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MAGNETIC NON-EQUIVALENCE IN SUBSTITUTED ALLYLPALLADIUM COMPOUNDS IN RELATION TO MOLECULAR REARRANGEMENTS

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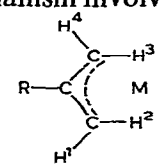
SUMMARY

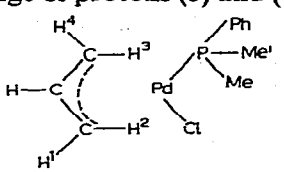
The rearrangement reactions of substituted allylpalladium salts have been studied on complexes carrying magnetically non-equivalent groups on the alkyl substituents. The study proved that in one of the reactions, the π,σ-rearrangement, the intermediate is a σ-form. Rearrangement was not found to occur in the case of chloro-(2-isopentyl-π-allyl)(triphenylphosphine)palladium and the 2-isobutyl compound, which is attributed to steric hindrance.

INTRODUCTION

It is well-known that in most of the π-allyl–metal complexes the *syn*-protons (1,4) and *anti*-protons (2,3) interchange under certain conditions[1-4]. NMR measurements on allyl or 2-methylallyl compounds indicate that *syn–anti* isomerization takes place in the line-broadening time scale, but do not provide detailed information on the mechanism involved.

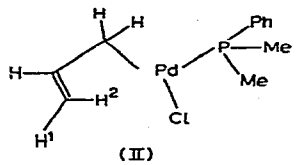


In two previous short communications[5] we described methods of studying this reaction of allyl–metal complexes. These methods make use of the fact that the two methyl groups of dimethylphenylphosphine are non-equivalent in a complex having no plane of symmetry through the phosphorus atom of the ligand. This property has often been used for determining the structure of hexacoordinate complexes containing various ligands[6,7]. In the fluxional molecule π-$C_3H_5PdCl(MeMe'PPh)$ (I) the exchange of the non-equivalent methyl groups is simultaneous with the *syn–anti* exchange of protons (3) and (4):



(I)

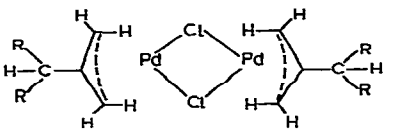
This shows that at higher temperatures the molecule behaves as if the plane Pd–P–Cl is a plane of symmetry. For the underlying mechanism it means that the allyl plane is converted into its mirror image during the (3,4) exchange, which is in agreement with the formation of a σ-intermediate[1] (II):



(II)

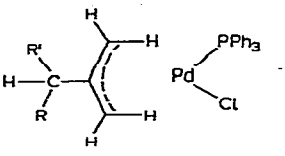
The second method[5] is particularly suited for use with complexes that do not contain phosphine ligands, but in which the asymmetric substituent is attached to the allyl group itself. The same method was also applied by Marks and Cotton[8] to π-benzylic molybdenum carbonyls [(1,2,7-*trihapto*-3,5-diisopropylbenzyl)(*pentahapto*-cyclopentadienyl)dicarbonylmolybdenum]. It should be added here that in some cases the reactivity of the substituted allylic complexes differs from that of the parent compound so that care should be taken in comparing the two.

Two types of substitution can be distinguished, *viz.* substitution at carbon-1 (terminal atom) and carbon-2 (central atom). The asymmetric substituent may be isopropyl, ethyl, isopentyl, or in general CR_2H or CH_2R. In a 2-substituted compound of formula (III):



(III)

the R-groups are equivalent due to the presence of the symmetry plane perpendicular to the $PdCl_2$ plane and the allyl plane. (The dihedral angle between the latter two planes amounts to about 110°.) Treatment of this dimeric compound with triphenyl phosphine results in the formation of the monomer (IV):



(IV)

in which the R-groups are evidently non-equivalent. Interchange of R and R' may take place via (*a*) ligand exchange with loss of configuration[1], (*b*) formation of a σ-bonded intermediate, after which the Pd moves to the other lobes of the double bond, and (*c*) a "flip"[9] of the allyl plane with respect of the Pd–Cl–P plane.

In complexes which are asymmetrical as a consequence of the presence of an extra substituent on carbon-1, we have similar phenomena of non-equivalence in the HRR'C-group at carbon-2. In the corresponding monomer, reaction (*a*) gives rise

to exchange of chemically distinct compounds. With similar consequences the substituent $-CRR'H$ can be attached to carbon-1 (or -3).

