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PALLADIUM-PROMOTED ADDITION REACTIONS OF 1,3-DIENES

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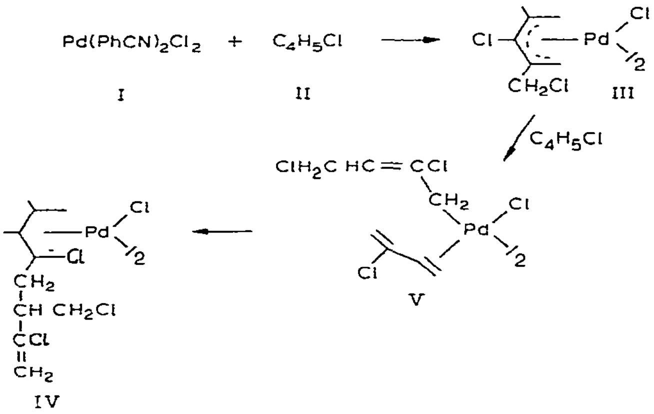
1,3-Dienes are known to undergo insertion reactions with palladium π-allyl complexes to yield new π-allyls[1-3]. In principle, the insertion reaction could be a propagation step in a metal-catalysed polymerisation It has been reported that branched chain products containing up to 19 carbon atoms (four insertion steps) are obtained on reaction of butadiene with π-allylpalladium chloride dimer under stringent conditions[1,2]. These brief reports excepted, little is known of reactions involving more than one diene insertion into palladium–π-allyl bonds This present paper describes the results of an investigation of the reactions of palladium π-allyl complexes with, mainly, 2-chlorobutadiene in which multiple insertion products containing up to 40 carbon atoms have been obtained under mild reaction conditions

A. RESULTS AND DISCUSSION

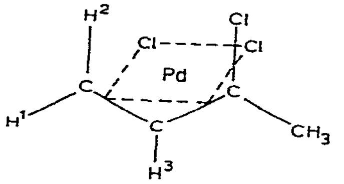
Reaction of Pd(benzonitrile)$_2$Cl$_2$, I, with 2-chlorobutadiene, II, in benzene solution at room temperature yields as a major component a yellow crystalline material shown by elemental analysis, IR and ^{1}H-NMR spectra and molecular weight measurements to be the chloride bridged dimer IV, comprising a π-allyl bond between each palladium atom and each C_8 unit This structure contrasts with that of the product of reaction of Na_2PdCl_4 with butadiene, in which the π-allyl moiety is contained in a C_4 unit, i e no dimerisation of diene has occurred[4]. By analogy with the butadiene reaction and other results to be described below it is proposed that IV is formed in a two-stage reaction, the first step being the formation of the simple π-allyl complex, III, derived from the diene, the second step being a rapid insertion of a second molecule of diene to yield IV. Attempts to isolate the intermediate III were unsuccessful, as were attempts to prepare it by other routes.

In the course of a study designed to confirm the structure of compound IV and its proposed formation via intermediate III, the reactions of various pre-formed palladium–π-allyl complexes [π-allyl PdCl]$_2$ with various 1,3-dienes were examined. In the former, the allylic group included unsubstituted π-allyl, π-1-chloroallyl, π-2-chloroallyl, π-1-chloro-1-methallyl, π-1,1′-dimethyl-2-chloroallyl, π-1,1′,3,3′-tetramethyl-2-chloroallyl

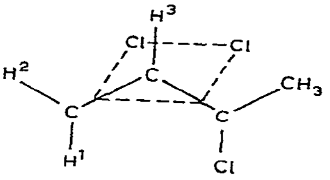


and π-1-carbomethoxyallyl The dienes included butadiene, 2-chlorobutadiene, isoprene and 2,3-dimethylbutadiene. From the results of experiments carried out two generalisations may be made (*1*) the presence of a chlorine substituent in the reactant π-allyl greatly enhances the rate of the insertion reaction. Medema et al.[2] have previously reported that reaction rate increases with increasing electron-withdrawing properties of substituents in the π-allyl. (*2*) when the insertion product itself contains a chlorine substituent in the π-allyl group, reaction proceeds beyond the first insertion step under conditions of room temperature and pressure.

