

New aspects of the carbonylation of allylpalladium complexes

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Abstract

The carbonylation of (η^3 -allyl)palladium(II) chloride dimer in the presence of an excess of ylide, such as $\text{Ph}_3\text{PC}(\text{H})\text{COR}$ ($\text{R} = \text{Me}$ or Ph) ($\text{Pd}:\text{ylide} = 1:5$) in MeOH or EtOH , at a CO pressure of 4 atm at room temperature occurs with reduction of the palladium(II) complex to palladium metal and with formation of the corresponding alkyl 3-butenolate with a high yield. The ylide does not give rise to any carbonylation product. When the carbonylation is carried out in the presence of PPh_3 ($\text{Pd}:\text{PPh}_3 = 1:2-3$), there is also formation of the unsaturated ester, although in lesser amount, together with $[\text{Pd}_3(\text{PPh}_3)_n(\text{CO})_3]$ ($n = 3$ or 4) or $[\text{Pd}(\text{PPh}_3)_2(\text{CO})]$ and *trans*- $[\text{Pd}(\text{PPh}_3)_2(\text{COOR})\text{Cl}]$ ($\text{R} = \text{Me}$ or Et). These products also form when the carbonylation is carried out in the presence of NEt_3 or PrCOONa , in place of the ylide, and of PPh_3 .

It has also been found that $[\text{Pd}(\text{PPh}_3)_2\text{Cl}_2]$ reacts in MeOH or EtOH at a CO pressure of 4 atm at ambient temperature in the presence of an excess of ylide to give the corresponding carbalkoxy complex *trans*- $[\text{Pd}(\text{PPh}_3)_2(\text{COOR})\text{Cl}]$. These findings suggest that the ylide probably promotes formation of carbalkoxy species, as do NEt_3 or PrCOONa because the ylide can behave as a base ($\text{p}K_a \approx 7$). They are strong support for the suggestion that the carbonylation of (allyl)palladium complexes occurs via a (carbalkoxy)palladium species.

Key words: Palladium; Allyl; Carbonylation

1. Introduction

A key step in the catalytic cycle of the reactions that lead to the formation of carbalkoxy-containing organic molecules [1] is the formation of an M-carbalkoxy intermediate or the insertion of CO into an $\text{M}-\text{C}$ σ bond to form an acyl intermediate, which yields the product upon attack of an alcohol [2]. Such M-carbalkoxy species are believed to be involved in the product-forming step of the carbonylation of allyl chloride to butenoate esters catalysed by palladium complexes, in the presence of a base such as a tertiary amine, or of a carboxylate anion [3].

The carbonylation of (η^3 -allyl)chloro or acetato complexes to yield unsaturated esters can be accomplished even under conditions as mild as carbon monoxide pressure of 3 atm at room temperature, if

carboxylic acid anions, such as PrCOO^- are present [4]. In the absence of carboxylate anions the reaction requires more severe conditions, is slow and gives low yields of carbonylation products [3]. Since the carboxylate anions are capable of forming carbalkoxy intermediates with an $\text{M}-\text{COOR}$ bond [5], it has been proposed that the carbonylation reaction occurs via an (allyl)(carbalkoxy)palladium intermediate. Alternatively, the formation of unsaturated esters can occur via insertion of carbon monoxide into the $\text{Pd}-\text{C}$ of the (allyl)palladium moiety. Such an insertion is by η^1 -allyl systems [6].

It has also been found that PPh_3 inhibits the carbonylation reaction, and with $\text{Pd}:\text{PPh}_3 = 1$ both the carbonylation rate and the selectivity for the unsaturated ester are lower [3].

In this work we have extended the study of carbonylation reactions by using an ylide as a base, in order to discover whether the ylide promotes the carbonylation of the allyl or whether it can itself give rise

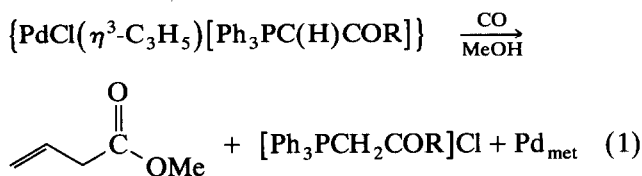
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to any carbonylation product. Ylides are a specific type of base because they can vary their basicity with the substituents on the ylidic carbon atom [7]. In addition, ylides can coordinate to a metal through the methine carbon, forming an M–C(ylide) σ bond [8,9] which, in principle, could undergo insertion of CO.

