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NMR SPECTRA OF THE π-ALLYLIC COMPLEXES [(π-C_4H_7- AND π-C_3H_5)Pd(PPh_2R)$SnCl_3$]

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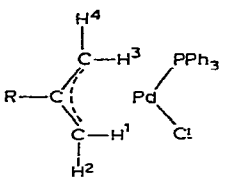
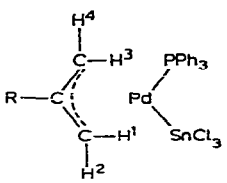
SUMMARY

The NMR spectra of the π-allylic complexes (π-C_4H_7- and π-C_3H_5)Pd-(PPh_3)$SnCl_3$] (III) at room temperature in $CDCl_3$ strongly resemble those of the symmetrical complexes [(π-C_4H_7- and π-C_3H_5)PdCl]$_2$ (I), and are markedly different from those of complexes [(π-C_4H_7- and π-C_3H_5)Pd(PPh_3)Cl] (II). The coupling constants $J(P-H^1)=J(P-H^3)=6.0$ Hz and $J(P-H^2)=J(P-H^4)=$ca. 3 Hz are about half of the *trans* coupling constants $J(P-H^1)$ and $J(P-H^2)$ observed in complexes (II), respectively.



(II)



(IIIa), R = CH_3
(IIIb), R = H

The spectrum of more soluble complex [(π-C_4H_7)Pd(PPh_2Me)$SnCl_3$] (V) shows a similar $A_2M_2X_3$ pattern at room temperature, but changes at low temperature to an $ABCDX_3$ system consistent with a "frozen" unsymmetrical structure. The effects of addition of $SnCl_2$ to the complexes (II) have also been studied. The spectrum of the system (II)/$SnCl_2$ or (II)/(III) depends upon the mole ratio of $SnCl_2$/Pd atom. These results can be accounted for by a rapid inter- and intramolecular $SnCl_2$-transfer mechanism, involving the five-coordinated stannylene complex [(π-C_4H_7- or π-C_3H_5)PdCl(PPh_2R)$SnCl_2$] as an intermediate.

INTRODUCTION

A number of reports on NMR characteristics of π-allylic complexes have been published[1], because of the importance of NMR studies in the characterization of π-allylic systems. The NMR spectrum of bis(π-allylpalladium chloride) (Ib) shows an AM_2X_2 pattern, consistent with non-classical allylic structure[2], and is independent of temperature change, unless recorded in a solvent with co-ordinative ability such as

dimethyl sulfoxide[3]. As the π-allylic groups in the complexes [(π-C_4H_7- and π-C_3H_5)-$PdCl(PPh_3)$] (II) are expected to be distorted[4] by the differing *trans*-effects of the phosphine and chloro-ligands, their spectra show complex signal pattern (ABCDX), and vary significantly with temperature. These phenomena have been investigated by many workers[5] and explained in terms of a rapid σ–π-interconversion and ligand transfer.

The NMR spectrum[6] of the complex [(π-C_4H_7)$Pd(PPh_3)SnCl_3$] (IIIa) is abnormal in that the spectrum resembles that of the symmetrical complex (Ia), and is quite different from that of complex (IIa), although its molecular structure resembles that of the unsymmetrical complex (IIa) rather than that of (Ia). This result suggested that a rapid ligand-transfer process should exist in the solution of complexes (III), and the results of our studies on NMR spectra of complexes of type (III) and of mixtures of complexes (II) with $SnCl_2$ are described below.

EXPERIMENTAL

NMR spectra were run on JEOL, JNM-MH-60 and C-60 Spectrometers with variable temperature equipment in deuterochloroform solution with TMS as internal standard.

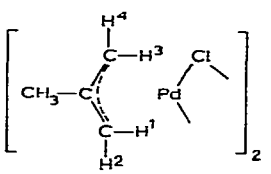
Reagents

Anhydrous stannous chloride was obtained by treatment of stannous chloride dihydrate with acetic anhydride. π-Allylic palladium complexes and their phosphine derivatives were prepared by the literature method[7–10]. (Trichlorostannyl)-π-allylic complexes (III) were prepared as described in our previous paper, and recrystallized from chloroform under nitrogen.

