Journal of Organometallic Chemistry, 66 (1974) 465–473

METAL π-ALLYL CHEMISTRY

III*. THE PREPARATION OF π-ALLYLPALLADIUM COMPLEXES FROM PALLADIUM(II) SALTS

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(Received July 9th, 1973)

Summary

A number of routes for the preparation of π-allylpalladium complexes from palladium(II) salts were investigated with a view to obtaining a quantitative yield. Quantitative yields were obtained rapidly when a stream of ethylene was passed through an aqueous solution of Na_2PdCl_4 and the allylic chloride, and more slowly on vigorously shaking an aqueous solution of Na_2PdCl_4 with a 3-fold excess of allyl chloride.

Spectroscopic evidence is presented to confirm that the first stage of the reaction of allylic compounds with palladium(II) salts involves the formation of an olefinic complex. It is found that such palladium(II)—olefin complexes of $CH_2{=}CH{-}CH_2{-}X$ are very much less susceptible to nucleophilic attack when $X = Cl$ than when $X = C_5H_{11}$, OH or OAc, which are all attacked rapidly by nucleophilic solvents, such as methanol, with deposition of palladium metal.

Introduction

The principal object of the present work was to attempt to find routes for the preparation of π-allylpalladium complexes in quantitative yield with a minimum of side products. It was decided first to investigate the use of palladium(II) salts as starting materials. Previous workers have shown that palladium(II) salts such as $PdCl_2$ or Na_2PdCl_4 yield π-allylpalladium chloride on treatment with allyl alcohol [1 - 3] or allyl chloride together with either water [4,5] or a reducing agent such as carbon monoxide [6,7] or stannous chloride [8] or a primary amine and carbon monoxide [9]. In addition π-allylic complexes substituted by an alkyl or aryl group at the central carbon atom can be

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formed by treating Na_2PdCl_4 in glacial acetic acid with a solution of the appropriate hydrocarbon olefin in the presence of sodium acetate [10].

Investigations of the mechanisms of the reactions with allyl alcohol [2,3] and allyl chloride in the presence of reducing agents [7 - 9] have shown that an essential step in the reaction involves the reduction of palladium(II) to palladium(0) at the expense of the organic species present. We have confirmed that water is essential in order to promote the formation of π-allylpalladium chloride from allyl chloride and either Na_2PdCl_4 or $[(PhCN)_2PdCl_2]$. Furthermore the role of the water is to take part in oxidative hydrolysis of the initially formed palladium(II)—allyl chloride π-olefin complex yielding palladium(0) and CH_3COCHO as the principal organic component. The palladium(0) then reacts by oxidative addition with further allyl chloride to yield π-allylpalladium chloride. During the course of this work a similar mechanism was postulated independently by Jira and Sedlmeier [11] and accordingly in the present work we have focussed our attention on providing evidence for the formation of the initial π-olefin complex.

Experimental

$PdCl_2$ and Na_2PdCl_4 were prepared from K_2PdCl_4 as follows: A solution of K_2PdCl_4 (0.5 g) in water (50 ml) was passed through a BioRad AG50W-X8 cation exchange resin in the acid form and eluted with water. The H_2PdCl_4 eluent was then concentrated and dried to give purple $PdCl_2$ in 95% yield. Na_2PdCl_4 was prepared similarly in 90% yield using the cation exchange resin in the sodium form. The failure to obtain 100% yields is attributed to some covalent bonding between $[PdCl_4]^{2-}$ anions and the resin analogous to that observed previously between this resin and $[PtCl_4]^{2-}$ anions [12].

Thoughout this work the methanol used was that supplied by B.D.H. as specially dried for Karl—Fischer titrations. The acetic acid was of analytical reagent grade and was used without further purification. Allyl acetate was prepared from allyl chloride and silver acetate and like allyl chloride and allyl alcohol was fractionally redistilled before use. Ethylene was dried by slow passage through an acetone/carbon dioxide trap.