The mechanisms described above are useful in the study of a variety of allylic compounds with dynamic behaviour, especially those of which the underlying mechanism is not known[3,10]. Here, we shall concern ourselves with the reactions of monomeric palladium compounds (IV) with phosphines as ligands and acetates and chlorides as anions.

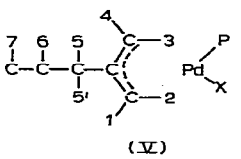
EXPERIMENTAL

The compounds studied were prepared by a method devised by Volger[11]. From the appropriate olefins we obtained bis[(alkylallyl)palladium chlorides] with alkyl = 2-isopropyl, 2-isobutyl, 2-isopentyl, 2-ethyl-1-methyl, or 1-isopropyl. The chlorides were converted into acetates by treating them with silver(I) acetate in acetone*. The monomers with triphenylphosphine and dimethylphenylphosphine were prepared from equivalent amounts of reactants in chloroform, and precipitated by addition of pentane.

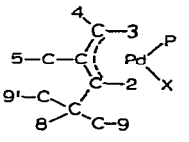
NMR spectra were obtained on Varian HA-100 and DP-60 Spectrometers using chloroform as solvent and tetramethylsilane as internal standard and lock-signal. The acetato adducts were measured as pure (substituted allyl)(triorganophosphine)-palladium acetates, or with a small excess of parent dimer; in the case of chloride monomer about 15 mole% of dimer was added (see Discussion).

RESULTS

The NMR data are given in Table 1. In some cases only the range of coinciding multiplets of second order absorptions is mentioned. The assignments are based on those given in previous reports[1]. The way in which the hydrogens are numbered is shown in (V) and (VI), with P = phosphine and X = Cl^- or OAc^-.



(V)



(VI)

Two classes of compounds can be distinguished: those giving a broadening of signals 3 and 4 at temperatures between -40 and $+10°$, and those not showing a reaction at these temperatures. At higher temperatures all the 2-substituted allyl compounds exhibit a broadening of signals 1, 2, 3 and 4.

As to the first class of compounds, the 3–4 exchange of the (2-isopropylallyl)-palladium acetates is independent of the concentration of the monomer or, if present, the dimer[12], whereas with the chlorides the concentration of the dimer does affect

* In general, allylpalladium acetates, when exposed to light and heat, decompose readily into metallic palladium and allyl acetates.

