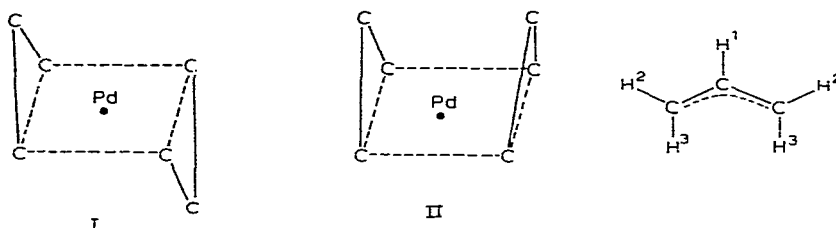


## PRELIMINARY NOTE

### Temperature dependence of the NMR spectrum of palladium bis- $\pi$ -allyl

The proton NMR spectrum<sup>1</sup> of  $\text{Pd}(\text{C}_3\text{H}_5)_2$  below  $0^\circ$  consists of two  $\text{AM}_2\text{X}_2$  patterns in the approximate ratio 3:1 and is believed to arise from an equilibrium mixture of the two forms (I) and (II). On raising the temperature of a benzene solution to  $60^\circ$  the doublets due to the *syn* and *anti* protons ( $\text{H}_2$  and  $\text{H}_3$  respectively) broaden, suggesting that these protons undergo a site exchange process. This was interpreted as an exchange between *syn* and *anti* sites occurring more rapidly in the minor than in the major component. However, acceleration of the equilibrium between forms (I) and (II) would also cause line broadening.



We have now made more detailed measurements on the line shapes, and carried out double resonance experiments, in an effort to determine which of the above exchange processes best accounts for the observed behaviour. Our results can be explained only by invoking both processes.

Line shapes were recorded under slow sweep conditions in benzene up to  $60^\circ$ ; less detailed observations were also made in chloroform up to  $20^\circ$ . Above these temperatures in the given solvents, decomposition was too rapid to permit measurements. The shapes of the two  $\text{CH}_2$  doublets were compared with theoretical line shapes for each of the alternative exchange processes, calculated from the general two-site exchange shape functions for unequal site populations in the form given by Gutowsky and Holm<sup>2</sup>, assuming the spin-lattice relaxation time  $T_1$  for the central proton of each allyl group to be sufficiently long that relaxation of this proton can be neglected compared with the other rate processes.

In benzene at temperatures up to  $30^\circ$  the experimental line shapes can be satisfactorily fitted to either exchange process; at higher temperatures the theoretically predicted line shapes diverge one from the other, the shapes for isomer equilibration giving a somewhat better fit than those for *syn-anti* exchange (see Fig. 1). The situation at these temperatures is unfortunately complicated by additional broadening due to precipitated solids resulting from the onset of decomposition.

More specific information about the exchange processes is obtained from frequency sweep double resonance experiments in which the doublet assigned to protons  $\text{H}_2$  in the major isomer ( $\tau$  5.85 in benzene) is saturated while observing the doublets in the region  $\tau$  7.3 to 7.8 (*i.e.* protons  $\text{H}_3$  in both isomers). Under these conditions any exchange between the saturated and observed proton sites at a rate

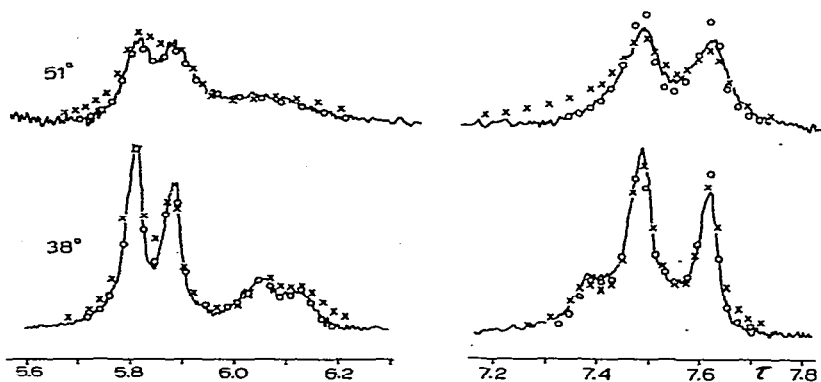


Fig. 1. Observed line shapes for the  $\text{CH}_2$  protons of  $\text{Pd}(\text{C}_3\text{H}_5)_2$  in  $\text{C}_6\text{H}_6$  at  $38^\circ$  and  $51^\circ$ , compared with theoretical line shapes for isomer equilibration (circles) and *syn-anti* exchange (crosses).