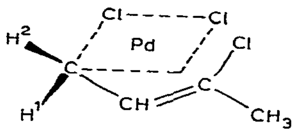
The ^{1}H-NMR spectra of the reactant π-allyls and of the various diene addition products afforded useful information on the mechanisms of the addition reactions. Palladium π-allyl complexes are known to undergo dynamic *syn* ⇌ *anti* exchange[5,6]. There now seems general agreement[6] that the mechanism of exchange involves the participation of a σ-bonded allylic intermediate which permits rotation about the adjacent carbon–carbon bond, and hence exchange of *syn* and *anti* positions. The situation may be illustrated by the complex [π-1-methyl-1-chloroallylPdCl]$_2$. As prepared, this complex exists as a mixture of *syn*-methyl (*anti*-chloro) and *syn*-chloro (*anti*-methyl) isomers (VI, VII) The 50°C ^{1}H-NMR spectrum (Fig 1(a)) clearly shows the two sets of resonances corresponding to the two isomers As the temperature is raised (spectra (b) and (c), Fig 1), the 1 1 1 quartets of the central allylic protons (H^3) collapse to 1 2 1 triplets, the two resonances remaining separate. The singlets due to the *syn* and *anti* methyl groups remain unaltered. Clearly, it is protons H^1 and H^2 which are exchanging positions, and from this it is inferred that in the transition state the σ-bond is to the unsubstituted carbon atom, as indicated in structure VIII, a suggested intermediate for the exchange process This intermediate assumes a donor bond from the vinylic double bond to the palladium atom. This interaction, if it occurs at all, is expected to be rather weak because the chelate ring formed thereby is three-membered (considering the vinyl group as one coordinating centre) and therefore rather strained. While coordination of the vinylic group may serve to satisfy, at least partially, the preferred coordination



VI



VII



VIII

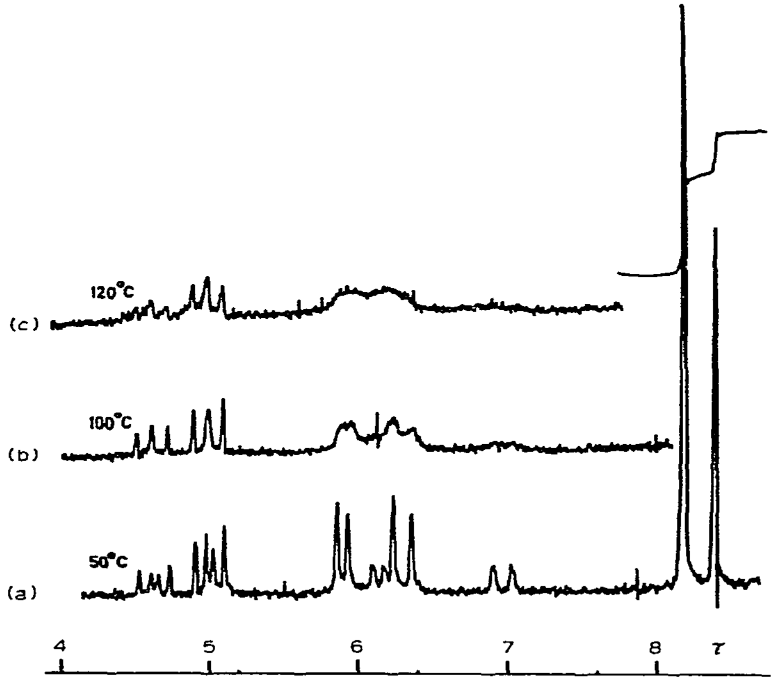
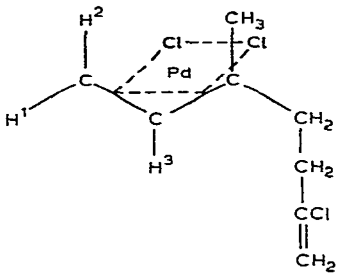


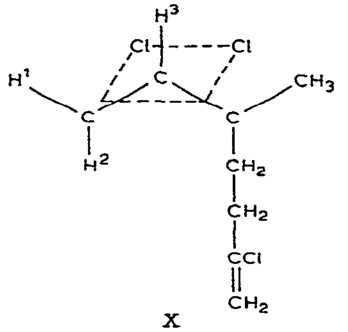
Fig. 1. The ^{1}H-NMR spectra of [π-1-chloro-1-methylPdCl]$_2$ in an o-/p-dichlorobenzene mixture at three temperatures. (The singlets at τ8.15 and τ8.40 due the *syn* and *anti* methyl protons are omitted in spectra (b) and (c) for clarity, these resonances are, however, the same as in spectrum (a))

number of four of the metal ion, it should be noted that the π-bond cannot remain intact during all stages of the rotation about the carbon—carbon bond.