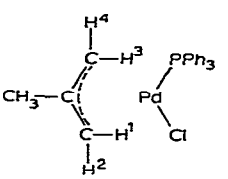
RESULTS

1. *NMR spectra of the complexes* (π-C_4H_7)- *and* (π-C_3H_5)$Pd(PPh_3)SnCl_3$ *at room temperature*

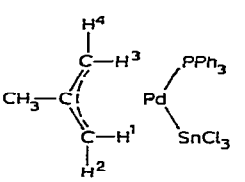
The NMR spectra of the three types of the π-methallyl complexes (Ia), (IIa) and (IIIa) at room temperature in $CDCl_3$ are shown in Fig. 1.



(Ia)



(IIa)



(IIIa)

The spectrum of complex (IIIa) is quite different from that of (IIa), although (IIIa) and (IIa) have similar unsymmetrical structures. *Anti*-protons H^1 and H^3 are magnetically equivalent, as are *syn*-protons H^2 and H^4. The former appear as a doublet due to the coupling with phosphorus atom [$J(P–H^{1,3})$ 6.0 Hz], and the latter as a slightly broad singlet, indicating that $J(P–H^2)$ or $J(P–H^4)$ is very small (nearly 3 Hz; half of the

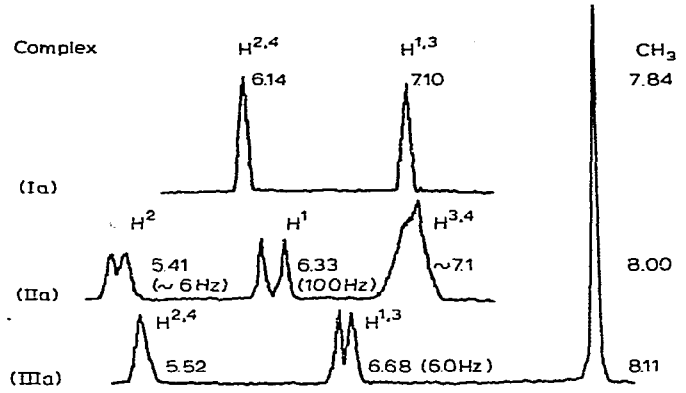


Fig. 1. NMR spectra of π-methallyl complexes (Ia), (IIa) and (IIIa) (20°, in $CDCl_3$). Resonance peaks due to methyl group were abbreviated, except for complex (IIIa), and the values under protons assigned show their chemical shifts (ppm).

half-width of the peak due to H^2 and H^4).

This assignment was confirmed by the spectrum of complex (IIIb), shown in Fig. 2, which has a strong resemblance to that of (Ib). *Anti*-protons H^1 and H^3 are

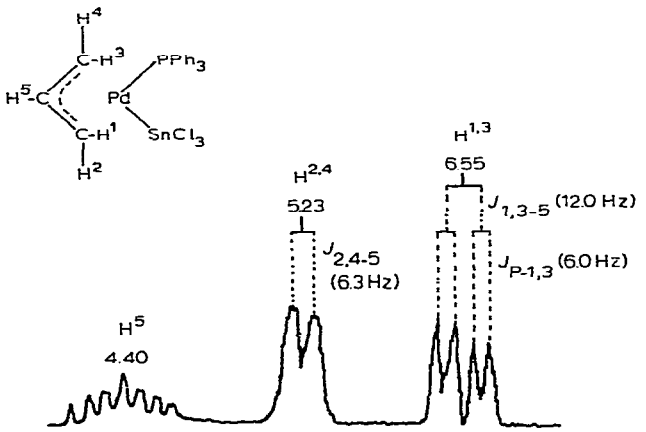


Fig. 2. NMR spectra of π-allyl complex (IIIb) (20°, in $CDCl_3$). The values under protons assigned show their chemical shifts (ppm).

equivalent, splitting to a double doublet by coupling with proton H^5 [$J(H^1–H^5)$ or $J(H^3–H^5)=12.0$ Hz] and with the phosphorus atom [$J(P–H^1)$ or $J(P–H^3)$ 6.0 Hz]. The *syn*-protons H^2 and H^4 are also magnetically equivalent and appear as a relatively broad doublet by coupling with H^5 [$J(H^2–H^5)$ or $J(H^4–H^5)=6.3$ Hz]. The proton–proton coupling constants in (IIIb) are similar to that in (Ib)[11].

