Oxidative Addition of Quadricyclene to Di-μ-chlorotetracarbonyldirhodium(I) and the Mechanism of the Rhodium(I)-catalysed Isomerization of Quadricyclene to Norbornadiene

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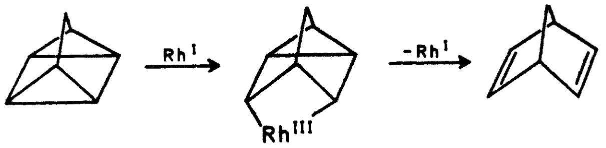
Summary Several new organorhodium compounds derived from the reaction of quadricyclene with di-μ-chlorotetracarbonyldirhodium(I) are described; it is concluded that the rhodium(I)-catalysed valence isomerization of quadricyclene to norbornadiene proceeds through a non-concerted mechanism involving an oxidative addition step.

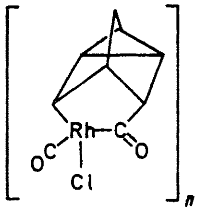
CONSIDERABLE interest has recently been evidenced in the catalysis by transition-metal compounds of reactions such as cyclobutane–diolefin transformations which are "thermally forbidden" according to the Woodward–Hoffmann rules of orbital symmetry conservation.[1] Examples include the rhodium(I)-catalysed valence isomerizations of quadricyclene to norbornadiene;[2] hexamethylprismane to hexamethyl-"Dewar-benzene";[3] cubane to *syn*-tricyclo-octadiene and of the latter to cyclo-octatetraene;[4] as well as several silver(I)-catalysed reactions.[5–7] Two alternative interpretations have been suggested for such catalysis, namely (1) removal of the symmetry constraints on the otherwise-"forbidden" concerted pathway, by interaction with appropriate *d*-orbitals of the catalyst,[5,8] or (2) opening up of a non-concerted reaction pathway involving the initial breaking of only one carbon–carbon bond through an "oxidative-addition" mechanism.[4,9]



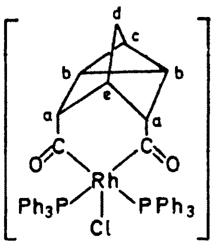
(I) (II) (III)

We have recently demonstrated that the rhodium(I)-catalysed transformation of cubane to *syn*-tricyclo-octadiene proceeds through a mechanism of the latter type[4] and, we now present evidence which favours a similar mechanism [(I) → (II) → (III)] for the valence isomerization of quadricyclene (I) to norbornadiene (III). The valence isomerization of quadricyclene is of special interest in this context since it has been used as a model reaction in several studies of the catalytic phenomena under consideration.[2,10] In addition, we describe several new compounds derived from the reaction of quadricyclene with $Rh_2(CO)_4Cl_2$.

The addition of an excess‡ of quadricyclene to a cyclohexane solution of $Rh_2(CO)_4Cl_2$ (*ca.* $1·5 \times 10^{-3}$ M) resulted in a stoicheiometric reaction marked by the disappearance over a period of 20 min. at room temperature of the yellow colour of the initial rhodium complex. Partial evaporation of the solution, followed by addition of petroleum resulted in the precipitation of a white product (80% yield) which, on the basis of its elemental analysis and its i.r. spectrum in CCl_4 (strong bands at 2070 and 1750 cm^{-1}, assigned to terminal and acyl carbonyls, respectively) is assigned the structure (IV). This compound presumably arises from oxidative addition of quadricyclene to the rhodinm to give an initial adduct analogous to (II) which undergoes the familiar "CO insertion" rearrangement to the acyl compound, (IV). Analogous acylrhodium adducts have been obtained from the reactions of cyclopropane[11] and of cubane[4] with $Rh_2(CO)_4Cl_2$. Although the molecular weight has not been established it seems likely, by analogy with the latter adducts, and because of the preference of rhodium(III) for co-ordination numbers greater than four, that (IV) has a Cl-bridged polymeric structure.



