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REACTIONS OF π-ALLYLIC COMPLEXES OF PALLADIUM WITH METHYL FORMATE

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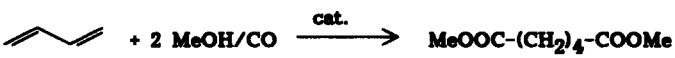
Summary

The reaction of methyl formate with various π-allylic palladium complexes is reported. Unsaturated carboxylic acid esters are formed in high yield and selectivity. A comparison of the reactivity of methyl formate with that of the hydroesterification substrate CH_3OH/CO reveals that methyl formate gives rise to a different product pattern. The addition of PPh_3 gives a new π-methallyl palladium complex $C_4H_7Pd(PPh_3)(CO_2CH_3)$, which is discussed as a model for the key intermediate in the reaction of π-allylic palladium complexes with methyl formate and with CH_3OH/CO.

Introduction

Research on C_1 chemistry, particularly for CO-based organic syntheses, has been of considerable interest in recent years. Various C_1 building blocks, among them methyl formate, have been forwarded as sources for CO/H_2 and CH_3OH/CO [1 - 5]. Lately, special attention has been devoted to the hydroesterification of butadiene, yielding the methyl ester of adipic acid according to eqn. (1), a reaction which is close to industrial realization [6].



(1)

It is believed that this reaction involves π-allylic complexes as intermediates. However, there is no general agreement on the elemental reaction steps involved [7].

We have demonstrated that methyl formate can be used instead of MeOH/CO in eqn. (1) [8], and we therefore became interested in the reaction of π-allylic complexes of palladium with methyl formate, a reaction which has attracted only little attention. The related reaction of π-allylic palladium complexes with alcohol/CO is long known (eqn. (2)), but for a long time was less useful because high CO pressures and high temperatures were required to give carbonylation products in low yields [9].

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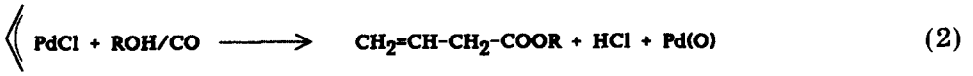


(2)

A breakthrough occurred when Milstein reported that in the presence of carboxylate salts a low pressure, low temperature carbonylation is feasible [10].

In this paper, we report results of reacting various π-allylic complexes of palladium with methyl formate. Results are also given to allow comparison of the reactivities of MeOH/CO and $HCOOCH_3$.

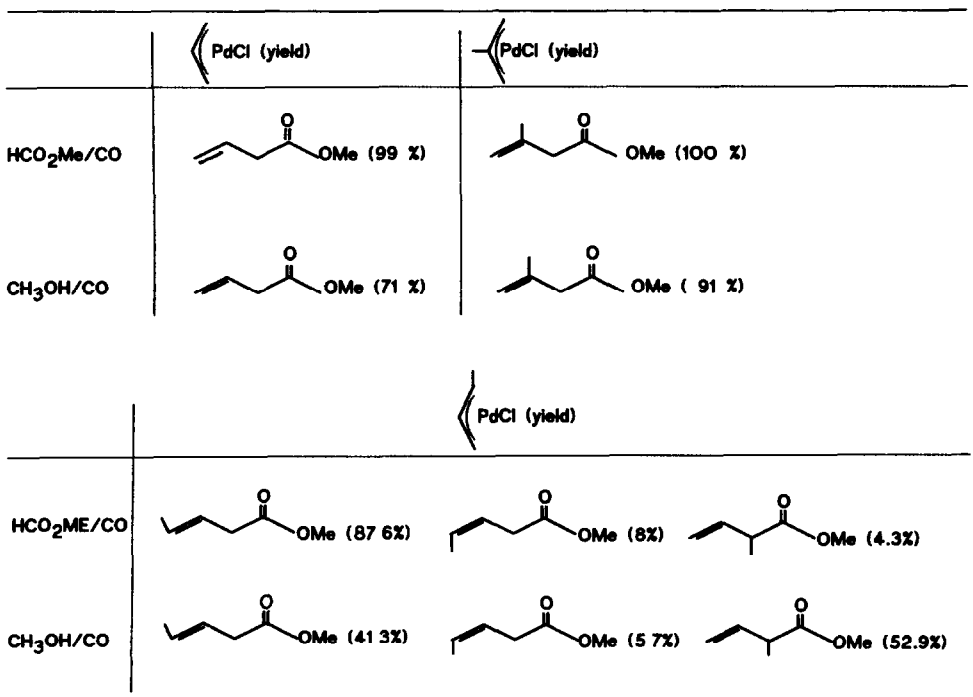
Results and discussion

Attempts to react π-allyl palladium chloride complexes with methyl formate revealed that for reaction to occur a nucleophile and additional, free CO must be present. If no CO is added, a rapid reduction of the Pd(II) complexes occurs, giving metallic palladium. This reduction has been used to prepare Pd(0) complexes [11].