The value of coupling constants of the phosphorus atom with *syn*- and *anti*-protons *trans* to it were reported to be nearly 6 and 12–14 Hz in complexes (II), respectively [5a,10]. The observed values of $J(P–H)$ for complexes (III) in this work were almost half of the respective *trans* coupling constants in (II). These facts suggest the existence of a rapid equilibrium, by which protons H^1 and H^3 (H^2 and H^4) became

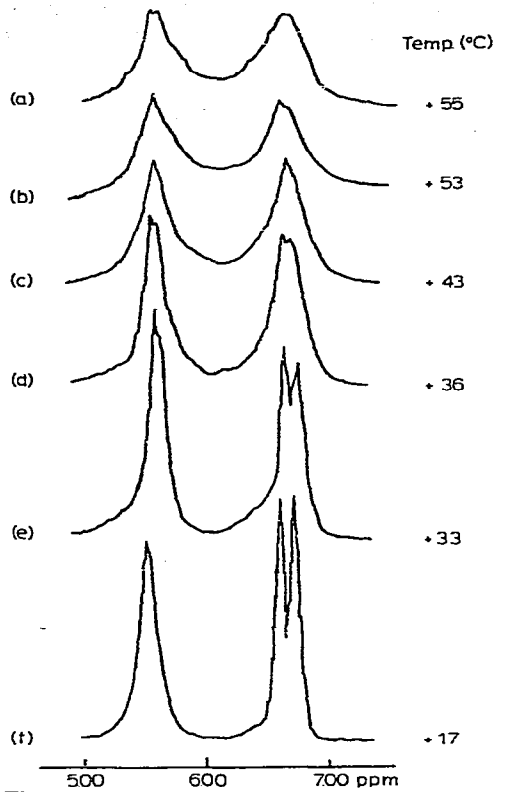


Fig. 3. Variable temperature NMR spectra of complex (IIIa) (in $CDCl_3$).

equivalent, and the non-existence of a σ–π-interconversion process, which would lead to a coalescence of the peaks due to *syn*- and *anti*-protons not observed in these cases.

2. *Variable temperature NMR spectra*

The spectrum of (IIIa) varies appreciably with the temperature as shown in Fig. 3. Broadening and coalescence of the peaks due to *syn*- and *anti*-protons occurs as the temperature is raised, and this can be easily explained by a σ–π-interconversion process.

At low temperature, the disappearance of the coupling with phosphorus atom and broadening of the peaks is also observed. The lower field peak broadened more rapidly.

As further information on NMR spectrum of complex (IIIa) at lower temperature could not be obtained because of its low solubility in chloroform, the spectrum of the more soluble complex $[(\pi\text{-}C_4H_7)Pd(PPh_2Me)\cdot SnCl_3]$ (V) was studied, and the results were shown in Fig. 4. The spectrum at room temperature was quite similar to that of complex (IIIa); the resonance peak due to the methyl group on the PPh_2Me ligand was observed as a doublet at τ 7.91 as a result of coupling with the phosphorus atom $[J(P\text{–}H)=9.0$ Hz]. At higher temperature broader peaks due to π-allylic protons were observed.

On the other hand, as the temperature was lowered, the two peaks of allylic

protons became broadened: at about −27° the lower field peak began to split into two broad peaks and at −44° the splitting of the higher field peak was observed. The spectrum at the lower limit of temperature (−57°) was consistent with the frozen unsymmetrical structure (V). The coupling of phosphorus–allylic protons could hardly be observed, but can be assigned as shown in Fig. 4h according to results obtained for complex (IIa)[5a,10].