Preparation of π-allylpalladium chloride

(i). In water. A solution of Na_2PdCl_4 (0.1068 g; 0.362 mmole) in water (12 ml) was vigorously shaken with allyl chloride (0.187 g; 2.44 mmole). The initial brown colour changed to yellowish-green and after an hour a yellowish-green precipitate was formed. After 16 h the solution was evaporated to dryness and extracted with benzene, which left a white solid (sodium chloride). Careful evaporation of the benzene yielded yellowish-green $[(\pi\text{-}C_3H_5)PdCl]_2$ (0.0660 g) in 99.5% yield based on Na_2PdCl_4. Methallyl chloride reacted similarly, although more slowly, taking 8 h to yield an initial precipitate of π-2-methylallylpalladium chloride. After 16 h a 100% yield of $[(\pi\text{-}C_4H_7)PdCl]_2$ was obtained.

(ii). In water in the presence of ethylene. Two routes were used: *(a)* A degassed solution of Na_2PdCl_4 (0.1350 g; 0.458 mmole) in water (20 ml)

under nitrogen was cooled to just above 0°. Ethylene, presaturated with allyl chloride, was then bubbled through the solution until a yellowish-green precipitate was deposited (after 1 h). A GLC trace of the aqueous solution on a 2 m glass column packed with diatomite coated with polypropyleneglycoladipate (15% w/w) that had been previously calibrated using methylethylketone as the internal standard indicated a yield of acetaldehyde of 98% based on palladium. Isolation of π-allylpalladium chloride by extraction from the aqueous solution into chloroform followed by cautious evaporation yielded 0.0835 g of $[(\pi\text{-}C_3H_5)PdCl]_2$, a yield of 99%. (*b*) A degassed solution of Na_2PdCl_4 (0.1430 g; 0.485 mmole) and methallyl chloride (0.2202 g; 2.42 mmole) in water (20 ml) under nitrogen was cooled to just above 0° and vigorously stirred. Ethylene was bubbled in and the reaction proceeded as above, only more rapidly. GLC analysis indicated a yield of acetaldehyde of 98% and the yield of $[(\pi\text{-}C_4H_7)PdCl]_2$ was 100%, both based on Na_2PdCl_4.

(iii). In acetic acid in the presence of ethylene and sodium acetate. Ethylene was bubbled slowly through a stirred solution of Na_2PdCl_4 (0.1766 g; 0.60 mmole) and allyl chloride (0.374 g; 4.89 mmole) in glacial acetic acid saturated with anhydrous sodium acetate (20 ml). After several hours the original red solution became yellowish-green. In early experiments this solution was treated with a mixture of water (to extract the acetic acid) and chloroform (to extract the π-allylic complex) and the chloroform layer separated off, neutralised with sodium carbonate or bicarbonate and cautiously evaporated. Since some decomposition to metallic palladium was observed during the neutralisation, this procedure was modified by evaporating the yellowish-green chloroform solution to dryness under reduced pressure and re-extracting the residue with chloroform. In this way 0.091 g of $[(\pi\text{-}C_3H_5)PdCl]_2$, a yield of 83% based on palladium, was obtained. π-2-Methylallylpalladium chloride was prepared similarly from methallyl chloride in 87% yield.

Spectra and chromatograms

Ultra-violet and visible spectra were recorded on a Unicam SP800 and NMR spectra on a Perkin—Elmer R12. Gas-liquid chromatograms were obtained using a Perkin—Elmer model 452 fitted with a flame ionisation detector.

Results

(i). The interaction of allyl chloride and Na_2PdCl_4 in methanol

Since one of the difficulties of the standard methods for the preparation of π-allylpalladium chloride from Na_2PdCl_4 and allyl chloride is the presence of a two-phase system we investigated the use of methanol as a solvent, firstly because it is possible to dissolve methanol in allyl chloride up to about 55% (v/v), and secondly because palladium(II)—olefin complexes react rapidly with methanol to yield palladium(0) and the corresponding methyl ether in a reaction analogous to the oxidative hydrolysis observed in water. However, although Na_2PdCl_4 reacted rapidly with allyl chloride in dry methanol the product obtained was not the desired π-allylic complex but rather a simple olefin