TABLE 1

NMR-DATA FOR SOME SUBSTITUTED ALLYLPALLADIUM COMPLEXES IN CHLOROFORM

Compound	Temp. (°C)	Chemical shifts (ppm downfield from TMS)										Coupling constants (Hz)		
		1	2	4	5	5,5'	6,6'	7,7'	8	9,9'	x			
(2-Methylallyl)PdCl(PPh_3)[1]	−45	4.50	3.62	2.80	2.89	1.96						J(P-H_1) 6.5	J(H_1-H_4) 2.9	J(P-H_2) 9.8
(2-Methylallyl)PdOAc(PPh_3)[12]	−40	4.97	4.21	2.51	2.84	2.01					1.75	J(P-H_1) 7.0	J(H_1-H_4) 2.5	J(P-H_2) 9.5
[(2-Isopropylallyl)PdCl]$_2$	25	3.92	2.84	2.84	3.92	2.42	1.24					J(H_5-H_6) 7.0		
(2-Isopropylallyl)PdCl(PPhMeMe')	−40	4.41	3.36	2.50	3.15	2.24	1.07, 1.01	(Me: 1.97; Me': 1.94)				J(P-H_1) 6.5	J(H_1-H_4) 3.0	J(P-H_2) 10.0
												J(H_5-$H_{6,6'}$) 7	J(P-Me,Me') 9.5	
[(2-Isopropylallyl)PdOAc]$_2$	25	3.67	2.58	2.58	3.67	2.61	1.25				2.00	J(H_5-H_6) 6.5		
(2-Isopropylallyl)PdOAc(PPh_3)	−30	4.59	3.79	2.56	2.92	2.41	1.22, 1.02					J(H_5-$H_{6,6'}$) 6.5	J(P-H_1) 6.5	J(P-H_2) 9
												J(H_1-H_4) 3.5		
(2-Isopropylallyl)PdOAc(PPhMeMe')	−40	4.35	3.55	2.47	2.87	2.65	1.18, 1.02	(Me: 1.80; Me': 1.84)			2.23	J(H_1-H_4) 3	J(P-H_1) 6.5	J(P-H_2) 10.5
												J(H_5-$H_{6,6'}$)7.5	J(P-Me, Me') 9.5	
[(2-Isobutylallyl)PdCl]$_2$	25	3.81	2.89	2.89	3.81	2.18	1.81	1.01				J(H_5-H_6) 6.5	J(H_6-H_7) 6.5	
(2-Isobutylallyl)PdCl(PPh_3)	−40	4.52	3.62	2.80	2.80	(2.20 1.80)		0.99, 0.94				J(H_1-H_4) 2.0	J(P-H_1) 6.5	J(P-H_2) 10
[(2-Isobutylallyl)PdOAc]$_2$	25	3.63	2.70	2.70	3.63	2.29	1.82	0.99			2.00	J(H_5-H_6) 7	J(H_6-H_7) 7	
(2-Isobutylallyl)PdOAc(PPh_3)	−30	4.49	3.73	2.47	2.87	(2.20 1.80)		0.96, 0.90			1.80	J(P-H_1) 6.5	J(P-H_2) 9	J(H_1-H_4) 3
[(2-Isopentylallyl)PdCl]$_2$	25	3.77	2.88	2.88	3.77	2.19		0.96						
(2-Isopentylallyl)PdCl(PPh_3)	−25	4.48	3.62	2.81	2.81	2.23, 1.77		0.95				J(P-H_1) 6.5	J(H_1-H_4) 2.5	J(P-H_2) 10
												J(H_5-$H_{5'}$) 12		
[(2-Isopentylallyl)PdOAc]$_2$	25	3.60	2.69	2.69	3.60	2.32		0.98			2.01			
(2-Isopentylallyl)PdOAc(PPh_3)	−30	4.50	3.73	2.53	2.84	2.44, 2.24[a]		0.95			1.81	J(P-H_1) 6	J(P-H_2) 9	J(H_1-H_4) 2
												J(H_5-$H_{5'}$) ≈ 10		
(2-Isopentylallyl)PdOAc(PPhMeMe')	−25	4.35	3.44	2.60	3.10	2.10, 1.76[a]		(Me, Me': 1.79, 1.81)				J(P-Me, Me')9.5	J(H_5-$H_{5'}$) 12	
[(1-Isopropyl-2-methyl-π-allyl)PdCl]$_2$	25		3.39	2.57	3.66	2.10			~2.08	1.24, 1.06		J(H_8-H_2) ≈ 9	J(H_8-H_9) 6.5	
(1-Isopropyl-2-methyl-π-allyl)PdCl(PPh_3)	−25		4.17	2.49	2.60	1.97			~2.75	1.60, 1.21		J(P-H_2) 9.5	J(H_8-H_9) 6.5	J(H_2-H_8) 9.5

[a] AB-spectrum.

this exchange (and hence the temperature at which the NMR time-scale is reached). The following results have been obtained on solutions with a 15 per cent excess of dimer. The 3,4-interchange was observed with the following compounds: (2-isopropylallyl)(dimethylphenylphosphine)palladium(II) chloride (−20°, −0°), the corresponding acetate (−33°, +20°), (2-isopropylallyl)(triphenylphosphine)palladium(II) chloride (−14°, −0°), the corresponding acetate (−18°, +20°), (1-isopropyl-2-methylallyl)(triphenylphosphine)palladium(II) chloride (−8°, +52°). The upper limit indicates the temperature at which other reactions begin to occur. For the last-mentioned complex this reaction is a phosphine exchange between monomer and dimer, and for the other complexes it is the broadening of signals 1, 2, 3 and 4. As can be seen in Table 1 and Fig. 1 (two doublets at about 1.0–1.2 ppm) the two methyl groups of the isopropyl substituent are inequivalent in the monomer. In all cases it can be seen that the methyl groups broaden at the same rate as protons 3 and 4.