Table 1 lists the results obtained by applying various π-allylic complexes of palladium. Under very mild conditions high yields of esters are

TABLE 1

Hydroesterification of different allylic systems[a]



[a] 25 °C; $P(CO)$ = 3.5 bar; t = 2 h; 0.25 mmol Pd complex, 8 ml HCO_2Me(MeOH); 2.5 mmol Na butyrate.

observed. Interestingly, the linearity of the esters obtained by reacting crotyl complexes amounts to 95%. For comparison, Table 1 contains the data found using MeOH/CO instead of methyl formate under otherwise identical conditions. As can be seen, the use of MeOH/CO gives slightly lower yields and the differences observed are small. However, with π-crotyl palladium chloride a branched ester is formed in about 53% yield when using CH_3OH/CO. Here methyl formate yields predominantly the linear ester. This appears noteworthy, because it implies that methyl formate reacts quite differently than MeOH/CO in hydroesterification reactions. It also suggests that methyl formate does not react via transformation to MeOH/CO according to eqn. (3).

$$HCO_2CH_3 \xrightarrow{\text{"Pd"}} CH_3OH + CO \qquad (3)$$

In this connection it appeared of interest to use various formates (HCOOR, R = ethyl, n-butyl, n-hexyl). Starting from π-methallyl palladium chloride, the yields to the corresponding esters decreased from 100% (R = Me) to 75% (R = ethyl), 45% (R = n-butyl) and to 35% (R = n-hexyl).

Use of different nucleophiles

The hydroesterification of π-methallyl palladium chloride was carried out using carboxylates (Fig. 1) and alkoxides (Fig. 2) as nucleophiles. The ester formation is quantitative with basic carboxylates; butyrate gave the best results. Alkoxides of low basicity such as phenoxide also gave excellent results. This is in contrast to the results of Milstein, who reported that practically no reaction occurs with alkoxides [10]. It is crucial to carry out the

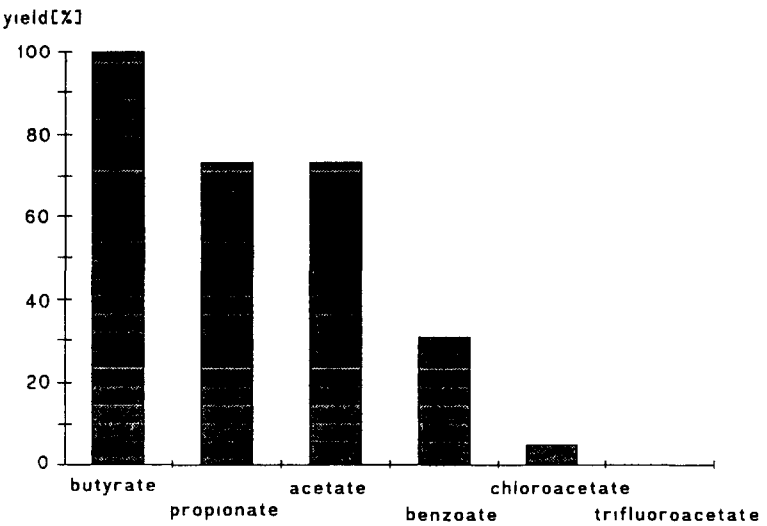


Fig. 1. Hydroesterification of $[(\pi\text{-methallyl})\text{—Pd—Cl}]_2$ with HCO_2Me/CO yielding 3-methyl-3-butenoic acid methyl ester· variation of the carboxylate (T = 25 °C, $P(CO)$ = 3 5 bar, t = 2 h; 0.25 mmol $[(\pi\text{-methallyl})\text{—Pd—Cl}]_2$, 8 ml MeOH, 2 5 mmol nucleophile).