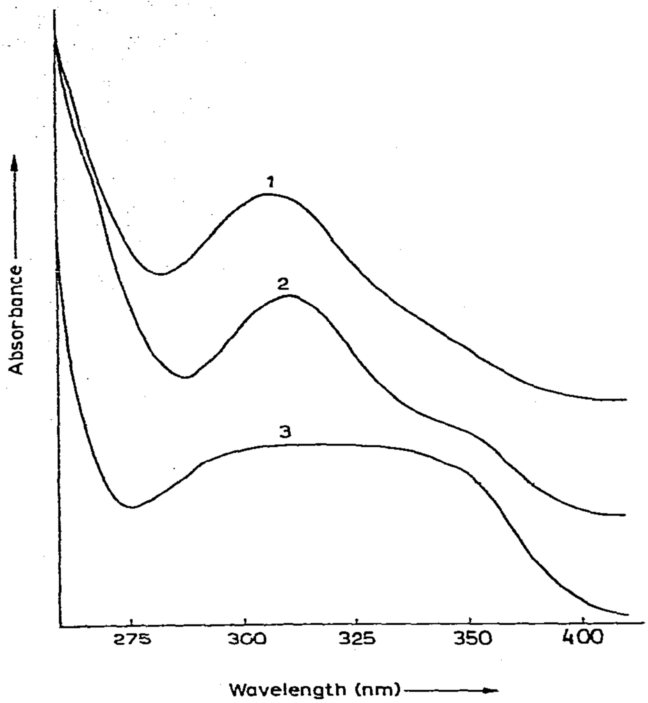

Fig. 1. Ultra-violet and visible spectra: 1. π-olefin complex formed between allyl alcohol and Na_2PdCl_4 in glacial acetic solution. 2. π-Olefin complex formed between allyl chloride and Na_2PdCl_4 in methanol solution. 3. $[(\pi\text{-}C_3H_5)PdCl]_2$ in methanol solution. (Note there is a wavelength scale change at 350 nm.)

complex as shown by comparison of its ultra-violet and visible spectrum with firstly the known spectrum of π-allylpalladium chloride in methanol [13] and secondly the initial product of the reaction of 1-octene with a solution of Na_2PdCl_4 in methanol* (see Fig. 1 and Table 1).

The dry methanolic solution of allyl chloride and Na_2PdCl_4 was stable for at least a week showing no signs of decomposition to palladium metal. Addition of water to this solution yielded either two or three layers depending on the relative proportions of allyl chloride, methanol and water. In both cases the bottom layer was aqueous and the top layer contained allyl chloride; when present the intermediate layer was milky and contained no palladium. Ultra-violet and visible spectroscopy showed that the aqueous layer contained π-allylpalladium chloride whereas the allyl chloride layer contained only the π-olefinic allyl chloride-palladium(II) complex formed in dry methanol. No decomposition to palladium metal was observed. Although this result shows that the initially formed allyl chloride-palladium(II) π-olefin complex is susceptible to nucleophilic attack by water to yield π-allylpalladium chloride, and thus provides strong supporting evidence for Jira and Sedlmeier's mechanism

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[*] The spectrum of the 1-octenepalladium(II) complex in methanol was obtained in sections using the rapid scanning mode of a Unicam SP800 spectrophotometer. Decomposition to palladium metal was noticeable within one minute and complete within about four minutes at room temperature.

TABLE 1

THE ULTRA-VIOLET AND VISIBLE SPECTRA (250—550nm) OF PALLADIUM(II)—OLEFIN AND —π-ALLYL COMPLEXES

Olefin	Solvent	Peaks (nm)
Olefin complexes		
1-Octene	MeOH	315, 430(sh)
1-Octene	CH_3COOH	306, 430(sh)
$CH_2=CHCH_2Cl$	MeOH	311, 350(sh), 430(sh)
$CH_2=CHCH_2Cl$	CH_3COOH	292, 340(sh), 420(sh)
$CH_2=CHCH_2OH$	MeOH	310, 350(sh), 440(sh)
$CH_2=CHCH_2OH$	CH_3COOH	312, 345(sh), 435(sh)
$CH_2=CHCH_2OAc$	MeOH	325, 440(sh)
$CH_2=CHCH_2OAc$	CH_3COOH	305, 345(sh), 440(sh)
π-Allylpalladium complexes		
$[(\pi\text{-}C_3H_5)PdCl]_2$	MeOH	290, 335
$[(\pi\text{-}C_3H_5)PdCl]_2$	CH_3COOH	305, 335
$[(\pi\text{-}C_3H_5)Pd(OAc)]_2$	MeOH	325(sh)
$[(\pi\text{-}C_3H_5)Pd(OAc)]_2$	CH_3COOH	328(sh)

