New Methods for Studying the Mechanism of the π,σ-Reaction in Allylic Metal Complexes

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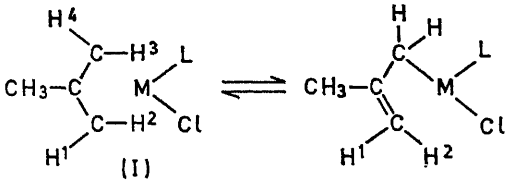
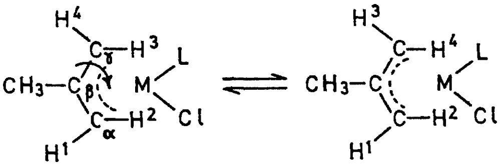
Summary The n.m.r. spectrum of the compound (π-C_4H_7)-PdCl(PPhMeMe′) reveals two simultaneous interchange reactions—interchange of the two nonequivalent methyl groups and interchange of allyl protons (3) and (4)—thus proving that the intermediate of the (3)–(4) interchange reaction contains a σ-bonded methallyl group.

IN many asymmetric π-(meth)allylpalladium complexes of the form (I) an interchange of the protons (3) and (4) is observed in the n.m.r. spectrum under certain conditions. Two mechanisms have been put forward for this interchange process:

(1) A rearrangement *via* a short-lived σ-intermediate where the γ-carbon atom [the one with protons (3) and (4)] remains bonded to the metal atom:



(2) A process involving rotation about the C–C bond with the maintenance of two metal–carbon (α,β) bonds:



Although the first mechanism, from which stems the name π–σ reaction, seems to be favoured by most investigators,[1–4] the second mechanism was claimed[5] to be supported by the n.m.r. parameters for the rearrangements in Zr(allyl)$_4$. But then, similar behaviour was found[6] for methyl-substituted allyl complexes, and here a C–C rotation would be very difficult for steric reasons. In short, the supporting evidence for either mechanism is not very well defined.

At first sight the net effect would seem to be the same in both cases. There is, however, a marked difference between the two mechanisms. In both cases it is assumed that the γ- and α-carbon atoms retain their positions with respect to L and Cl. But in mechanism (2) the configuration of the γ-carbon atom is changed, and the configuration of the other carbon atoms is retained, while in the first mechanism the reverse holds. This can easily be checked by looking along the metal–carbon bond. As a result of mechanism (2) it will be found here that the allyl plane does not change its orientation with respect to the square-plane of the molecule (dihedral angle about 120°) during the C–C rotation. As a result of the π–σ reaction, on the other hand, the allyl plane ends up in a position which is a mirror image of its original position, with the square-plane as the mirror plane. It thus seems that the π-bond is loosened and after a rotation around the σ-bonds of the γ-carbon is re-attached by its other lobes.

Consider, for example, the allyl compound with M = Pd and L = PMe$_2$Ph. The free ligand here has a plane of symmetry, but once the ligand is attached to the palladium complex the plane of symmetry disappears and hence the two methyl groups are nonequivalent. (This can be compared with ethyl groups in organic molecules where there is no mirror plane coinciding with the plane of symmetry of the ethyl group, thus leading to an ABC$_3$ system.) In the n.m.r. spectrum, therefore, two methyl peaks should occur irrespective of any rotation of the phosphine. However, when by some mechanism the allyl plane interconverts rapidly with its mirror image (the MLCl-plane being the mirror plane), the complex does have a plane of symmetry in a certain time-scale, and the two methyl groups become equivalent in the same time-scale, provided that the sterically most stable structure is obtained if no rotation of the phosphine should occur.