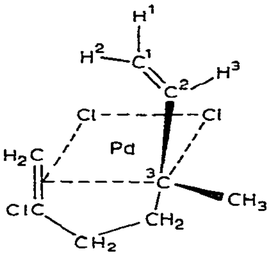
In contrast to the above, the insertion products of dienes with [π-allylPdCl]$_2$ complexes behave quite differently in their dynamic *syn* $\rightleftharpoons$ *anti* interconversions. The insertion product formed from [π-2-chloroallylPdCl]$_2$ and isoprene provides a typical example As prepared in benzene at 20°C the complex exists once again as a mixture of *syn*-methyl (*anti*-chloro) and *syn*-chloro (*anti*-methyl) isomers (IX, X). Variable-temperature ^{1}H-NMR experiments have shown[7] that exchange of *syn* and *anti* positions occurs preferentially at the substituted allylic carbon atom, indicating that in the transition state the σ-bond is formed preferentially to the substituted carbon atom. The relatively low barrier isomerisation ($\Delta G^{\ddagger} = 17.3$ kcal.mole^{-1} for the case cited) has been interpreted in terms of the intramolecular chelated transition state XI which allows for retention of the preferred coordination number of four of the palladium atom *at all stages* of the rotation about C^2–C^3. Note, also, that the chelate ring is five-membered and therefore much less strained than in the case described above



IX



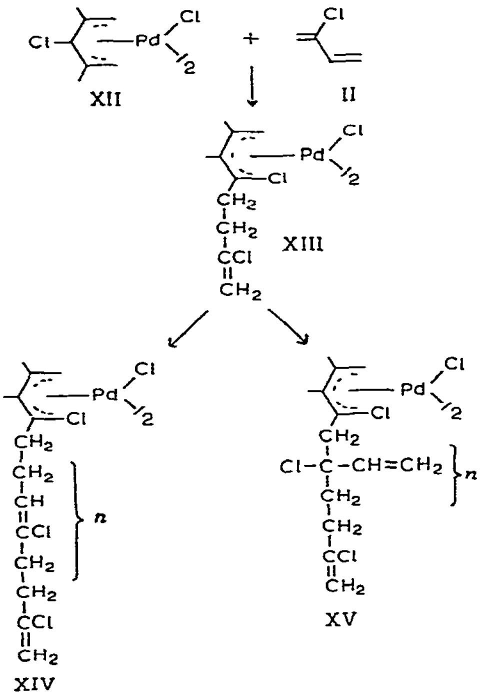
X



XI

The mechanisms of the *syn* $\rightleftharpoons$ *anti* interconversions in the differently constituted π-allyl complexes have important implications for the mechanism of the insertion process. It has been postulated by other workers that a primary step in the insertion process is coordination of the reactant diene by one of its double bonds. According to Medema et al.[2] this is the rate-determining step in the overall reaction. However, Hughes and Powell[8] have shown that coordination of diene is a rapid step and that it is the actual insertion step that is rate-determining. They further point out a correlation between the life-time of the σ-allyl intermediate (in *syn* $\rightleftharpoons$ *anti* exchange) and the rate of product formation, the longer lived the σ-intermediate, the faster the reaction rate We therefore expect that insertion occurs when the allyl complex is in its σ-bonded form, and that the diene joins to the allylic carbon atom which is not σ-bonded. A possible intermediate for the case of the first insertion step is V. Note that the diene enters the allyl moiety at its substituted end.

The mode of addition of diene in the second and subsequent insertion steps is expected to be different, i.e. to the unsubstituted end of the allyl, because as shown above, the σ-bond in the intermediate in the *syn* $\rightleftharpoons$ *anti* exchange is to the substituted carbon atom. Thus, for the case of reaction of $[\pi\text{-2-chloroallylPdCl}]_2$, XII, with 2-chlorobutadiene, II, the expected product is XIII. Further insertions will yield a



product XIV having a linear chain of repeating unit $-[CH_2-CH=CCl-CH_2]-$ containing one trisubstituted olefinic function and four aliphatic protons to every olefinic proton. If the diene were to add to the substituted end of the allyl group (as in the first insertion step) the branched chain product XV would result. Here, further insertions would produce a repeating unit of $-[CCl(CH=CH_2)-CH_2]-$ containing one vinylic double bond and an aliphatic olefinic proton ratio of 2 3. (These considerations assume that 2-chlorobutadiene joins to the allyl group via the C^1 carbon atom. This appears to be so in practice.) The two modes of diene addition represent 1,4- and 1,2-addition respectively. It is possible to distinguish between them by means of ^{1}H-NMR and IR spectroscopy Figure 2(a) shows the ^{1}H-NMR spectrum of compound XIII. The presence of *syn* and *anti* isomers can once again be clearly seen in the resonances of the allylic protons. Figure 2(b) shows the spectrum of a multiple insertion