[11], preparatively this route offers no advantages for the synthesis of π-allylpalladium chloride over the classical synthesis in 50% aqueous acetic acid solution [5] in that the yields of the two routes are comparable.

(ii). The interaction of allyl alcohol and allyl acetate with Na_2PdCl_4 in methanol

Solutions of allyl alcohol and allyl acetate in methanol or isopropanol reacted with Na_2PdCl_4 to give π-olefin complexes, as shown by their ultraviolet and visible spectra which were virtually identical to that of a solution of 1-octene and Na_2PdCl_4 in methanol. Both the allyl alcohol and the allyl acetate solutions decomposed to palladium metal after a few minutes. Thus the chloride group in allyl chloride appears to stabilise the palladium(II)—allyl chloride π-olefin complex to nucleophilic attack by methanol whereas the hydroxyl, acetate and pentyl (in 1-octene) groups permit nucleophilic attack to occur rapidly.

(iii). The interaction of allyl chloride and palladium(II) in acetic acid

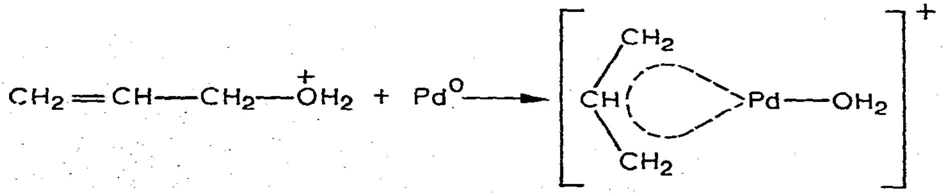
Since methanol was apparently insufficiently nucleophilic to react with the palladium(II)—allyl chloride π-olefin complex, it was decided to investigate the reaction between allyl chloride and palladium(II) in acetic acid using sodium acetate as the nucleophile. Acetic acid is a good solvent for both allyl chloride and Na_2PdCl_4 (which it dissolves to give a mixture of Na_2PdCl_4 and $Na_2Pd_2Cl_6$ [14]) and might therefore be expected to induce high yields of the π-allylic complex. Although water does not readily react with palladium(II)—olefin complexes in acetic acid [14,15] sodium acetate does; in the case of simple olefins such as ethylene or propene the olefin is oxidised and palladium(II) reduced to the free metal [16], whereas with 2-substituted propenes [$CH_2=C(R)CH_3$] the olefin is converted to the π-allylic complex [10]

$[(\pi\text{-}2\text{-R—C}_3H_4)PdCl]_2$. Treatment of a solution obtained by dissolving Na_2PdCl_4 in acetic acid with allyl chloride yielded a solution whose ultra-violet spectrum was similar to that of the π-olefinic complex of palladium(II) and allylic chloride in methanol except that the high energy peak at 311 nm in methanol was shifted to 292 nm in acetic acid. On addition of anhydrous sodium acetate to this solution the colour lightened dramatically and a spectrum with only one broad band at 315 nm was obtained. This spectrum was totally different to that of either $[(\pi\text{-}C_3H_5)PdCl]_2$ or $[(\pi\text{-}C_3H_5)Pd(OAc)]_2$ [17] wich were recorded for comparison (see Table 1). However it was very similar to the spectrum obtained when a solution of Na_2PdCl_4 in acetic acid was treated with allyl acetate, suggesting that the allylic chloride group was being replaced by acetate, a reaction that is known to be catalysed by palladium(II) complexes [18]. On either standing at room temperature overnight or on refluxing some decomposition to metallic palladium occurred.