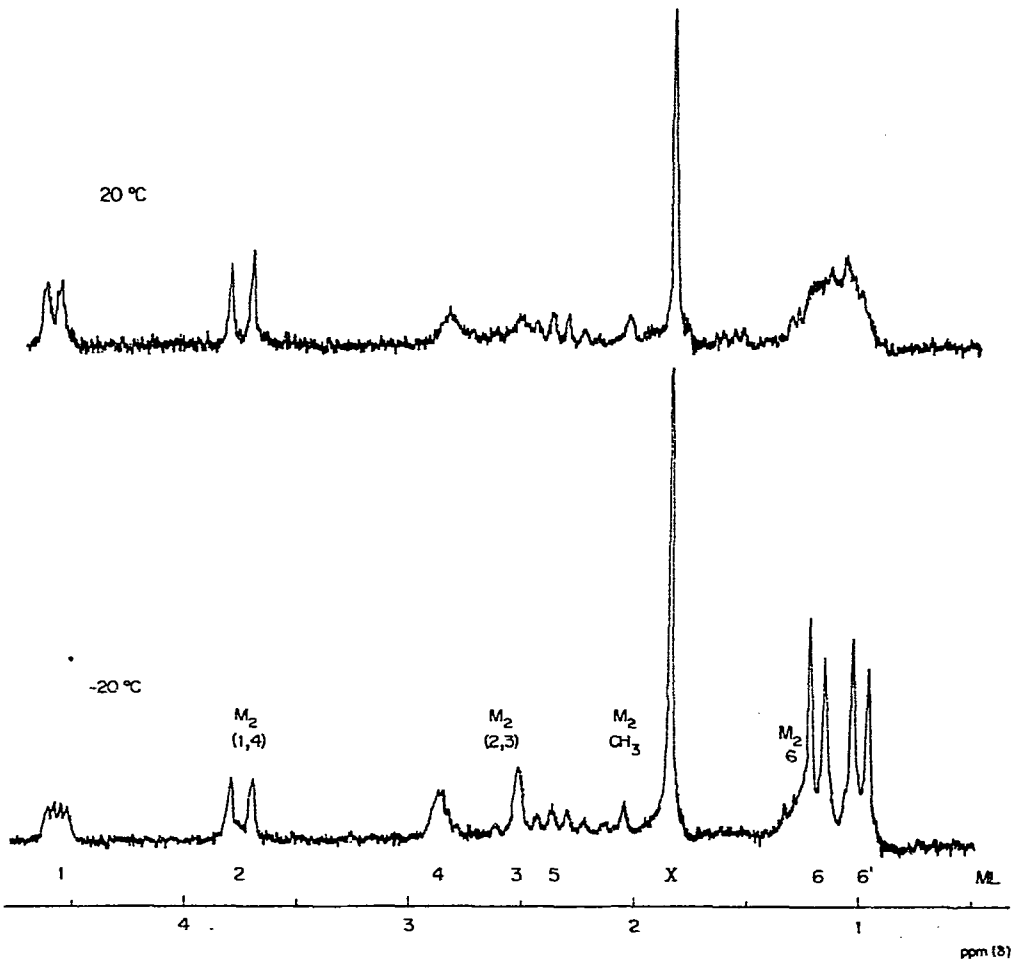


Fig. 1. NMR spectra of (2-isopropylallyl)(triphenylphosphine)palladium acetate at various temperatures in $CDCl_3$. For the numbering see formula (V).

Additionally, in the adducts with PPhMeMe' the non-equivalent Me- and Me'-groups interchange in the NMR time-scale in the same temperature range.

The temperature-dependent spectra of (1-isopropyl-2-methyl-π-allyl)(triphenylphosphine)palladium chloride are depicted in Fig. 2. The difference in chemical shift between the protons of the two methyl groups (H_9 and H_9') amounts to 0.41 ppm. Again a simultaneous broadening of the two methyl (H_9, H_9') and protons 3 and 4 is observed.

Fig. 3 shows the spectra of (2-isopentyl-π-allyl)(triphenylphosphine)palladium acetate, representing the clas s of compounds not showing a reaction between $-40°$ and $+10°$. The AB doublet of H_5 and $H_{5'}$ is centred at about 2.30 ppm. At $+20°$ exchange broadening is observed for signals 1, 2, 3, 4 and 5, 5'. Double resonance experiments[13] had proved that proton 1 interchanges with proton 4 only, and proton 2 with proton 3.

