

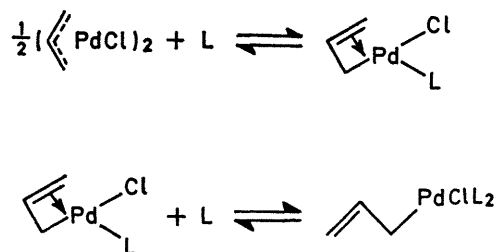
Laser Raman Study of the π - σ -Bond Conversion in π -Allylpalladium Complexes

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Summary The laser Raman spectra of π -allylpalladium chloride and its complexes with triphenylphosphine and dimethyl sulphoxide show that the co-ordination of these ligands with the Pd atom in π -allylpalladium complexes does not cause the conversion of the π -allyl group to the asymmetric of σ -bonded form, but that only a cleavage of the bridged Pd-Cl bond occurs.

In a number of papers¹ n.m.r. spectra of the allyl, methallyl, and crotyl complexes of palladium are interpreted in terms of a π - σ -bond conversion in the allylic ligand. It is assumed that addition of donor ligands stimulates rapid exchange reactions of the type



which are responsible for the transition of the A_2M_2X n.m.r. spectrum through an intermediate to A_4X .

To elucidate whether in palladium π -allyls the Pd co-ordination with such ligands as triphenylphosphine or dimethyl sulphoxide affects the allyl group bond structure, we investigated the Raman spectra of π -allylpalladium halides and some of their complexes with PPh_3 and DMSO .[†] We report here the solid-state Raman spectra of $(\pi\text{-all-PdCl})_2$, and PPh_3 , and of their adduct allPdCl, PPh_3 (Figure 2), as well as those of liquid Me_2SO and an Me_2SO solution of $(\pi\text{-allPdCl})_2$ (molar ratio 10:1, respectively) (Figure 1).

The Raman spectrum of a solution of $(\pi\text{-allPdCl})_2$ in Me_2SO shows no lines in the 1600—1640 cm^{-1} region attributable to $\nu_{\text{C}=\text{C}}$ of a σ -allylic group.⁴ The lines corresponding to the π -allyl modes are present virtually unchanged

particularly in the region 370—400 cm^{-1} (stretching modes of Pd- π -all), at ca. 500, ca. 1030, and ca. 1500 cm^{-1} (bending, symmetric, and antisymmetric stretching modes of the

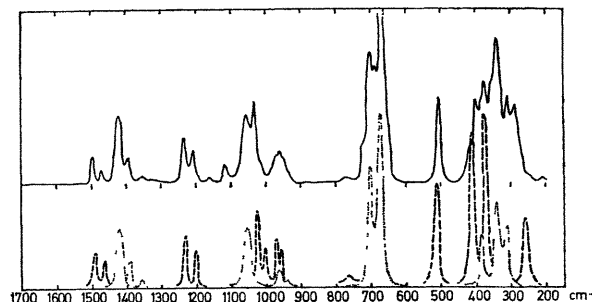


FIGURE 1. The Raman spectra of liquid dimethyl sulphoxide (.....), solid $(\pi\text{-allPdCl})_2$ (-----) and Me_2SO solution of $(\pi\text{-allPdCl})_2$ molar ratio 10:1, respectively (————).

π -allyl system, respectively). The spectrum exhibits some new lines in the region 290—350 cm^{-1} , while the strong line 258 cm^{-1} (stretching Pd-Cl bridged mode) is absent. In the spectrum of the solid adduct allPdCl, PPh_3 (Figure 2) an analogous situation is observed, but in this case it is not

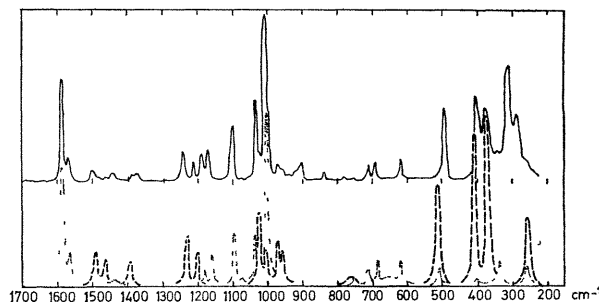


FIGURE 2. The Raman spectra of solids PPh_3 (.....), $(\pi\text{-allPdCl})_2$ (-----), and their adduct allPdCl, PPh_3 (————).

[†] While this manuscript was being prepared, Nakamoto² and Adams³ have reported the Raman spectra of $(\pi\text{-allPdX})_2$ where $X = \text{Cl, Br}$, which are in agreement with our results.

so obvious because of the overlapping of several lines in the spectra of the original compounds.

From these results, we conclude that the co-ordination of the donor ligand with the Pd atom in palladium allyls does not cause the conversion of the π -allyl group to the

asymmetric or σ -bonded form, but that cleavage of the bridged Pd-Cl bond occurs.

The Raman spectra were taken using a spectrometer of the modified DFS-12 type equipped with a He/Ne 50 mW laser.

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¹ J. C. Chien and H. C. Dehm, *Chem. and Ind.*, 1961, 745; R. G. Schultz, *Tetrahedron Letters*, 1964, 301; J. Powell, S. D. Robinson, and B. L. Shaw, *Chem. Comm.*, 1965, 78; G. L. Statton and K. C. Ramey, *J. Amer. Chem. Soc.*, 1966, 88, 1327, 4387; K. Vrieze, C. MacLean, P. Cossee, and C. W. Hibbers, *J. Organometallic Chem.*, 1966, 6, 672; F. A. Cotton, J. W. Faller, and A. Musco, *Inorg. Chem.*, 1967, 6, 179; J. Powell and B. L. Shaw, *J. Chem. Soc. (A)*, 1967, 1839.

² K. Shobatake and K. Nakamoto, *J. Amer. Chem. Soc.*, 1970, 92, 3339.

³ D. M. Adams and A. Squire, *J. Chem. Soc. (A)*, 1970, 1808.

⁴ Yu. P. Egorov, L. A. Leites, and V. F. Mironov, *Zhur. strukt. Khim.* 1961, 2, 562; A. N. Nesmeyanov, A. Z. Rubezhov, L. A. Leites, and S. P. Gubin, *J. Organometallic Chem.*, 1968, 12, 187.