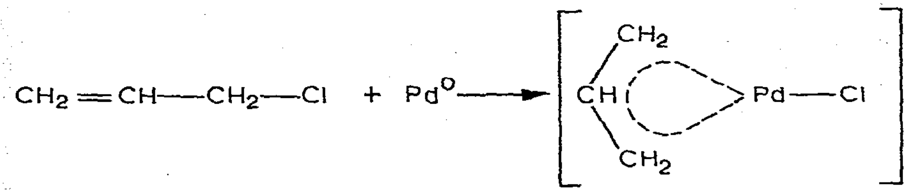
(iv). The interaction of allyl alcohol and palladium(II) in acetic acid

When allyl alcohol was added to a solution obtained by dissolving Na_2PdCl_4 in glacial acetic acid an immediate lightening of the colour occurred and the ultra-violet and visible spectrum (see Fig. 1) indicated that an olefin complex had been formed. On standing overnight the colour lightened still further, a small amount of metallic palladium was deposited and a gas (propene) was liberated. The spectrum then indicated that palladium was present as $[(\pi\text{-}C_3H_5)PdCl]_2$. However on attempting to isolate the product by evaporation to dryness under reduced pressure extensive decomposition to palladium metal occurred so that the method is of little preparative value.

The formation of $[(\pi\text{-}C_3H_5)PdCl]_2$ from allyl alcohol and Na_2PdCl_4 in glacial acetic acid is perhaps not surprising in view of its formation from allyl alcohol and Na_2PdCl_4 in 50% aqueous acetic acid [1] or in the absence of any added solvent [3]. However it is in contrast to the rapid reduction of Na_2PdCl_4 to palladium metal by allyl alcohol in methanol or in water at neutral pH. π-Allylpalladium chloride may well be formed in glacial acetic acid as a consequence of the base-strengthening properties of this solvent [19] which enable it to protonate the allyl alcohol to yield $CH_2{=}CHCH_2OH_2{}^+$. This can then react with the palladium(0) that has been formed by the reduction of Na_2PdCl_4 by allyl alcohol to yield the π-allylic palladium complex by an oxidative-addition reaction (reaction 1) analogous to that observed for the reaction of allyl chloride with palladium(0) (reaction 2).



(1)



(2)

(v). The interaction between allyl chloride and Na_2PdCl_4 in the presence of ethylene

Since previous work has suggested that the formation of π-allylic complexes from allyl chloride and palladium(II) involves the intermediate formation of palladium(0) attempts were made to generate the palladium(0) in situ by bubbling ethylene into solutions of Na_2PdCl_4 containing nucleophiles.

Thus when ethylene was bubbled through the solution obtained by dissolving Na_2PdCl_4, allyl chloride and anhydrous sodium acetate in acetic acid, the initial orange colour gradually became greenish-yellow and on work-up π-allylpalladium chloride was obtained in 83% yield. Our initial procedure for isolating the π-allylic complex, which involved treating the acetic acid with a mixture of chloroform and water, separating off the chloroform layer, neutralising it with sodium carbonate or bicarbonate and then evaporating off the chloroform layer, was unsatisfactory because the addition of either sodium carbonate or bicarbonate, which was necessary in order to neutralise the acetic acid, caused some decomposition. Accordingly the π-allylic products were isolated by evaporating the chloroform solution to dryness under reduced pressure at temperatures below 40° and extracting the residue into either chloroform or benzene.

In an attempt to improve the 83 - 87% yield obtained in acetic acid the use of water was investigated. Two approaches were used and both gave virtually quantitative yields. In the first a stream of dry ethylene saturated with the allylic chloride was bubbled through a solution of Na_2PdCl_4 in water and in the second, which was the more rapid, the allylic chloride was added to the reaction flask as the neat liquid and then dry ethylene was bubbled in with vigorous stirring. Both allyl chloride and methallyl chloride gave π-allylic complexes in 99 - 100% yield based on palladium. GLC analysis of the solution showed that 1 mole of acetaldehyde was formed per mole of palladium(II) initially present indicating that the reaction involved the quantitative reduction of palladium(II) to palladium(0) (reaction 3) followed by oxidative-addition of the allylic chloride to palladium(0) (reaction 4).