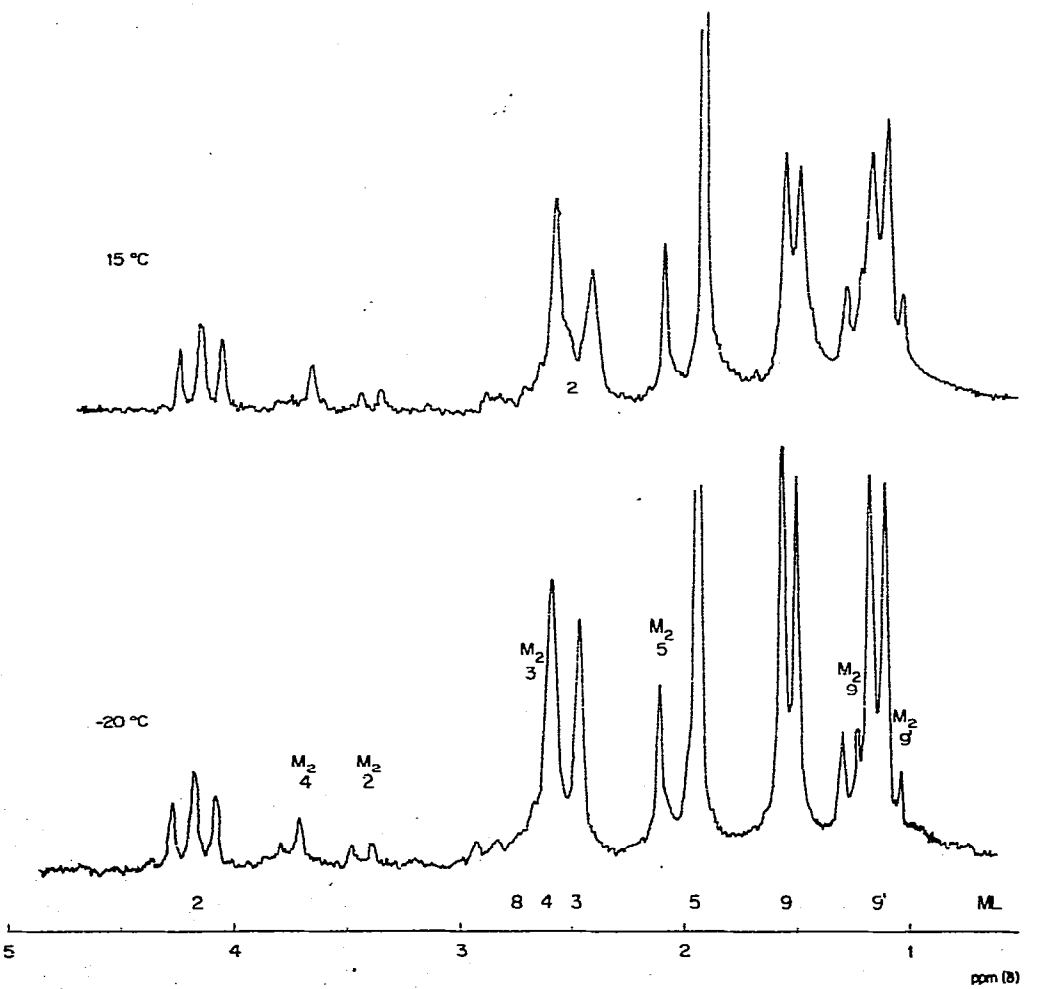


Fig. 2. NMR spectra of (1-isopropyl-2-methylallyl)(triphenylphosphine)palladium chloride at various temperatures in $CDCl_3$. The numbers (M_2) refer to the protons of the dimers. See also (VI).

