclo-octa-1,3-diene reacts with dichlorobis(benzonitrile)palladium(II) to give a mixture of dichlorocyclo-octa-1,5-dienepalladium(II) and dichlorocyclo-octa-1,4-dienepalladium(II), whereas with Pt^{II} only the cyclo-octa-1,5-diene complex is obtained: evidence for the formation of cyclo-octa-1,4-diene during the rearrangement of cyclo-octa-1,3-diene to cyclo-octa-1,5-diene in the palladium system is presented.

CYCLO-OCTA-1,5-DIENE isomerises to the 1,3-diene *via* the 1,4-diene in the presence of a mixture of palladium(II) or platinum(II) complexes and tin(II) chloride.[1] The reverse rearrangement, namely, the isomerisation of cyclo-octa-1,3-diene to the 1,5-diene has been observed in rhodium(I) systems[2] and in palladium(II) and platinum(II) complexes.[3] The failure to detect cyclo-octa-1,4-diene among the decomposition products of the metal–olefin complexes led to the suggestion[2,3] that a step-wise mechanism for the isomerisation of cyclo-octa-1,3-diene to the 1,5-diene is not operative. More recently evidence was given for the formation of a π-cyclo-octenyl complex as an intermediate in the isomerisation of cyclo-octa-1,3-diene in iridium(I) system.[4] But, it is reported[4] that, in the iridium(I) system too, cyclo-octa-1,4-diene is not involved in any of the isomerisation steps, except when used as a starting material.

We report that cyclo-octa-1,4-diene is formed as an intermediate in the rearrangement of cyclo-octa-1,3-diene to the 1,5-diene in palladium(II) systems. The reaction of cyclo-octa-1,3-diene with dichlorobis(benzonitrile)palladium(II), $PdCl_2(PhCN)_2$, (I) in benzene solution or without a solvent yielded a product, which upon treatment with aqueous KCN and extraction of the organic layer with petroleum ether gave a mixture of cyclo-octa-1,5-diene and cyclo-octa-1,4-diene. The n.m.r. spectrum of dichlorocyclo-octadienepalladium(II) obtained from the reaction of (I) with cyclo-octa-1,3-diene consisted of a spectrum similar to that of cyclo-octa-1,5-diene superimposed on a spectrum similar to that of the 1,4-diene.† This also suggests that, like cyclo-octa-1,5-diene, the steric arrangement of the 1,4-diene is little affected by co-ordination.

The ratio of the 1,5- to the 1-4-diene in dichlorocyclo-octadienepalladium(II) varied according to (i) the time of stirring of the reaction medium and, (ii) the amount of cyclo-octa-1,3-diene used in the reaction. When a large excess of 1,3-diene was used in benzene solution [25 ml of 1,3-diene with a solution of 1·0 g of (I) in 20 ml benzene] the ratio of 1,5- to 1,4-diene in the decomposition product was 10 : 1. The same ratio was obtained when an excess of cyclo-octa-1,3-diene was treated with (I) without a solvent. When 20 ml of the 1,3-diene were used with 4·0 g of (I) in benzene solution, the ratio of 1,5- to 1,4-diene in the decomposition product was 2 : 3. Stirring the diene complex in which the ratio of 1,5- to 1,4-diene was 2 : 3 in a mixture of 1,3-diene and benzene for 2 h gave a complex involving a 1 : 1 mixture of 1,5- and 1,4-diene.

The reaction of cyclo-octa-1,3-diene with K_2PtCl_4 or K_2PtCl_6 in the presence of a reducing agent gave a platinum–olefin complex which, when decomposed by KCN, gave the 1,5-diene exclusively. This result agrees with the findings of other investigators.[3]

We believe that cyclo-octa-1,4-diene is involved in the rearrangement of the 1,3- to the 1,5-diene. The fact that it was not detected in the platinum–olefin system does not necessarily imply that it was not formed during the reaction. It is possible that cyclo-octa-1,4-diene is formed in the platinum system but rearranges to the 1,5-diene very quickly.

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† The n.m.r. spectrum and other physical properties of cyclo-octa-1,4-diene along with methods of its preparation will be the subject of a forthcoming publication.

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