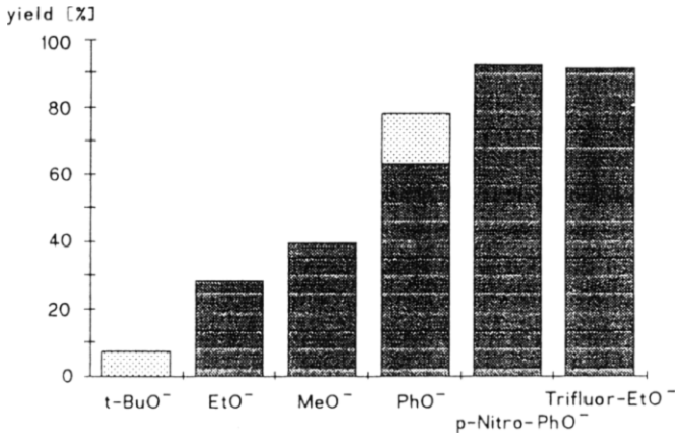


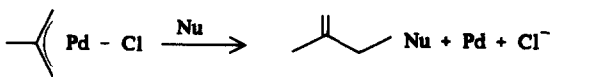
Fig. 2. Hydroesterification of $[(\pi\text{-methallyl})\text{—Pd—Cl}]_2$ with HCO_2Me/CO yielding 3-methyl-3-butenoic acid methyl ester (■) and 3-methyl-2-butenoic acid methyl ester (□): variation of the alkoxide (conditions as for Fig. 1).

reaction in the right sequence by adding the alkoxides at the end; otherwise reduction of the palladium complexes will occur.

Alkoxides also induce a double bond isomerization of the primary product 3-butenoic acid ester to the α,β-unsaturated ester. This isomerization product is obtained in 90% yield in the hydroesterification using MeOH/CO and $t\text{-}BuO^-$ as nucleophile.

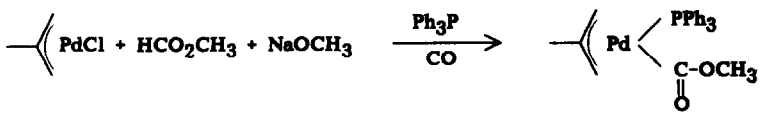
Addition of phosphines

A well-studied reaction is the attack of the allylic ligand by nucleophiles according to eqn. (4) [12].



(4)

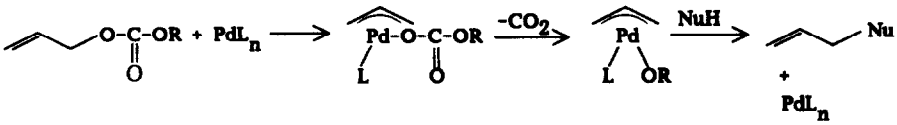
This becomes the major reaction path upon addition of PPh_3. Indeed, in the presence of sodium butyrate, methallyl butyrate is formed quantitatively. If the nucleophile is phenoxide, the corresponding phenyl methallyl ether is also formed exclusively. However, if MeO^- is applied, we were able to isolate the novel carbomethoxypalladium complex 1 (eqn. 5)).



(5)

This complex, which is quite unstable at room temperature, was characterized by IR and NMR analysis (see Experimental part), and the spectra are in agreement with those of analogous complexes of palladium [13], rhodium [14] and iridium [14]. To verify the composition of complex 1, a reaction of 1 with CH_3I was carried out. As expected, $CH_3CO_2CH_3$ was formed.

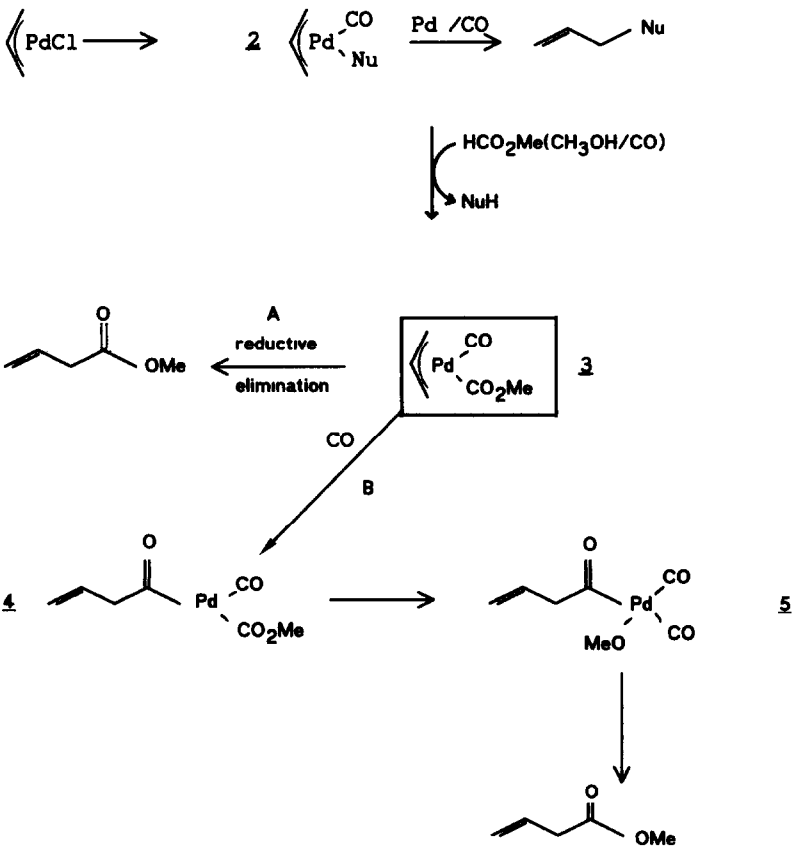
The formation of complex 1 exhibits certain parallels to a related reaction, namely, the cleavage of allyl–oxygen bonds in allyl carbonates followed by decarboxylation and nucleophilic attack at the allylic ligand, a reaction useful for allylation of nucleophiles (eqn. (6)) [15].