From the spectrum in Fig. 4, the coupling constant of the methyl group with

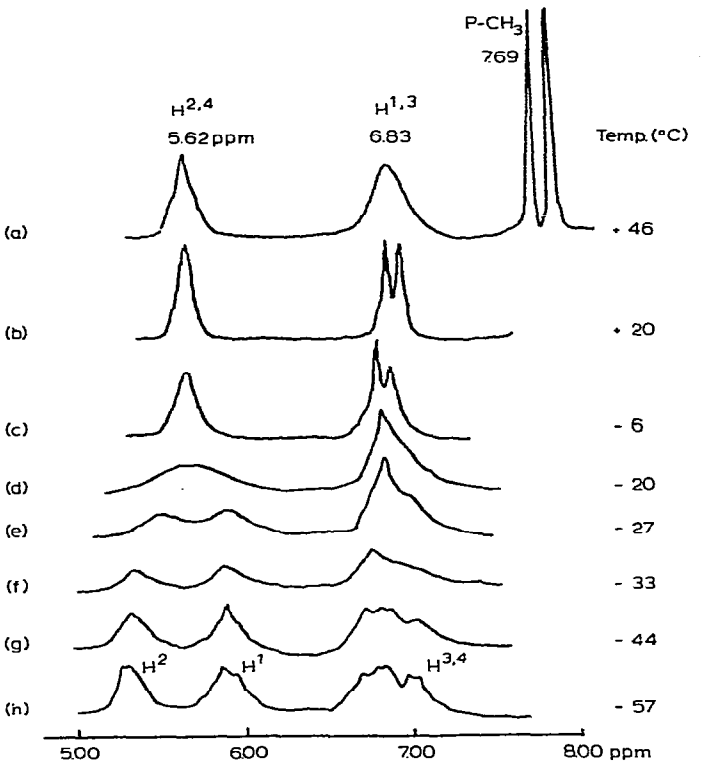


Fig. 4. Variable temperature NMR spectra of complex (V) (in $CDCl_3$).

the phosphorus atom [J(P–H) 9.0 Hz] was found to be much larger than that in free PPh_2Me [J(P–H) 3.7 Hz in benzene], and was independent of the temperature. These results suggest that an equilibrium involving dissociation of the phosphine ligand from the palladium atom plays a minor role in the variation of the spectra, and so an equilibrium arising from Pd–Sn bond dissociation appears to be involved.

3. *Additive effects of $SnCl_2$ on the NMR spectra of complexes (II)*

As a $SnCl_2$-transfer mechanism is indicated by the results described above, effects of addition of $SnCl_2$ on the NMR spectra of complex (IIa) were examined, and the results are shown in Fig. 5. The addition of as little as 0.036 mole of $SnCl_2$ per Pd atom to a deuterochloroform solution of the complex (IIa) caused the complete disappearance of the phosphorus coupling with H^1 and H^3, and a significant broaden-

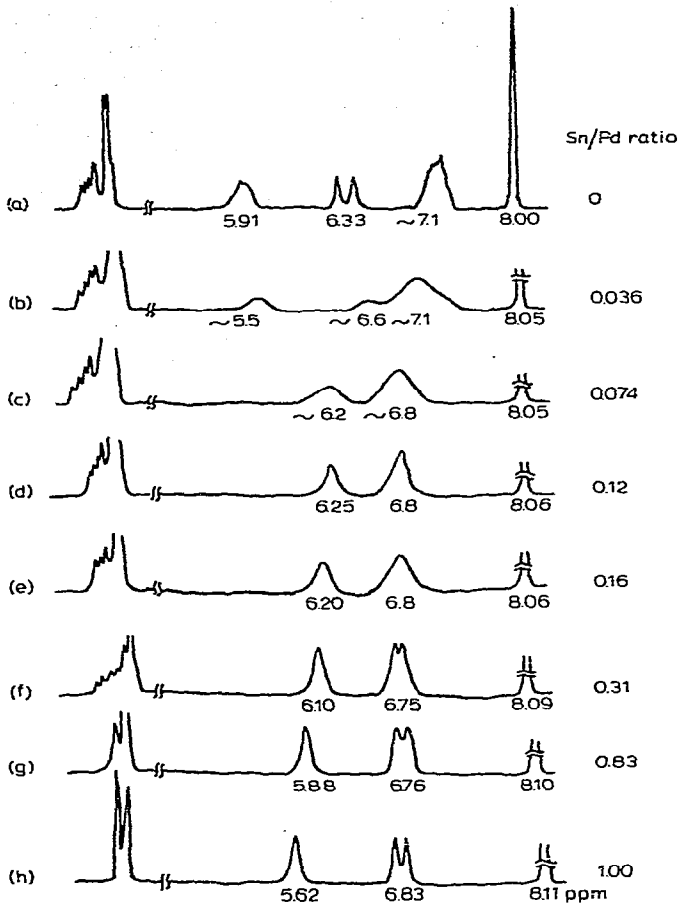


Fig. 5. NMR spectra of complex (IIa) with increasing added $SnCl_2$ (in $CDCl_3$).

ing of H^2 and H^4. The addition of 0.074 mole of $SnCl_2$ per Pd atom caused collapse of the peaks due to the H^1 and H^3, the shape and position of which were consistent with a mechanism whereby H^1 exchanged its position with H^3 and H^2 with H^4, relative to the position of the co-ordinated phosphine and chloro-ligand in complex (IIa).