$$C_2H_4 + H_2O + Na_2PdCl_4 \rightarrow CH_3CHO + Pd^0 + 2NaCl + 2HCl \qquad (3)$$

$$2\,Pd^0 + 2\,CH_2{=}CHRCH_2Cl \xrightarrow{(R = H,\, CH_3)} [(\pi\text{-}R{-}C_3H_4)PdCl]_2 \qquad (4)$$

An attempt to prepare π-allylpalladium chloride in methanolic solution by reducing Na_2PdCl_4 with ethylene failed to give reasonable yields. This was because, although Na_2PdCl_4 was reduced rapidly by the ethylene (cf. reaction 3) and subsequent oxidative addition of allyl chloride to palladium(0) occurred (reaction 4), the π-allylic complex was unstable in methanol and decomposed to palladium metal during the work-up.

(vi). The interaction between allyl chloride and Na_2PdCl_4 in water

An alternative, but rather slower, preparation of π-allylpalladium chloride in virtually quantitative yield involved vigorously shaking an aqueous solution of Na_2PdCl_4 with a 3-fold excess of allyl chloride. Methallyl chloride reacted similarly although more slowly to yield π-2-methylallylpalladium chloride. Part of the success of these routes was due to the work-up procedure. Instead of following previous workers and filtering off the product directly [11] and consequently losing some due to the appreciable solubility of π-allylpalladium chloride in water, the water was removed under reduced pressure and the solid residue extracted with benzene from which the π-allylic complex was recovered quantitatively.

When a solution of Na_2PdCl_4 in water was treated with allyl alcohol an immediate precipitate of palladium metal was formed, again demonstrating the much higher susceptibility to nucleophilic attack of palladium(II) olefinic complexes of allyl alcohol as compared to allyl chloride. In the presence of hydrochloric acid very little palladium metal was deposited and a smooth reaction between allyl alcohol and Na_2PdCl_4 took place, as observed previously [2], to yield mainly π-allylpalladium chloride.

Conclusions

The present work has provided conclusive evidence that the initial interaction of allylic compounds with palladium(II) salts involves the formation of an olefinic complex. For the formation of a π-allylic complex the palladium(II) must be reduced to palladium(0) and this can be effected either by nucleophilic attack on the allylic π-olefin complex or by the addition of an external reducing agent. Of the external reducing agents reported so far ethylene, as described in the present paper, seems to be the most effective and in combination with water as a solvent gives rise to the formation of π-allylic complexes from allylic chlorides and Na_2PdCl_4 in quantitative yields.

It is tempting to ascribe the resistance to nucleophilic attack of the palladium(II) π-olefinic complex of allyl chloride as compared to the high susceptibilities of the allyl alcohol, allyl acetate and 1-octene complexes, to the considerable electron-withdrawing ability of the chloro-group. However the inductive withdrawing abilities of the allylic substituents (Cl +0.47, $CH_3OCO \approx +0.32$, OH +0.25, alkyl ≈ -0.05)* suggest that such an explanation is probably too simple as they would predict a greater similarity between allyl chloride and allyl acetate than between allyl acetate and 1-octene.

Our earlier observations that acetic acid is a very good solvent for stabi-

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* Obtained from ref. 20. The approximate σ_I values quoted for acetate and alkyl are values actually reported for propionate and methyl respectively.

lizing the palladium(II)—olefin complexes of simple terminal olefins such as 1-octene [21] and also olefin complexes of the allylammonium cation [22] ($CH_2{=}CHCH_2NH_3^+$) have received further support in this work where the palladium(II)—olefin complexes of allyl chloride, allyl acetate and allyl alcohol are all stable with respect to decomposition to palladium metal in acetic acid, although the allyl alcohol-palladium(II) π-olefin complex does react slowly with excess allyl alcohol to yield π-allylpalladium chloride.

Acknowledgements

The authors wish to thank Mr. G.W. Searle for his help in setting up the gas-liquid chromatograph, Dr. D.E. Rogers for the loan of the ion-exchange resin, the S.R.C. for a studentship (to S.R.J.) and Johnson, Matthey and Co. Ltd. for their generous loan of the palladium salts used during this investigation.

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