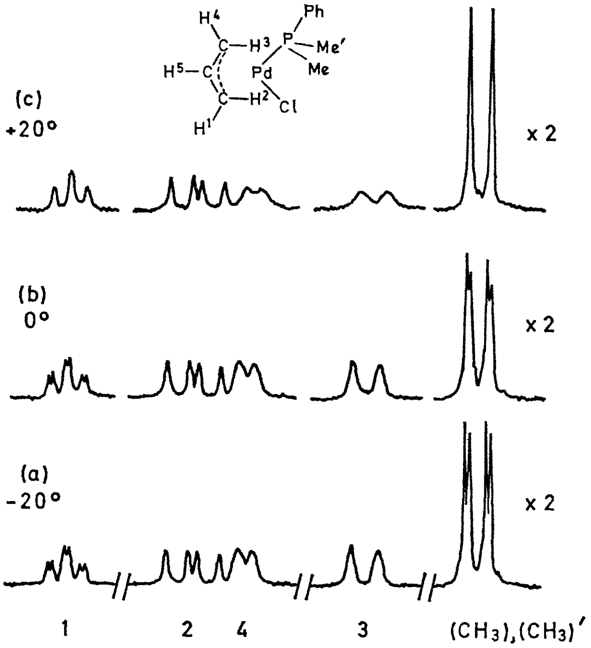


FIGURE. *The n.m.r. spectra of* (π-C_3H_5)PdCl(PMeMe′Ph) *in* CDCl$_3$ *with small amounts of parent dimer. The resonances of the methyl peaks and of protons* (1)—(4) *are shown.* $J[\text{P-H}(2)] = 10$ *Hz*; $\frac{1}{2}\{J[\text{P-H}(1)] + J[\text{H}(5)\text{-H}(1)]\} = 7$ *Hz*; $J[\text{H}(5)\text{-H}(4)] = 7$ *Hz*; $J[\text{H}(5)\text{-H}(2)] = 14$ *Hz*; $J[\text{H}(5)\text{-H}(3)] = 12$ *Hz*; $J[\text{H}(1)\text{-H}(4)] = 2{\cdot}5$ *Hz*; $\frac{1}{2}\{J[\text{P-CH}_3] + J[\text{P-CH}_3']\} = 9{\cdot}2$ *Hz.*

It is well known[4,6] that a (3)–(4) interchange occurs in allylpalladium(II) chloride–phosphine compounds in the presence of dimers, and recently a possible explanation has been given[7] for this reaction. In the Figure we show the n.m.r. spectra of a monomer–dimer mixture at several temperatures, and as expected the monomer spectrum ($L = PMe_2Ph$) shows the occurrence of two nonequivalent methyl groups [both split by a phosphorus coupling J ($P-CH_3$) 9 Hz], the difference in chemical shifts being about 2Hz (at 100 MHz). At −20° [Figure, (a)] no broadening is observed on the signals of protons (1), (3), and (4), or of the methyl groups. On all the signals a coupling due to the allylic proton is observable, and on proton (1) a small coupling (2·5 Hz) is observed due to proton (4); but when an exchange between (3) and (4) sets in, this latter coupling partly disappears even before a definite broadening of (3) and (4) is observed. In (b) and (c) the spectra at 0° and +20° are shown and it is seen that at these temperatures a π–σ reaction occurs at rates of 2 and 10 sec^{-1}. Synchronously with this process the methyl groups of the phosphine become equivalent, but evidently no ligand exchange takes place since the P-doublet of proton (2) remains very sharp even above 20°. This observation leads to the conclusion that simultaneously with the (3)–(4) exchange the absolute configuration of the β and α carbons is changed, *i.e.* after a (3)–(4) interchange the allyl plane is inverted with respect to the Pd–P–Cl plane, which definitely rules out the C–C rotation[5] mechanism in allylpalladium compounds.

The behaviour of methallyl and allyl complexes was found to be analogous, with the added advantage that since the couplings of (3) and (4) with the allylic proton are different the exchange at low rate can also be observed in the pattern of the latter proton. The nonequivalence of the methyl groups was not found when $PMePh_2$ was used, as was to be expected.

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