Addition of about 0.1 mole of $SnCl_2$/Pd gave the resonance pattern in Fig. 5d and 5e with two broad singlets at 6.26 (the mean value of τ_1 and τ_3) and 6.80 ppm (the mean value of τ_2 and τ_4). On further addition of $SnCl_2$, the two broad singlets became sharper, and coupling of the antiprotons H^1 and H^3 with phosphine became evident. $SnCl_2$/Pd ratios above 0.30, no further obvious variation was observed, except for the lower field shift of the peaks due to allylic protons, and the more clear-cut splitting of antiprotons H^1 and H^3 by coupling with phosphorus. On the other hand, the peak due to the methyl group in the allylic moiety tended to shift upfield with increasing $SnCl_2$/Pd ratio, and the difference of its chemical shifts between complex (IIa) and (IIIa) reached about 0.1 ppm. Similar results were also obtained with mixtures of complexes (IIa) and (IIIa).

These phenomena can be explained by a ligand-exchange process involving rapid intra- and inter-molecular transfer of the $SnCl_2$ entity. Similar results were also obtained with the system [(π-C_4H_7)Pd(PPh_2Me)Cl] (IV)/$SnCl_2$. In this case, also, the peak due to the methyl proton of the phosphine maintained its shape but tended towards lower field, as shown in Fig. 6. It can be concluded, therefore, that fission of

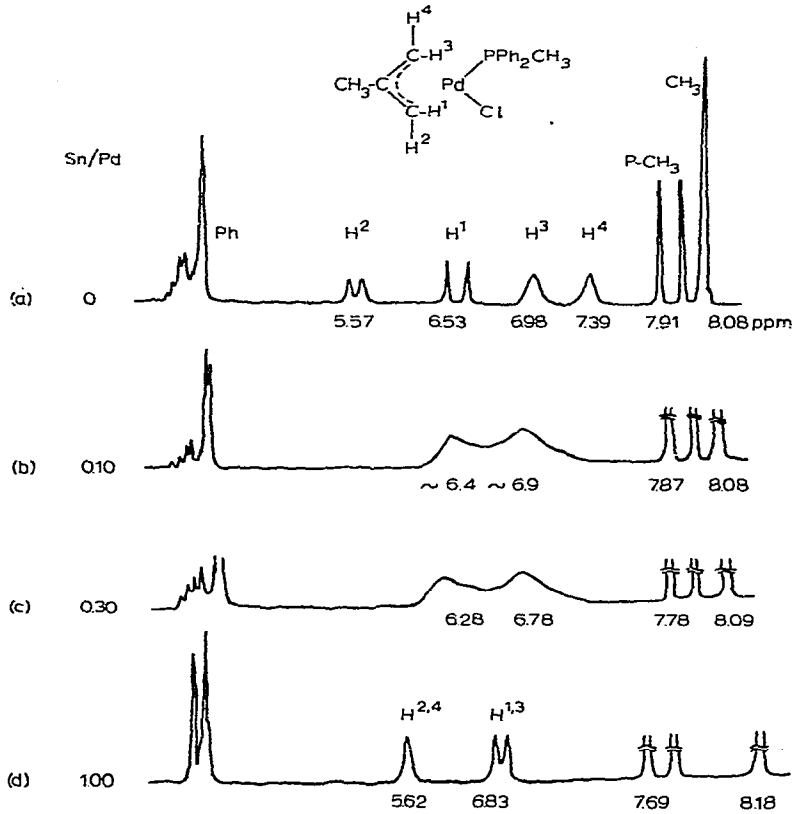


Fig. 6. NMR spectra of complex (IV) with increasing added $SnCl_2$.

the Pd–P bond is not involved in the equilibrium. Moreover, throughout all the cases, no coalescence of *anti*- and *syn*-protons was observed, suggesting that there was only a minor contribution of σ–π-interconversion processes to the NMR spectral change.