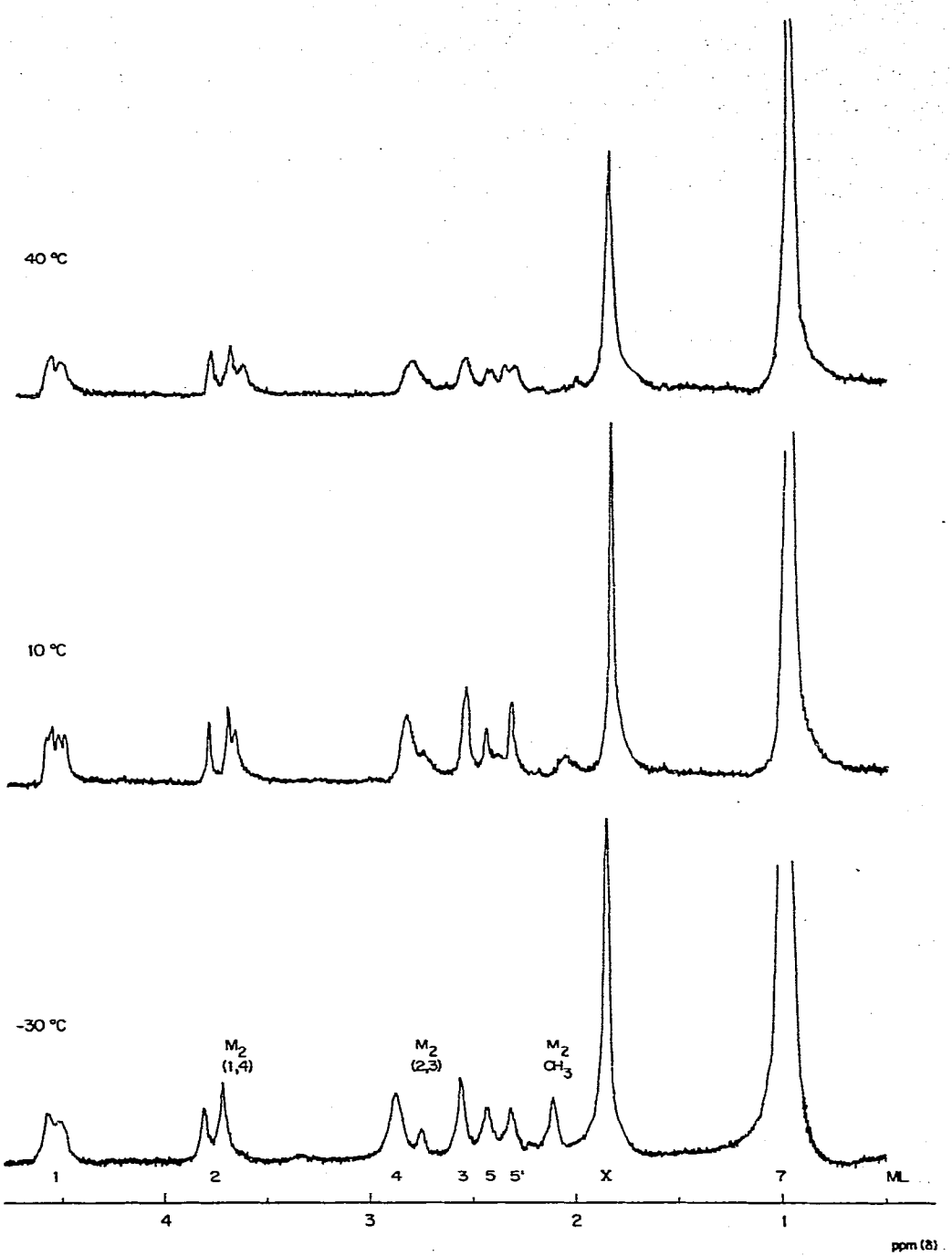
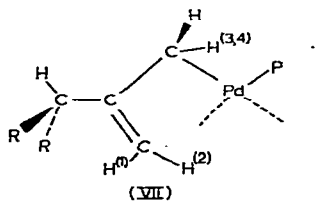


Fig. 3. The NMR spectra of (2-isopentylallyl)(triphenylphosphine)palladium acetate at various temperatures in $CDCl_3$.

DISCUSSION

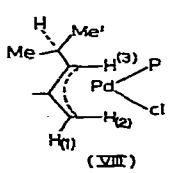
If an exchange is to take place between the non-equivalent R- and R'-groups in the 2-substituted complex, the reaction intermediate (or transition state) should possess a plane of symmetry passing through the carbon atom between R and R'. In the compounds studied such a plane may either be the plane through carbon-2 and palladium, perpendicular to the Pd–Cl–P-plane, or the allyl plane in a temporarily planar molecule, coinciding with the Pd–Cl–P-plane, provided that the phosphine used is symmetric. When either of these planes is present in an intermediate state, the two signals R and R' will show exchange broadening in the NMR spectrum. This is evidently the case in all 2-isopropyl-π-allyl monomers between $-30°$ and $+10°$, while the line widths of protons 3 and 4 increase to the same extent. The reaction rate of the chlorides is linearly dependent on the dimer concentration, as found previously by Vrieze *et al.*[14]. Presumably, the dimer acts as a Lewis acid on the chloride anion of the monomer, thus increasing the difference in *trans*-effect* between the two ligands (P, Cl), which facilitates σ-allyl formation. Other factors influencing the π,σ-reaction are dicussed in ref. 12. The transition state (VII) has a plane of symmetry. Exchange