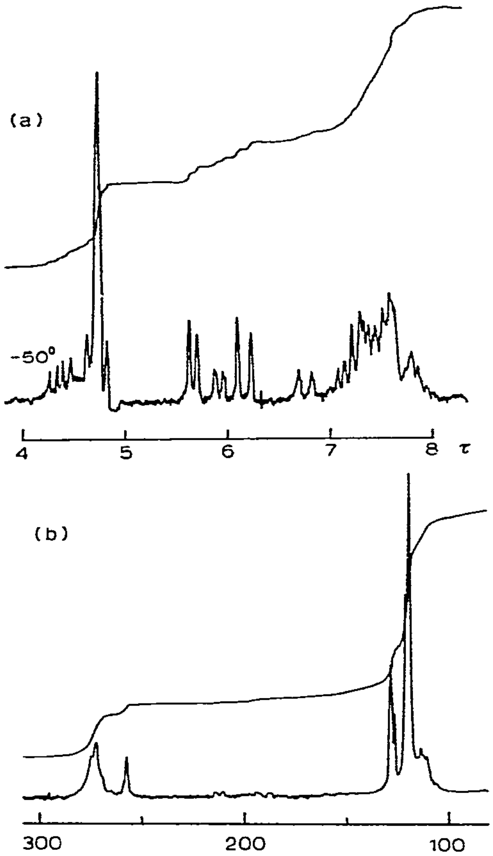


Fig. 2. The ^{1}H-NMR spectra in $CDCl_3$ of (a) compound XIII at 50° and (b) of compound XIV at 27°.

product obtained from the same reaction system. Several differences may be noted (*1*) the appearance of a new resonance at τ4.55 attributable to the proton in the olefinic function $-CH{=}CCl-$, (*2*) the reduced intensity of the signals due to the vinylic protons at τ4.8, (*3*) the reduced intensity of the two terminal allylic protons, between τ5 6 and τ7.0, and (*4*) the increased intensity of the aliphatic protons at τ7.0 –τ8.0. Table 1 lists the numbers of different kinds of protons (distinguishable by NMR) in the oligomer as a function of the number of insertion steps for each of the two modes of diene addition Comparison of the NMR integrals of the signals due to the vinylic and olefinic protons centred at τ4.55 and τ4.82, respectively, gives a ratio of 1 4. Since there are two vinyl protons present whatever the degree of oligomerisation this indicates the presence of eight olefinic protons, a result corresponding to an average of nine insertion steps. Similarly, comparison of the integrals of the olefinic and aliphatic proton resonances (τ4.55 and τ7.0–8.0, respectively) indicates the presence of 36 aliphatic protons, a result again corresponding to an average of nine insertion steps in the product. These proton ratios would be quite different (see Table 1) for the alternative mode of addi-

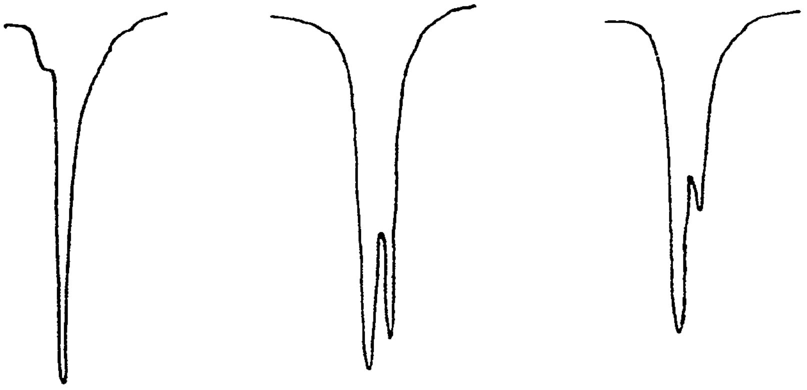
TABLE 1

Numbers of different types of proton in oligomers as function of degree of oligomerisation [Pd(π-Cl-allyl)Cl]$_2$ + 2-Cl-butadiene, where N = no. of diene additions. a = allyl, v = vinyl, o = olefinic and al = aliphatic.

N	Addition to unsubst. C atom of allyl				Addition to subst. C atom of allyl			
	a	v	o	al	a	v	o	al
1	3	2	0	4	3	2	0	4
2	3	2	1	8	3	5	0	6
3	3	2	2	12	3	8	0	8
4	3	2	3	16	3	11	0	10
5	3	2	4	20	3	14	0	12
6	3	2	5	24	3	17	0	14
7	3	2	6	28	3	20	0	16
8	3	2	7	32	3	23	0	18
9	3	2	8	36	3	26	0	20
10	3	2	9	40	3	29	0	22
11	3	2	10	44	3	32	0	24
12	3	2	11	48	3	35	0	26

tion (1,2-addition) in which the diene adds to the substituted end of the π-allyl moiety.

