

An Intramolecular, Four-co-ordinate, σ -Allyl Transition State in the *syn-anti* Exchange in a π -Allylpalladium Complex

By D. J. S. GUTHRIE, R. SPRATT, and S. M. NELSON*

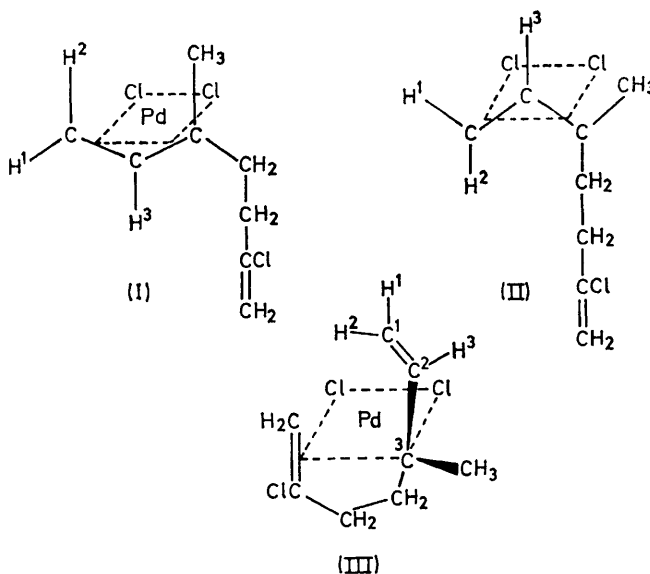
(Department of Chemistry, Queen's University, Belfast, BT9 5AG, N. Ireland)

Summary A novel instance of preferential *syn-anti* isomerisation about the substituted carbon atom of an asymmetrically substituted π -allylpalladium chloride dimer is accounted for in terms of an intramolecular, four-co-ordinate σ -allyl transition state.

SEVERAL mechanisms have been suggested for *syn-anti* isomerisation in π -allyl complexes. The currently favoured mechanism is one involving a σ -bonded intermediate which permits rotation about the adjacent carbon-carbon bond with resulting face exchange of the metal atom with respect to the π -allyl plane.¹ Rates of isomerisation are dependent on the nature of the allylic group, the nature of the other ligands, and on the presence or absence of other ligand molecules in the solutions. In particular, in the case where the allylic group is unsymmetrical it is observed that equilibration of *syn*- and *anti*-isomers always occurs at the unsubstituted (or less substituted) carbon atom.² We here report a novel instance of preferential isomerisation at the substituted carbon atom which provides strong evidence for an intramolecular four-co-ordinate σ -allyl transition state.

As prepared in benzene solution at room temperature the product of reaction of π -(2-chloroallyl)palladium chloride dimer with isoprene exists as *syn*- and *anti*-isomers (structures I and II). This is clearly shown by the 25° n.m.r. spectrum (see Figure) in an *o*-/*p*-dichlorobenzene mixture. Assignments of the proton resonances are as indicated in the Figure; they were made on the basis of established assignments in related compounds and of the expected coupling characteristics. As the temperature is raised the methyl resonances of the two isomers broaden and coalesce at 73°. An exchange rate of 60 s⁻¹ (73°) was calculated using an adapted Gutowsky programme³ for AB exchange (with $J_{AB} = 0$); this gives $\Delta G^\ddagger_3 = 17.3 \pm 0.2$ kcal mol⁻¹. The exchange is seen simultaneously in the collapse of the two multiplets (*syn* and *anti*) of the methylene group adjacent to the allyl group, and also in the broadening of the multiplet

due to the next methylene group at intermediate temperatures. The resonances of allylic protons 1, 2, and 3 remain unaltered to *ca.* 100°. Above this temperature there is



some broadening indicating the onset of exchange of protons 1 and 2. Accurate evaluation of the kinetic parameters for this exchange was not possible because of some decomposition at still higher temperatures. However, it is clear that the barrier (ΔG^\ddagger not less than 20 kcal mol⁻¹) is higher than for the first exchange.

