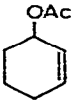
The mechanism of the reaction of nucleophiles with alicyclic olefin palladium complexes

An important industrial process for the direct conversion of ethylene into acetaldehyde involves[1] the reaction:

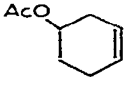
$$C_2H_4 + PdCl_2 + H_2O \longrightarrow CH_3\cdot CHO + Pd(O) + 2HCl$$

Related oxidation–reduction reactions have been observed with other nucleophiles; for example, acyclic olefin–palladium(II) complexes react with alcohols[2] to form acetals and vinyl ethers, and with sodium acetate in acetic acid[3] or with acetic acid and disodium hydrogen phosphate[4] to yield vinyl acetates.

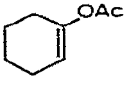
We now report that the palladium dichloride catalysed reaction of cyclohexene with sodium acetate in acetic acid at 20° in the presence of benzoquinone gives cyclohex-2-enyl acetate [I; 76 %] and cyclohex-3-enyl acetate [II; 24 %] (yields based on olefin converted into products) rather than the expected cyclohex-1-enyl acetate III.



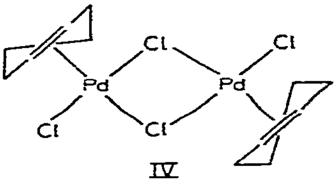
I



II



III



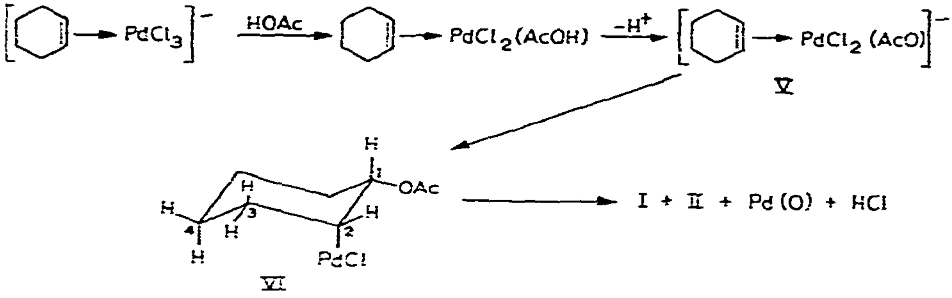
IV

With cupric chloride as oxidant at 20° the yields of I and II were 73 % and 27 %, suggesting that the product ratio is not influenced by the method of conversion of Pd(O) into Pd(II).

Control experiments showed that the compounds I–III were not isomerized under the conditions used. Similarly, the π-allylic complex di-μ-chloro-bis(cyclohexenyl)dipalladium(II), initially considered as a possible precursor of the acetates I and II, was unchanged on treatment with sodium acetate in glacial acetic acid under the conditions used.

The acetates I and II were obtained in 9 % and 40 % yields respectively from the room temperature reaction of di-μ-chlorodichlorobis(cyclohexene)dipalladium(II) IV with sodium acetate in glacial acetic acid; benzene (14 %), cyclohexane (25 %), phenylacetate (< 2 %), and cyclohexyl acetate (10 %) were also formed by palladium metal catalysed disproportionation. The marked change in the ratio of I:II should be noted.

Several mechanisms can be suggested for the previously reported reactions of olefin—palladium(II) complexes with nucleophiles, but there is little evidence available to distinguish one unambiguously from another, and more particularly to enable a general mechanistic interpretation to be derived which can enable useful predictions to be made and tested, as distinct from the rationalisation of experimental observations. The present work has established the unexpected absence of the vinylic acetate III, and this interesting difference in the type of product obtained from alicyclic and acyclic olefin complexes may be explained if the following assumptions are made concerning the mechanism. Firstly that chlorine on palladium in the complex is replaced by acetate, secondly that nucleophilic attack by the acetate on the coordinated olefins occurs *intramolecularly* within the complex V, and thirdly that a palladium-assisted 1,2-hydride shift occurs followed by, or concurrently with, proton loss from an adjacent carbon atom; a 1,2-hydride shift has been proposed following kinetic and deuterium-labelling studies with propylene[4].



The intermediate σ-complex VI would then have the palladium and the acetate groups *cis* to each other, and in such a complex it would not be possible for the hydrogen atoms in the 1-position to interact with the palladium as a prelude to a 1,2-hydride shift. Interaction with the 3- and 4-hydrogen atoms, *cis* to the palladium, can occur, and this would lead to the formation of the acetates I and II. Experiments are in progress to establish whether the above assumptions are valid and whether the acetate II arises by a 1,2- or a 1,3-hydride shift.

Di-μ-chloro-dichlorobis(cyclopentene)dipalladium(II) similarly gives cyclopent-2-enyl acetate (39 % yield) and cyclopent-3-enyl acetate (26 % yield), and it is again noteworthy that the vinylic compound cyclopent-1-enyl acetate is absent.

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