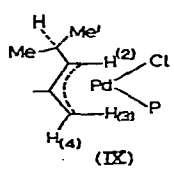
(VII)

of R-groups will occur when the Pd-atom is reattached to the other lobes of the π-bond, *i.e.* when it is bonded to the other face of the π-allyl plane. It is seen that protons 3 and 4 also interchange, but not protons 1 and 2. In this way we have now ruled out other possibilities for a 3,4-exchange[5]. Furthermore, we conclude that no "flip" mode[9] is carried out, since no broadening of R and R' is observed without simultaneous broadening of signals 3 and 4, (π,σ-reaction) or 1, 2, 3, and 4 (ligand exchange). (In a flip mode the metal atom moves to the other side of the allyl anion, without exchange between *syn*- and *anti*-protons taking place.)

We now turn to the compound bis(1-isopropyl-2-methylallylpalladium chloride). The behaviour of this dimer and of the corresponding (1-isopropylallyl)-palladium chloride was discussed in a previous communication** by Alexander *et al.*[5]. The monomeric phosphine adduct has two possible forms (VIII) and (IX):



(VIII)



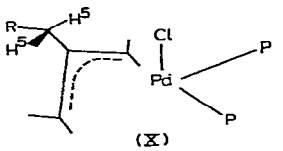
(IX)

* In the acetate the reaction is monomolecular. The acetates are included in this study because their tendency to π,σ-reactions is usually stronger than that of the chlorides[12].

** We are indebted to Dr. W. R. Jackson for informing us about his results prior to publication.

Comparison with other spectra[14] indicates that only IX is present. This could be due to steric factors. In addition it must be attributed to the manner of bonding. The phosphorus ligand induces to some extent a σ-form *cis* to it, and, as in general a metal–carbon σ-bond of the type $R-CH_2$–metal is more stable than the bond to a branched alkyl chain, we expect the isopropyl group positioned *trans* to the phosphorus. Clearly, no left–right interchange will be detected in the spectrum of the monomer when isomer (IX) is much more stable than isomer (VIII) (which holds only for phosphine complexes). The spectra show that the methyls in the isopropyl group, and protons 3 and 4 exchange at the same rate. This is an argument in favour of a σ-bonded allylpalladium system in an intermediate state.

Finally, we shall now consider the compounds that do not exhibit a π,σ-rearrangement in the usual temperature region. All complexes with a 2-isopentyl or 2-isobutyl substituent, even the acetates, belong to this group. If we look at a model of these compounds, it is clear that the very large substituent at carbon-2 will certainly not point in the direction of the palladium atom, but will occupy the position on the other face of the allyl plane. What happens during a π,σ-reaction is that the palladium atom moves to the other face of the allyl group. Therefore, the isopentyl or isobutyl substituent will also have to change its position. The rotation of this group, however, is seriously hindered by the protons (1) and (3,4). It is therefore not surprising that no π,σ-reactions are found to occur under the usual conditions. Although the difference in activation parameters may be very small, it is clearly reflected in the NMR spectra. The broadening of all four signals (1–4), together with a collapse of the AB doublet at 2 ppm is caused by the left–right interchange in the monomer, probably accompanied by anion exchange[12]. The same spectral phenomena are found when excess phosphine is added. There is no exchange of phosphine with retention of configuration[14], and it is likely that in the intermediate state the two exchanging ligands, and also the protons 5 and 5', are equivalent (X).



(X)

Vrieze *et al.*[1,14] concluded from the second-order behaviour of the exchange reaction that the reaction intermediate is five-coordinate (X).

CONCLUSIONS

All the compounds studied in this investigation show a π,σ-reaction (exchange of the *syn*- and *anti*-protons), and/or a left-right interchange. No indications have been found of other reactions or mechanisms. The rotation of the isopentyl and isobutyl groups at carbon-2 of the allyl group is sterically hindered. Prochiral substitution provides a good method of studying reactions in allyl–metal systems.

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