The relatively low-barrier isomerisation about the substituted allylic carbon may be interpreted in terms of the σ -bonded intermediate (III). This structure for the intermediate fulfils two important functions: (1) co-ordination of the chloro-vinyl group allows for retention of the preferred co-ordination number of the palladium atom, and

(2) the vinyl group can remain co-ordinated *at all stages* of the rotation about the C-2-C-3 bond, thereby lowering the potential barrier. The suggested chelate intermediate is

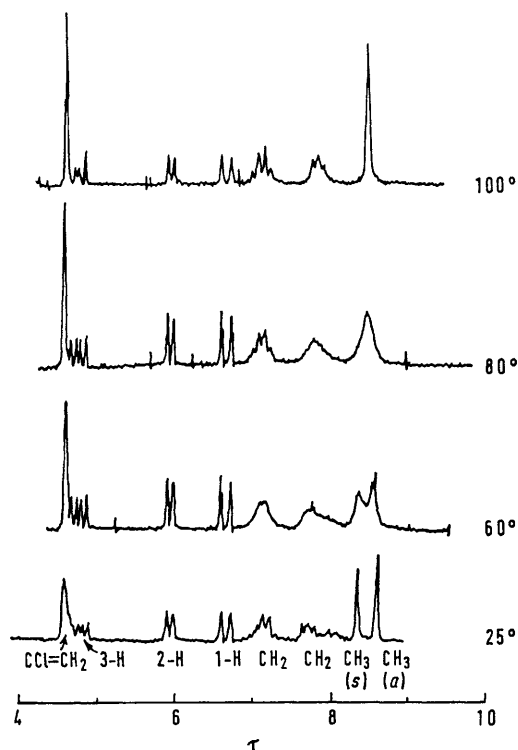


FIGURE. The *n.m.r.* spectra of the π -allylpalladium chloride dimer in an *o/p*-dichlorobenzene solvent mixture at various temperatures. (The slight broadening of the resonances at 25° is due to the low solubility of the complex in the solvent mixture at this temperature.)

¹ J. C. W. Chien and H. C. Dehm, *Chem. and Ind.*, 1961, 745; K. Vrieze, A. P. Pratt, and P. Cossee, *J. Organometallic Chem.*, 1968, 12, 533; P. W. van Leeuwen and A. P. Pratt, *Chem. Comm.*, 1970, 365; C. W. Alexander, R. Spratt, and W. R. Jackson, *J. Amer. Chem. Soc.*, 1970, 92, 4990; D. L. Tibbetts and T. L. Brown, *ibid.*, p. 3031.

² The slow isomerisation of *anti*-2-methyl-1-*t*-butyl- π -allylpalladium chloride to the *syn*-isomer, reported by J. Lukas, S. Coren, and J. E. Blom, *Chem. Comm.*, 1969, 1303, might, at first sight, seem an exception. However, there is no evidence that this is an equilibrium exchange process.

³ H. S. Gutowsky, *J. Chem. Phys.*, 1965, 42, 3396 (adapted for use on the Queen's University ICL 1907 digital computer by Dr. W. B. Jennings).

⁴ M. A. Bennett, H. W. Kouwenhoven, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 1964, 4570, and subsequent papers.

⁵ D. Medema, R. van Helden, and C. F. Kohll, *Inorg. Chim. Acta*, 1969, 3, 255; Y. Takahashi, S. Sakai, and Y. Ishii, *J. Organometallic Chem.*, 1969, 16, 177.

five-membered (considering the vinyl group as one co-ordinating centre) and may be compared with the stable (five-membered) chelates of various *o*-styryl-phosphines and -arsines, studied by Bennett *et al.*, containing one co-ordinated σ -donor (P or As) and one or more co-ordinated vinyl groups. Inspection of framework molecular models reveals that a stabilising interaction of the vinyl group with the metal atom (in a seven-membered ring) is also possible for the alternative intermediate in which the metal is σ -bonded to the unsubstituted allylic carbon atom, C-1. In this case, however, rotation about C-1-C-2 can only occur if the bond between the metal and the vinyl group is broken, *i.e.* to give a three-co-ordinate transition state. The same considerations apply to a σ -bonded intermediate involving interaction of the metal with an olefinic function localised between C-2 and C-3 or C-1 and C-2.

To date, we have also observed preferential isomerisation at the substituted allylic carbon for the insertion products of π -(1-chloroallyl)palladium chloride dimer with isoprene, π -(2-chloroallyl)palladium chloride dimer with 2-chlorobutadiene, and for the π -allyl formed by the open-chain dimerisation 2-chlorobutadiene in the presence of bis(benzonitrile)palladium(II) dichloride. All contain a terminal vinyl group in the substituent chain; preparations and properties will be described elsewhere.

These results strongly suggest that the same kind of four-co-ordinate σ -intermediate responsible for the *syn-anti*-interconversions in these compounds may also play an important role in their formation from π -allyl and diene, the difference being that in the latter case the intermediate is bimolecular.⁵

We thank the Du Pont Co. (U.K.) Ltd. for the gift of the 2-chlorobutadiene, and Dr. W. R. Jackson for helpful discussion.

(Received, March 29th, 1971; Com. 414.)