comparable with, or faster than, spin-lattice relaxation of the latter, causes a reduction in signal intensity owing to transfer of spin depolarisation<sup>3,4</sup>. The effects found at two temperatures in benzene solution are shown in Fig. 2. The reduction in intensity of the doublets proves that exchange of protons between *syn* and *anti* sites is occurring at a rate which increases with temperature. Furthermore, the fact that the major and minor doublets are both reduced by about the same factor shows that a comparatively rapid isomer interconversion ( $\text{I} \rightleftharpoons \text{II}$ ) also occurs. This is confirmed by the

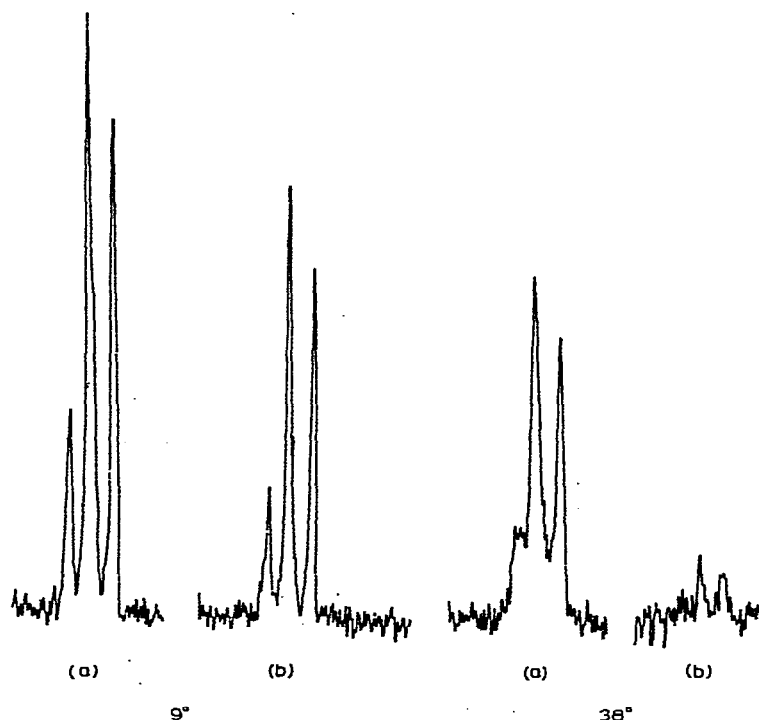


Fig. 2. Resonances of the *anti*  $\text{CH}_2$  protons of  $\text{Pd}(\text{C}_3\text{H}_5)_2$  in  $\text{C}_6\text{H}_6$ ; (a) normal, (b) with double irradiation saturating the *syn* protons at  $\tau$  5.85.

dependence of the effect on the frequency of the saturating r.f. field; the intensities of the  $H_3$  proton resonances have two distinct minima corresponding to passage of the saturating frequency through each of the two  $H_2$  doublets.

As already reported<sup>1</sup> the rates of exchange indicated by broadening of the  $CH_2$  resonances are considerably higher in chloroform than in benzene at a given temperature. The *syn-anti* proton exchange rates obtained by double resonance show a similar solvent dependence, being approximately 10 times faster in chloroform than in benzene at 15°. This solvent dependence contrasts with the situation for *syn-anti* exchange in  $Zr(C_3H_5)_4$ , in which we find the same coalescence temperature in a range of solvents ( $CFCl_3$ ,  $CDCl_3$ ,  $CH_2Cl_2$ ,  $CS_2$  and cyclopentane). Thus, although *syn-anti* exchange is observed in both these compounds, the mechanisms by which it occurs may be different.

Quantitative results on the exchange lifetimes have so far been insufficiently reproducible to determine whether the *syn-anti* exchange and isomer equilibration processes in  $Pd(C_3H_5)_2$  involve a common or different mechanisms. If they occurred by a common mechanism this would most probably involve a short lived  $\sigma$ -bonded intermediate, as proposed to explain *syn-anti* exchange found for allyl palladium complexes in the presence of basic ligands<sup>5</sup>.

Spectra were measured at 100 Mc/s on a Varian HA-100 spectrometer; line shape calculations were carried out using an English Electric KDF-9 digital computer.

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