The IR spectra, in the 1500–1700 cm^{-1} region, of the oligomers support the conclusions gained from the NMR spectra. Figure 3(a) is a spectrum of the first insertion product, XIII The single band at 1640 cm^{-1} is characteristic of the carbon–carbon stretching frequency of the chlorovinyl $-CCl{=}CH_2$ group. Spectrum (c) of Fig 3 is of the same oligomer (XIV) whose NMR spectrum is given in Fig. 2(b) Here, the

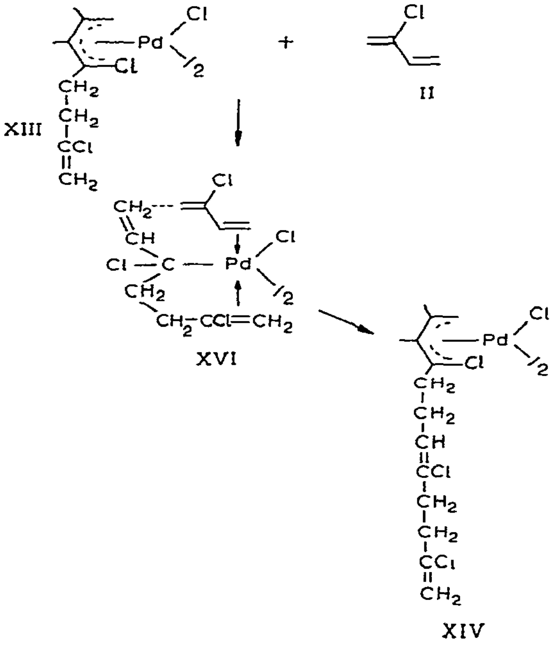


(a) (b) (c)

Fig. 3. The infrared spectra (KBr pellets and thin films) of (a) compound XIII, (c) compound XIV and (b) an oligomer of intermediate chain length.

1640^{-1} band has greatly diminished in intensity at the expense of a new band at 1660 cm^{-1} characteristic of a non-terminal double bond, –CH=CH– or –CH=CCl– Spectrum (b) of Fig. 3 is of a fraction eluted from the column separation of the reaction products of [π-2-chloroallylPdCl]$_2$ and 2-chlorobutadiene after the multiple insertion product already referred to but before the first insertion product Here, the relative intensities of the 1640 and 1660 cm^{-1} absorptions indicate, as expected, that this material is an oligomer of intermediate chain length.

The foregoing results strongly suggest that the same kind of σ-allylic intermediate which provides a pathway for *syn* ⇌ *anti* exchange or isomerisation also plays a part in an initial stage in the insertion reaction. A further related inference is that the mode of diene addition is controlled by the lower energy σ-allylic intermediate. For the first insertion step we have seen that this is one in which the σ-bond is to the unsubstituted carbon atom, whereas in subsequent steps the σ-bond is to the carbon atom having a potentially coordinating alkenyl group in the substituent chain A possible intermediate for the second insertion step in that shown in XVI. Certain features of the proposed intermediate are, of course, speculative. For example, it assumes a coordination number of five without rupture of metal–chlorine bonds. However, it does indicate correctly how the diene becomes linked to the unsubstituted end of the allylic group. A five-coordinate intermediate also suggests a possible explanation for the apparently reduced reaction rate for second and subsequent insertion steps compared to the first.



In the σ-intermediate XVI, suggested for *syn* ⇌ *anti* isomerisation of the insertion product, coordination of the alkenyl group in a five-membered chelate ring will satisfy the coordination number four of the palladium atom more effectively than will the allylic double bond of intermediate V proposed for the reactant π-allyl. Thus, the affinity of the palladium atom for coordinating a solute diene (an assumed necessary first step to addition) might well be less in the former case

While our results to date accord without exception to the view that the occurrence of an alkenyl group in the π-allyl substituent chain of the insertion products directs the incoming diene to add to the other end of the π-allyl group there is no particular reason to believe that this need always be the case Rather, it is to be expected that this is merely one among other unexplored influences that the reacting π-allyl and diene are subject to. In this connection we note that Medema et al.[2] have reported the isolation of 5-ethylnonane on hydrogenation of the insertion products of butadiene with $[\pi\text{-allylPdCl}]_2$, a result which indicates addition of the second butadiene molecule to the substituted π-allylic carbon atom in this case These and related reactions are under continuing investigation and will be reported in greater detail elsewhere

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