Mechanistic investigations of palladium-catalysed single and double carbonylation of aryl and vinyl halides by methyl formate

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Abstract

The palladium-catalysed methoxycarbonylation of PhCH=CHBr in the presence of HCO_2CH_3, NEt_3 and CO has been investigated and compared to that of PhI. Methyl cinnamate was the only product observed. Model reaction studies were conducted on the possible intermediates [(PhCH=CH)Pd(PPh_3)$_2$Br] (**1**), [(PhCH=CHCO)Pd(PPh_3)$_2$Br] (**2a**), and [(PhCO)Pd(PPh_3)$_2$I] (**3**). The results suggest that the high alcoholysis rate of complex **2a** is responsible for the lack of double carbonylation product from PhCH=CHBr. NMR studies of the catalytic systems in the presence of HCO_2CH_3 revealed the presence of the suggested aroylpalladium complexes (**2a** and **3**) in conjunction with [$PdCl(PPh_3)_2(CO_2CH_3)$] (**4**). Both stoichiometric and catalytic experiments indicated that complex **4** is a possible intermediate in the formation of both simple esters and α-keto esters, but that the latter arise mainly from classical aroylpalladium(II) complexes. The activation pathway of HCO_2CH_3 has been studied and a dramatic influence of CH_3OH concentration in the reaction medium has been found. These results suggest that CH_3OH arising from smooth decarbonylation of HCO_2CH_3 under the reaction conditions is the main alkoxy-transfer agent.

Key words: Palladium; Catalysis; Carbonylation

1. Introduction

Palladium-catalysed carbonylation reactions of aryl or vinyl halides have been extensively studied in recent years [1]. These reactions are useful for introducing either one (monocarbonylation process) or two (dicarbonylation process) CO molecules into a substrate in a single step. Such processes are therefore widely used in organic synthesis to produce various mono- and α-di-carbonyl compounds. In this area, special interest has been devoted to alkoxycarbonylation that gives simple esters [2] and α-keto esters [3] (eqn. (1)). These products are in general more readily hydrolyzable than amide derivatives and are therefore more convenient starting materials for the synthesis of various compounds by further functionalisation.

$$ArX + CO + ROH \xrightarrow[\text{base}]{\text{Pd catalyst}} ArCO_2R + ArCOCO_2R \quad (1)$$

$$PhI + CO + HCO_2CH_3 \xrightarrow[NEt_3]{[PdCl_2(PPh_3)_2]} PhCO_2CH_3 + PhCOCO_2CH_3 \quad (2)$$

Almost all these palladium-catalysed carbonylations are traditionally carried out using carbon monoxide and an alcohol. However, in the last decade, alkyl formates have attracted considerable interest as possible sources of these reactants. Among them, methyl formate is important since it is produced on a very large scale and can be considered an alternative synthon in C1 chemistry [4]. Many examples of metal-catalysed conversions of various substrates into car-

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boxylic esters using alkyl formates have been reported [5,6]. In some cases, especially for alkoxycarbonylation of organic halides, it proved essential that CO was added [6]. Therefore, in these cases, formate esters appear more likely to be active as alkoxy transfer agents. We have recently reported that HCO_2CH_3 is a better agent than CH_3OH for the double carbonylation of iodobenzene catalyzed by $[PdCl_2(PPh_3)_2]$ [7] (eqn. (2)), but the activation pathway of HCO_2CH_3 is not well understood. The present paper reports the latest results of our continuing and fundamental work in this area.

2. Results and discussion

The selectivities in double carbonylation in the production of α-keto esters from organohalides are usually lower than those observed in the corresponding α-keto amide synthesis from secondary amines. Furthermore, vinylic halides are by far much less selective substrates than classical aryl halides, so that the production of vinylglyoxylate esters is still marginal [3c]. Consequently, β-bromostyrene (PhCH=CHBr) is a challenging substrate for evaluation and comprehension of double carbonylation with methyl formate as reagent. Both catalytic and stoichiometric aspects of this reaction have been examined.

Despite the interesting selectivities observed earlier for the double carbonylation of iodobenzene [7], applying a similar procedure with PhCH=CHBr as substrate was ineffective and only methyl cinnamate, the mono carbonylation product, was obtained. Small amounts of methyl phenyl-2-succinate were also observed (maximum selectivity 4%). The formation of this side product can be rationalized by the combination of methoxycarbonylation followed by hydroesterification of the resulting methyl cinnamate (eqn. (3)). Figure 1 illustrates the influence of the CO pressure on the yield of methyl cinnamate after 24 h in a catalytic system with CH_2Cl_2 as solvent. In the absence of CO, the reaction did not proceed at all and this result reported earlier [6,7] confirms that HCO_2CH_3 is not the source of the carbonyl function in the ester. As shown in Fig. 1, under the conditions employed the yield of methyl cinnamate increases with pressure though with pressures above 20 atm the yield becomes almost constant. It is noteworthy that the double carbonylation product, methyl β-styrylglyoxylate, was never detected in this system, even at elevated pressure (130 atm).