2. Results and discussion

We carbonylated (η^3 -allyl)palladium(II) chloride dimer in MeOH or EtOH, in the presence of an excess of ylide, such as $\text{Ph}_3\text{PC(H)COR}$ ($\text{R} = \text{Me}$ or Ph) ($\text{Pd}:\text{ylide} = 1:5$) which is known to split the bridged complex to yield $[\text{PdCl}(\eta^3\text{-C}_3\text{H}_5)(\text{Ph}_3\text{PC(H)COR})\text{Cl}]$ [10–12]. In this complex the ylide ligand behaves as a nucleophile and it coordinates to the metal through the ylide carbon atom.

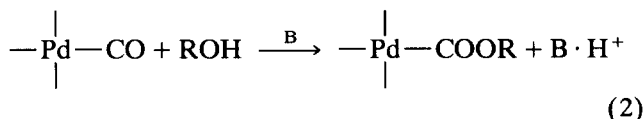
The reaction conditions are reported in Section 3. The product solution contained principally the 3-butenolate ester (52% methyl ester) together with trace amounts of the coupling product 2-propenyl *n*-butyrate. The ^1H and ^{31}P NMR spectra showed the presence of a phosphonium salt in addition to the excess of the free ylide. Thus, even though there is no carbonylation product from the ylide ligand, it promotes the carbonylation of the allyl moiety as do carboxylate anions. The reaction can be depicted as follows:



In addition, we carried out the carbonylation of (η^3 -allyl)palladium(II) chloride dimer in the presence of the ylide and of PPh_3 ($\text{Pd}:\text{PPh}_3 = 1:2$), under the same conditions. The reaction medium contained a brick-red precipitate, whose IR spectrum displayed several $\nu(\text{C}=\text{O})$ bonds at *ca.* 1850–1820 cm^{-1} due to $[\text{Pd}_3(\text{PPh}_3)_{3,4}(\text{CO})_3]$ [13], and $\nu(\text{C}=\text{O})$ at *ca.* 1670 and 1650 cm^{-1} [14,15] owing to the carbalkoxy complex *trans*- $[\text{Pd}(\text{PPh}_3)_2(\text{COOR})\text{Cl}]$ ($\text{R} = \text{Me}$ or Et). GLC/MS analysis of the solution showed only a trace of the unsaturated ester. Thus it appears that PPh_3 prevents the formation of the carbonylation product, probably because the phosphine competes with CO for coordination. When an excess of PPh_3 was employed ($\text{Pd}:\text{PPh}_3 = 1:3$) a mixture of $[\text{Pd}(\text{PPh}_3)_3(\text{CO})]$ [13] and *trans*- $[\text{Pd}(\text{PPh}_3)_2(\text{COOR})\text{Cl}]$ was isolated.

All these findings, together with the fact that in the absence of the ylide the butenoate ester does not form at all, further supports the suggestion that, under the reported conditions, the carbonylation of (allyl)palladium complexes occurs via the (carbalkoxy)palladium

species. The formation of carbalkoxy species is favoured by a base, *e.g.* a tertiary amine or a carboxylate anion [5,13,14,16]. It has been suggested that the role of the base is to neutralize the acid that forms in equilibrium (2) and to increase the concentration of MeO^- which attacks the coordinated CO to form the PdCOOR moiety [17]:



In the present case, it is likely that the ylide plays such a role because of its base properties ($\text{p}K_{\text{a}} = 7.50$ or 6.65 for the methyl or the phenyl phosphonium salts [18] respectively).

Reaction (1) deserves more comment. The only carbonylation product is the unsaturated ester, and there is no formation of dialkyl carbonate or of dialkyl oxalate. These last two products form when $[\text{Pd}(\text{AcO})_2]$ is carbonylated at room temperature in methanol. It has been suggested that the carbonate forms via attack of MeO^- on a species with a $\text{Pd}(\text{COOMe})$ moiety, while the oxalate would form upon reductive elimination from a dicarbomethoxy species, *e.g.* $\text{Pd}(\text{COOMe})_2$ [19]. Thus, if reaction (1) occurs via the intermediacy of a species having a carbalkoxy moiety, it would appear that reductive elimination of the unsaturated ester is faster than nucleophilic attack of RO^- on the carbalkoxy species that could lead to the formation of the carbonate.

