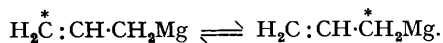


## Intermediates in the Conversion of $\pi$ - into $\sigma$ -Allylic Palladium(II) Complexes

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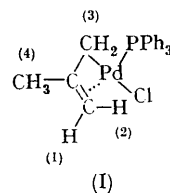
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CHIEN and DEHM found, by nuclear magnetic resonance spectroscopy, that bridged  $\pi$ -allylic chloropalladium(II) complexes of the type  $[\text{Pd}_2\text{Cl}_2(\text{all})_2]$  (all = allylic ligand) in dimethyl sulphoxide solution were converted by the solvent into  $\sigma$ -allylic complexes.<sup>1</sup> The spectra were similar to those of allylic Grignard reagents in which the allylic ligand is believed to undergo rapid exchange;<sup>2</sup> *e.g.*,



We have found that some double-bonding ligands, such as triphenylphosphine, convert bridged  $\pi$ -allylic halogenopalladium(II) complexes into  $\sigma$ -allylic complexes and also form intermediate complexes. When triphenylphosphine is added, in increasing amounts, to  $\pi$ -methallylpalladium

chloride in chloroform solution the corresponding nuclear magnetic resonance spectra are as shown in Figures (I)—(VI).



The two sharp singlets obtained with a 2:1 ratio of  $\text{PPh}_3$  : Pd (Figure VI) have intensity ratios 4:3. This and the absence of magnetic coupling between the allylic protons and the phosphorus

<sup>1</sup> J. C. W. Chien and H. C. Dehm, *Chem. and Ind.*, 1961, 745.

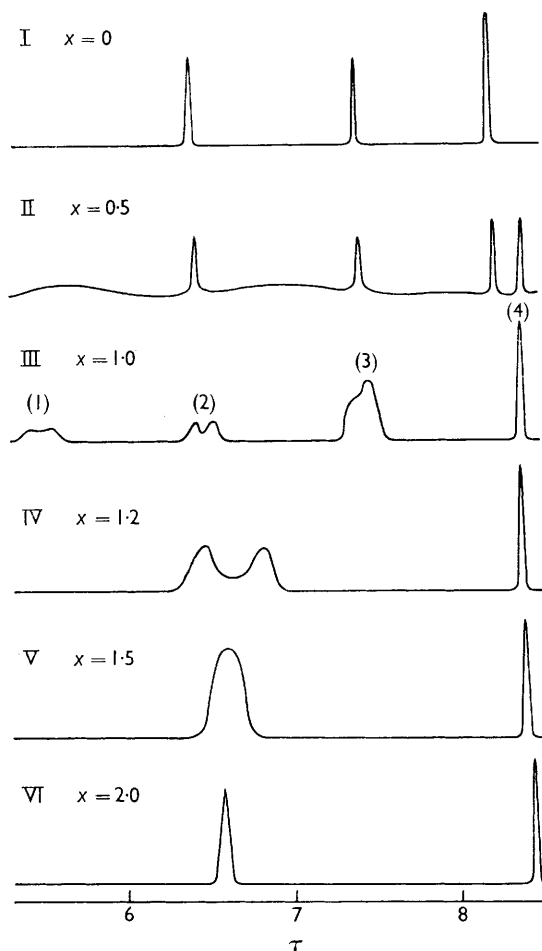
<sup>2</sup> G. M. Whitesides, J. E. Nordlander, and J. D. Roberts, *Discuss. Faraday Soc.*, 1962, **34**, 185.

indicate a  $\sigma$ -allylic ligand undergoing rapid exchange, as in allylic Grignard reagents.<sup>2</sup> The solution deposited nearly half of its palladium as dichlorobis(triphenylphosphine)palladium(II) after several hours but the nuclear magnetic resonance spectrum of the mother liquors was virtually as in Figure (VI). Presumably these mother liquors contain a bis(methallyl)palladium(II) complex, but this we have not yet isolated.

A stable crystalline monomeric complex  $[\text{PdCl}(\text{methallyl})(\text{PPh}_3)]$  was however readily isolated by treating methylpalladium chloride with triphenylphosphine (1 mole per palladium g-atom) in benzene or acetone. The nuclear magnetic resonance spectrum of this complex was as in Figure (III) with three broad doublets and a sharp singlet, intensity ratios 1:1:2:3. We suggest this compound has a structure approximating to (I), intermediate between a  $\pi$ - and a  $\sigma$ -methallyl complex with two carbon atoms only weakly bonded to the palladium. The protons numbered in (I) correspond to the numbered resonances in Figure (III). Resonances of protons (1) and (2) are split by coupling with phosphorus and protons (3) either by similar coupling or by restricted rotation. Broadening corresponds to fairly rapid position interchange of protons (1) and (2) and a slower interchange of these with protons (3). Addition of triphenylphosphine increases these interchange rates, Figures (IV)–(VI).

Chien and Dehm<sup>4</sup> reported the nuclear magnetic resonance spectrum of allylpalladium chloride in dimethyl sulphoxide to be a quintet and a doublet,  $J(\text{H-H}) = 9.8$  c./sec., but we find a quintet  $J(\text{H-H}) = 9.8$  c./sec. and a fairly broad singlet. However this singlet is separated by 8.5 c./sec. from a singlet caused by C-13 splitting of the dimethyl sulphoxide resonance and the two can give the appearance of a doublet. We suggest that in dimethyl sulphoxide solution at 33.5° the terminal hydrogens of allylpalladium chloride are not interchanging positions sufficiently rapidly to give a doublet. The resonance pattern of methallylpalladium chloride in dimethyl sulphoxide solution was very similar to Figure (IV).

The structure of the complex  $[\text{PdCl}(\text{methallyl})(\text{PPh}_3)]$  is being determined by X-rays.



*Nuclear magnetic resonance spectra of methallylpalladium chloride plus x mole of triphenylphosphine per g-atom of palladium in chloroform at 33.5°. Measured at 60 Mc./sec.*

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