(IV)



(V)

The compound (IV) undergoes a rapid stoicheiometric reaction with triphenylphosphine in chloroform solution to yield a compound (m.p. 175° dec.) which, on the basis of elemental analysis, i.r. spectrum [bands at 1680 (m), 1615 (s), and 1590 (w) cm^{-1} in $CHCl_3$], and ^1H n.m.r. spectrum [δ_a, 0·8—1·5; δ_b,δ_c, 0·0—0·6 (unresolved); δ_d, 2·15; δ_e, 0·83; δ (PPh_3), 7·0—7·9 p.p.m.] is assigned the structure (V). Recrystallization of this compound from methylene chloride–petroleum in the presence of an excess of triphenylphosphine yielded well-formed yellow crystals of the composition $(V)_2$, CH_2Cl_2 which are at present being subjected to single crystal *X*-ray structure analysis.

When the reaction between quadricyclene and $Rh_2(CO)_4Cl_2$ in cyclohexane was carried out under an atmosphere of carbon monoxide the reaction was accompanied by the absorption of approximately one mole of CO per mole of Rh (one-half of which was taken up in the first hour and the rest much more slowly over a period of about 20 hr.). Partial evaporation of the solution yielded a white precipitate which was washed with petroleum and dried under vacuum (80% yield, m.p. 180° dec.). The i.r. spectrum of this product in CCl_4 solution exhibited both terminal (2070 cm^{-1}) and acyl [1690 (vs), 1700 (sh), 1725 (sh)]

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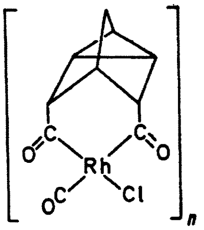
‡ A slight excess is necessary since the reaction with $Rh_2(CO)_4Cl_2$ is accompanied by some loss of quadricyclene through isomerization to norbornadiene, especially if the quadricyclene is initially contaminated by norbornadiene. The presence of the latter promotes the formation of $Rh_2(norbornadiene)_2Cl_2$ which is a powerful catalyst for the isomerization reaction.

carbonyl bands, consistent with the structure (VI). Treatment of (VI) in $CHCl_3$ solution with an excess of triphenylphosphine yielded, as expected, the compound (V).



(VI)

As reported previously, the isomerization of quadricyclene to norbornadiene (I → III) is catalysed by Rh_2(norbornadiene)$_2Cl_2$.[2] Kinetic measurements at 40°, using n.m.r. to follow the reactions, yielded the second-order rate-law, $-d[\text{quadricyclene}]/dt = k[\text{quadricyclene}][Rh_2(\text{norbornadiene})_2Cl_2]$ with $k = 2{\cdot}2 \pm 0{\cdot}2\ \text{M}^{-1}\ \text{sec}^{-1}$ in $CHCl_3$ ($1{\cdot}8\ \text{M}^{-1}\ \text{sec}^{-1}$ in CCl_4). The rate was unaffected by the addition of an excess of norbornadiene, demonstrating that reversible displacement of the norbornadiene ligand from the catalyst by quadricyclene is not a feature of the mechanism. In view of the demonstrated oxidative addition of quadricyclene to the closely related complex, $Rh_2(CO)_4Cl_2$, and by analogy with the recently elucidated mechanism of the corresponding rearrangement of cubane to *syn*-tricyclooctadiene,[4] we consider it highly likely that the Rh_2(norbornadiene)$_2Cl_2$-catalysed isomerization of quadricyclene to norbornadiene proceeds through the non-concerted mechanism, depicted above, involving a rate-determining oxidative addition step. The apparent catalytic activities of compounds (V) and (VI) for the isomerization of quadricyclene were much lower (< 5%) than that of Rh_2(norbornadiene)$_2Cl_2$ and may well be due to small amounts of the latter formed by reaction with quadricyclene.

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