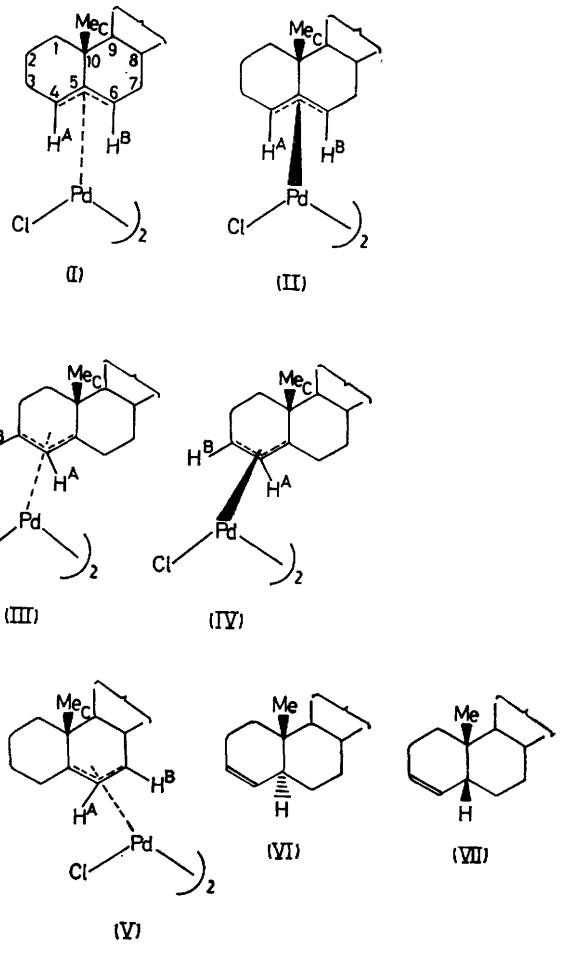
Stereochemistry of Formation and Reduction of π-Allyl Palladium Chloride Complexes from Steroidal Olefins

By D. NEVILLE JONES* and SIMON D. KNOX
(*The Chemistry Department, The University, Sheffield* S3 7HF)

Summary The regioselectivity and stereoselectivity of palladium π-allyl chloride complex formation from steroidal olefins was apparently controlled by steric effects, and both cholest-4-ene and cholest-5-ene gave diastereoisomeric complexes; two of the complexes were reduced to olefins by lithium aluminium hydride stereospecifically with retention of configuration.

PALLADIUM π-allyl complexes are potentially important synthetic intermediates,[1] but the paucity of information about the regioselectivity of the formation and reactions of complexes derived from cyclic olefins,[2] and nescience of the stereoselectivity of these processes has limited their exploitation. Until recently,[2] investigations have been hampered by difficulties in preparing complexes from cyclic olefins.[3]

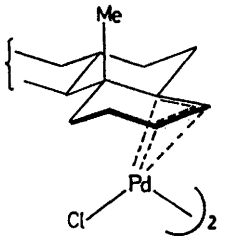
Treatment with bis(benzonitrile)palladium dichloride (1 equiv.) in boiling chloroform for 24—48 h (conditions A) provided a mild and efficient method for converting steroidal olefins into palladium π-allyl complexes. The presence of inorganic bases, added as catalysts for reaction with acyclic olefins,[4,5] was not necessary. Cholest-4-ene gave a mixture of the α-4—6η complex (I) (46%) (τ_A and τ_B 6·24, m; τ_C 8·88, s)† and the β-4—6η complex (II) (14%) (τ_A and τ_B 6·39, m; τ_C 8·45, s), whereas cholest-5-ene gave only (I) (71%). With disodium tetrachloropalladate in acetic acid–acetic anhydride (16:1) containing sodium acetate at 50° for 96 h (conditions B) (*cf.* ref. 5) cholest-4-ene gave (I) (26%), (II) (8%), the α-3—5η-complex (III) (5%) (τ_A 4·88, d, J 6·5 Hz; τ_B 5·19, m, $W_{\frac{1}{2}}$ 15 Hz; τ_C 9·10, s), and the β-3—5η-complex (IV) (18%) (τ_A 4·72, d, J 6·5 Hz; τ_B 5·15, m, $W_{\frac{1}{2}}$ 15 Hz; τ_C 8·58, s), whereas cholest-5-ene gave (I) (4%), (II) (4%), and the α-5—7η-complex (V) (12%) (τ_A 4·86, d, J 7 Hz; τ_B 5·45, dd, J 7 Hz, J' 1 Hz; τ_C 9·02, s). The complexes,‡ which were yellow solids, were separated by a combination of chromatography on alumina and fractional crystallization from light petroleum. These reactions provide the first examples of the isolation of diastereoisomeric palladium π-allyl complexes formed by attack of palladium(II) on the diastereotopic faces of an olefin. 5α-Cholest-6-ene under conditions A and B gave only (V) (80% and 70% respectively), whilst 5α-cholest-3-ene (VI) gave only (III) (80%).