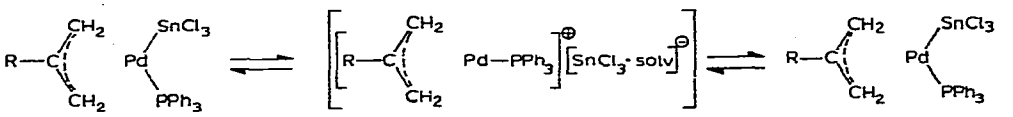
On the other hand, a different tendency was observed in (IIb)/$SnCl_2$ system. The addition of only a small amount of $SnCl_2$/Pd caused coalescence of the peaks to a single broad peak. This could not be explained by ligand exchange process alone. It is reported that the coalescence temperature of complex (IIb) is about 70° lower than that of corresponding complex (IIa)[5]. The proton H^5 in (IIb)/$SnCl_2$ system showed a relatively clear-cut quintet (AX_4 pattern), and therefore, the additional σ–π-interconversion process appears to operate only in the case of the system (IIb)/$SnCl_2$.

DISCUSSIONS

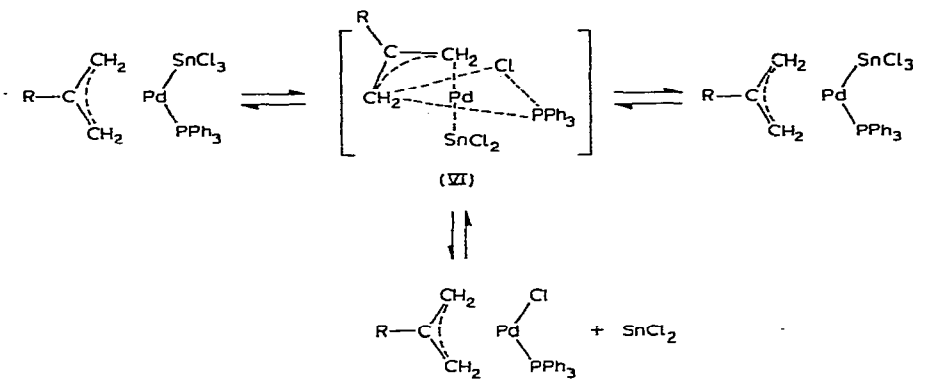
All the results obtained can be accounted for by the rapid equilibrium in-

volving dissociation and re-formation of the Pd–Sn bond. Two mechanistic schemes one, ionic (Scheme 1) and one carbene-like (Scheme 2), are possibilities.

Scheme 1



Scheme 2



The complex $CpNi(PPh_3)SnCl_3$[12] was reported to be converted into an ionic compound $[CpNi(PPh_3)][SnCl_3 \cdot Solv]$ in polar solvents (Solv), and to have a tendency to dissociate into $CpNi(PPh_3)Cl$ and $SnCl_2$ in solution, but complexes (III) and (V) are fairly stable in solution.

Conductivity measurement on complex (IIIb) indicated that it was virtually non-ionic[13]. The Sn–Cl stretching bands[6] at near 300 cm^{-1} also indicate that the complexes are non-ionic[14], and thus the existence of ionic process as in (Scheme 1) in our system can be excluded.

The carbene-like mechanism (Scheme 2) is the most probable. Recently, many carbene complexes have been prepared by Fischer and his co-workers[15], and in some cases have been assumed to be intermediates in the reactions of carbene-source with metal complexes[16–18]. Divalent dichlorotin can be considered as a singlet carbene analogue, so that stannous chloride could co-ordinate to the palladium atom, for which trigonal bipyramidal coordination would be preferred. With complexes (III) [or (V)] an intermediate (VI) can be postulated, in which the plane of allylic moiety is vertical to the plane of coordination Cl–Pd–P. This intermediate, through which a rapid ligand exchange might be possible, would readily account for the equivalence of H^1 and H^3, and that of H^2 and H^4, respectively, and furthermore for the intermolecular $SnCl_2$-transfer by dissociation.

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