(6)

Mechanistic considerations

To account for the ester formation described in Table 1 using methyl formate, a reaction sequence as shown in Scheme 1 is proposed. Here complex 2 is a key intermediate from which the nucleophilic addition product



Scheme 1 Mechanistic proposal for the hydroesterification of [(π-allyl)—Pd—Cl]$_2$ with HCO_2Me/CO.

can be derived. In the presence of HCO_2Me or CH_3OH/CO, complex 3 is formed. However, there must be a difference when methyl formate rather than CH_3OH/CO is used, because with π-crotyl palladium complexes (Table 1) other products are obtained.

Reductive elimination from 3 can yield the observed esters (pathway A). It is also conceivable that a CO insertion with complex 3 (pathway B) — this would account for the necessity of additional CO — yields 4, which via decarbonylation gives 5, from which reductive elimination leads also to the ester obtained.

To distinguish between pathways A and B, an experiment with ^{13}CO was carried out. The results show that the carbonyl group of the product ester originates exclusively from free CO, not from HCO_2Me; this result is consistant with pathway B, but not A.

This reaction proposal is further supported by the isolation of complex 1 which bears a close similarity to 3. Obviously, the reaction course is quite complex. By using ethyl formate in eqn. 5 we were able to isolate the corresponding (π-methallyl) palladium $(C_4H_7)(PPh_3)PdC(O)OC_2H_5$ complex, a result which is also consistent with the proposed mechanism.

Experimental

$[(\pi\text{-allyl})\text{—Pd—Cl}]_2$ complexes were prepared according to published procedures [16]. The nucleophiles were made by conventional methods. The hydroesterification reactions were carried out in a glass autoclave (100 ml). A mixture of Pd–complex, HCO_2Me (or MeOH) and nucleophile was stirred at room temperature for 30 min. Upon addition of 3.5 bar of CO, the reaction takes place within 2 h. Alkoxides as nucleophile were added under CO pressure through a glass finger. After the reaction, the internal standard (valeric acid methyl ester) was added, the reaction mixture filtered, and the resulting colourless liquid analysed by GLC (50 m Carbowax or 50 m FS-WG 11). For detailed data, see the corresponding Tables and Figures.

Synthesis of complex 1

In a 100 ml glass autoclave a mixture of 200 mg of $[(\pi\text{-methallyl})\text{—Pd—Cl}]_2$, 580 mg PPh_3 and 14 ml HCO_2Me was stirred at room temperature for 30 min.. After adding successively 3.5 bar CO and 270 mg NaOMe, the mixture was stirred for another 2 h, yielding a suspension, which was filtered; the orange solution was stored under argon at −25 °C for at least 2 days. The resulting orange solid, which is soluble in CH_2Cl_2 and $CHCl_3$, was characterized by spectroscopic data and elemental analysis: band at 1670/1655 cm^{-1}. The ^1H NMR spectrum ($CDCl_3$) showed a singlet at 2.38 ppm for the methyl group in $PdCOOCH_3$. In addition, the characteristic resonances for the π-methallylic group are observed. Sharp NMR peaks were observed only below 10 °C; ^{13}C spectra (SEFT) also confirmed the structure.

IR (KBr) cm^{-1}: 1670/1655(ν(COO))
^1H NMR ($CDCl_3$) δ: 7.3 - 7.8 (15 H); 2.38 s (3 H = OCH_3); 4.52 dd (1 H); 3.61 d (1 H); 2.86 s (1 H); 2.75 s (1 H); 1.97 s (3 H);
^{13}C NMR ($CDCl_3$) δ: 184.30 ($-COO^-$); 23.15 (CH_3); 30.75 (OCH_3)

Elemental analysis (anal. calcd.: C, 59.70; H, 5.22%. Found: C, 59.74; H, 4.59%).

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