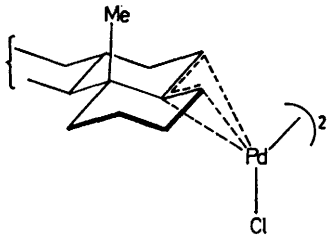
† N.m.r. data refer to solutions in $CDCl_3$.

‡ Satisfactory microanalytical data were obtained for all the complexes.

None of the complexes interconverted under the reaction conditions, indicating that they were formed under kinetic control, and they were dimeric in chloroform, according to osmometry.



(G)



(H)

Steric effects apparently are important in determining the stereochemical course of the reactions. The β-face of the olefins is more sterically hindered than the α-face,[6] and the β-face of cholest-5-ene is more hindered than that of cholest-4-ene, and accordingly cholest-4-ene furnished mostly (I) and some (II) under conditions A, whereas cholest-5-ene gave only (I). Furthermore, models of the steroidal palladium π-allyl complexes incorporating the known geometrical features of palladium π-allyl systems[7] revealed that 'endocyclic' π-allyl complexes (*e.g.* III; G) are more sterically compressed than 'exocyclic' complexes (*e.g.* I; H). The formation of (I) and (II), but not (III) and (IV) from cholest-4-ene, and the formation of (I) but not (V) from cholest-5-ene under conditions A becomes rational if the relative steric compressions in the transition states connecting π-complexes with π-allyl complexes reflect those in the products. Finally the greater regioselectivity and stereoselectivity of palladium π-allyl complex formation under conditions A than B may be attributed partly to the greater steric demands of the ligands in $[(PhCN)_2PdCl_2]$ than in $PdCl_4^-$, and in the π-complexes derived from them.

The n.m.r. characteristics of the π-allyl protons in the steroidal palladium π-allyl complexes were in accord with the structures allocated (*cf.* refs. 2,7). Assignment of α- or β-orientation to palladium followed from the greater deshielding of the 10-methyl protons in the β-isomers than in the respective α-isomers due to the closer proximity of these protons with the palladium atom in the β-isomers. Deshielding of protons by proximate palladium in π-allyl systems was hitherto unknown, although examples in other palladium complexes were recently reported.[8]

The structural allocations were substantiated by the nature of the olefins obtained on reduction of the complexes with lithium aluminium hydride. Both (I) and (II) gave a mixture of cholest-4-ene (30%) and cholest-5-ene (70%), whilst (V) gave cholest-5-ene quantitatively. The α-3—5η-complex (III) gave a mixture of cholest-4-ene (74%) and 5α-cholest-3-ene (VI) (26%), whereas the β-isomer (IV) gave cholest-4-ene (76%) and 5β-cholest-3-ene (VII) (24%), illustrating for the first time that palladium π-allyl complexes can be reduced by lithium aluminium hydride stereospecifically with retention of configuration.

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