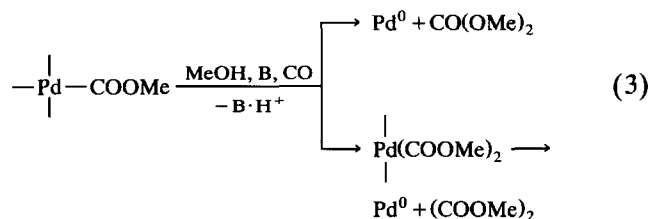
Further support for the suggestion that the carbonylation of allyl complexes of palladium can occur via the formation of carbalkoxy intermediates is as follows. When the (η^3 -allyl)palladium(II) chloride is carbonylated as above but in the presence of NEt_3 rather than the ylide ($\text{Pd}:\text{N} = 1:5$), there is also a significant yield (about 45%) of the butenoate ester. Moreover, when such a carbonylation is carried out in the presence of PPh_3 ($\text{Pd}:\text{PPh}_3 = 1:2\text{--}3$), the palladium precursor gives rise to a mixture of Pd^0 complexes and $[\text{Pd}(\text{PPh}_3)_2(\text{COOR})\text{Cl}]$ and the butenoate ester forms in trace amounts.

Analogous results are obtained when the carbonylation of the (η^3 -allyl)palladium(II) chloride– PPh_3 system ($\text{Pd}:\text{P} = 1:2\text{--}3$) is carried out in the presence of $^n\text{PrCOONa}$ in place of the ylide or of NEt_3 . When the carbonylation is carried out in the presence of a smaller amount of PPh_3 ($\text{Pd}:\text{PPh}_3 = 1:1$), the butenoate ester forms in significant amounts, together with coupling product allyl butanoate (41% and 47% respectively [3]).

It has also been reported that carbalkoxy complexes of the type *trans*- $[\text{Pd}(\text{PPh}_3)_2(\text{COOR})\text{Cl}]$ can be synthesized by carbonylating *trans*- $[\text{Pd}(\text{PPh}_3)_2\text{Cl}_2]$ suspended

in an alkanol in the presence of a base such as NEt_3 [14,16] or PrCOO^- [20]. We have found that these complexes ($\text{R} = \text{Me}$ or Et) can also be synthesized when $\text{trans-[Pd(PPh}_3)_2\text{Cl}_2]$ is carbonylated in the presence of the ylide ($\text{Pd}:\text{ylide} = 1:5$; $P_{\text{CO}} = 4$ atm; 30 min) in place of NEt_3 or PrCOO^- . Moreover, we have found that $\text{trans-[Pd(PPh}_3)_2(\text{COOMe})\text{Cl}]$ suspended in MeOH reacts with CO (40 atm) at $95\text{--}100^\circ\text{C}$ in the presence of the ylide ($\text{Pd}:\text{ylide} = 1:5$) to give dimethyl carbonate, together with trace amount of dimethyl oxalate, and Pd^0 complexes of the type $[\text{Pd}_3(\text{PPh}_3)_n(\text{CO})_3]$ ($n = 3$ or 4) or $[\text{Pd}(\text{PPh}_3)_3(\text{CO})]$ when the reaction is carried out also in the presence of PPh_3 ($\text{Pd}:\text{PPh}_3 = 1:3$).

These observations are similar to those observed when $\text{trans-[Pd(PPh}_3)_2(\text{COOMe})\text{Cl}]$ is allowed to react with CO under the same conditions, but in the presence of NEt_3 in place of the ylide [15,17]. Since $\text{trans-[Pd(PPh}_3)_2(\text{COOMe})\text{Cl}]$ is stable in the absence of NEt_3 even under these rather severe conditions, it has been suggested that the base exerts a promoting role by increasing the concentration of the nucleophile MeO^- that attacks the carbomethoxy ligand with formation of the carbonate [15,17]. Thus it appears that the ylide also acts as a base in promoting the following reaction:



3. Experimental details

3.1. Materials

Carbon monoxide was purchased from the S.I.O. Company. The solvents, NEt_3 and ${}^n\text{PrCOONa}$ were commercial grade. $[\{\text{Pd}(\eta^3\text{-C}_3\text{H}_5\text{Cl})_2\}]$ [21], $\text{trans-[Pd(PPh}_3)_2\text{Cl}_2]$ [22] and $\text{trans-[Pd(PPh}_3)_2(\text{COOR})\text{Cl}]$ [15] were prepared as reported in the literature.

3.2. General procedure

The carbonylation reactions were carried in a magnetically stirred glass bottle placed into a stainless steel autoclave, previously purged with CO . For reactions above room temperature the autoclave was placed in a heated oil bath. The working temperature was reached in about 15 min.

IR spectra were recorded on a Perkin-Elmer model 683 spectrometer. The ${}^1\text{H}$ NMR spectra were recorded

on a Bruker 200 AC spectrometer in CD_2Cl_2 , using TMS as internal standard. ${}^{31}\text{P}$ NMR spectra were recorded on a Varian FT 80 A instrument.

GC analysis was performed using a Hewlett-Packard gaschromatograph model 5890 series II, equipped with a HP 3396 series II integrator, using a $30\text{ m} \times 0.53\text{ mm} \times 1.0\ \mu\text{m}$ HP-FFAP (cross-linked FFAP) column, with helium as carrier gas.

The carbonylation reactions were carried out using a magnetically stirred stainless autoclave thermostatted in an oil bath.

3.3. Carbonylation of $[\{\text{Pd}(\eta^3\text{-C}_3\text{H}_5\text{Cl})_2\}]$

The dimer (37 mg, 0.2 mmol) and the ylide (318 mg, 1 mmol) dissolved in MeOH or EtOH (5 ml) were allowed to react with carbon monoxide (4 atm) at room temperature for 30 min. The black suspension of palladium metal was filtered off. The solution was analysed by GC and NMR spectroscopy.

When the carbonylation was carried out in the presence of PPh_3 ($\text{Pd}:\text{PPh}_3 = 1:2\text{--}3$) following this procedure, the reaction medium contained a brick-red or pink precipitate. After filtering, the solution was analysed by GC and NMR spectroscopy. The IR spectrum of the precipitate showed the presence of $[\text{Pd}_3(\text{PPh}_3)_n(\text{CO})_3]$ ($n = 3$ or 4) or $[\text{Pd}(\text{PPh}_3)_3(\text{CO})]$ together with $\text{trans-[Pd(PPh}_3)_2(\text{COOR})\text{Cl}]$. Analogous results were obtained when employing NEt_3 or ${}^n\text{PrCOONa}$ in place of the ylide.

3.4. Carbonylation of $\text{trans-[Pd(PPh}_3)_2\text{Cl}_2]$ in ROH ($\text{R} = \text{Me}$ or Et) in the presence of the ylide

The title complex (140 mg, 0.2 mmol) and $\text{PPh}_3\text{CHCOCH}_3$ (320 mg, 1 mmol) suspended in 5 ml of ROH were allowed to react with CO (4 atm) for 30 min at room temperature. The white-cream suspension was filtered. The solid was identified by IR spectroscopy as $\text{trans-[Pd(PPh}_3)_2(\text{COOR})\text{Cl}]$ (ca. 70% yield), together with small amounts of the starting complex. The solution analysed by GC did not show the presence of carbonate in an appreciable amount.

3.5. Carbonylation of $\text{trans-[Pd(PPh}_3)_2(\text{COOMe})\text{Cl}]$ in MeOH in the presence of the ylide

The title complex suspended in MeOH was pressurized with 40 atm of CO at 100°C for 2 h in the presence of $\text{PPh}_3\text{CHCOCH}_3$ ($\text{Pd}:\text{ylide} = 1:5$, molar ratio) and of 2 mol of PPh_3 per Pd atom. After cooling, the white-cream suspension was filtered. The solution showed the presence of dimethyl carbonate (ca. 70% yield with respect to the starting complex). The IR spectrum of the solid showed the presence of $[\text{Pd}(\text{PPh}_3)_3(\text{CO})]$ and of some unreacted carbomethoxy complex. In the absence of the ylide, the carbonate

formed only in trace amounts and the starting complex was recovered unreacted.

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