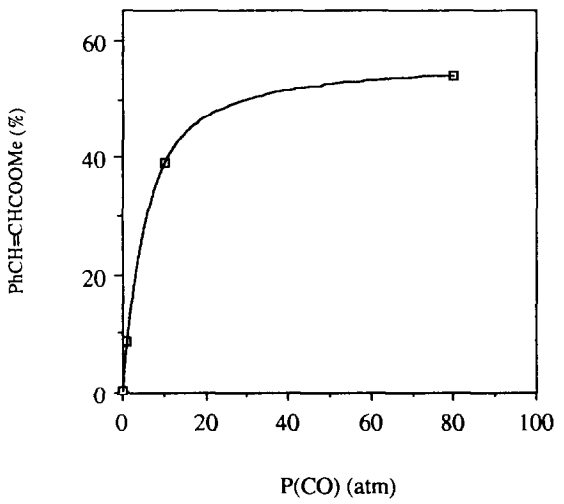


Fig. 1. Influence of CO pressure on the yield of methyl cinnamate. Reaction conditions: PhCH=CHBr (7.8 mmol), HCO_2CH_3 (320 mmol), NEt_3 (11.5 mmol), $[PdCl_2(PPh_3)_2]$ (0.031 mmol), CH_2Cl_2 (20 ml), 80°C, 24 h.

$$\mathrm{PhCH{=}CHBr + CO + HCO_2CH_3} \xrightarrow[\mathrm{NEt_3}]{[\mathrm{PdCl_2(PPh_3)_2}]} \mathrm{PhCH{=}CHCO_2CH_3} + \mathrm{PhCH(CO_2CH_3)CH_2CO_2CH_3} \quad (3)$$

2.1. Syntheses and reactivities of supposed catalytic intermediates

In order to gain a better insight into the double carbonylation reaction, the palladium complexes traditionally suggested as the predominant species during carbonylation processes [3b] were prepared, and their reactivities investigated. Indeed, model reactions of isolated phenyl- and benzoyl-iodopalladium(II) complexes under double carbonylation conditions revealed improved selectivities for α-keto ester formation in catalytic experiments [3b,3d,7]. The reactivities of *trans*-[{(*E*)-PhCH=CH}Pd$(PPh_3)_2$Br] (**1**) and *trans*-[{(*E*)-PhCH=CHCO}Pd$(PPh_3)_2$Br] (**2a**) were examined. Both are proposed intermediates in the catalytic reaction of PhCH=CHBr with HCO_2CH_3 and CO and we have established by $^{31}P\{^1H\}$ NMR spectroscopy the presence of complex **2a** in the catalytic system (see below). The (bromo)styrylpalladium(II) complex (**1**) was prepared by oxidative addition of PhCH=CHBr to $[Pd(PPh_3)_4]$ according to the method described previously [8] (eqn. (4)). To the best of our knowledge, the synthesis and characterization of cinnamoylpalladium(II) complexes have not yet been reported. The (bromo)cinnamoylpalladium(II) complex (**2a**) was prepared for the first time by carbonylation of complex **1** under atmospheric pressure in CH_2Cl_2 (eqn. (5)). The reaction, which could be followed by IR spectroscopy by monitoring the increase in the intensity of the carbonyl band, was found to take place readily at room temperature. Total conversion of **1** was achieved in 30

minutes, and complex **2a** was isolated in 90% yield as a yellow powder. The $^{31}P\{^1H\}$ NMR spectrum of **2a** shows a singlet at 19.3 ppm, consistent with a *trans* configuration. This was confirmed by the ^1H NMR spectrum which exhibits a β-vinyl proton signal at δ 5.39 as a doublet of triplets due to coupling with the α-(*E*)-CH ($^3J(H-H) = 16.0$ Hz) and the two PPh_3 ligands ($^4J(P-H) = 1.2$ Hz). In the $^{13}C\{^1H\}$ NMR spectrum, the carbonyl carbon signal is a triplet at δ 231.3 with $^2J(P-C) = 3$ Hz.

$$PhCH{=}CHBr + [Pd(PPh_3)_4] \longrightarrow [(PhCh{=}CH)Pd(PPh_3)_2Br] \quad (4)$$

$$[(PhCH{=}CH)Pd(PPh_3)_2Br] + CO \longrightarrow [(PhCH{=}CHCO)Pd(PPh_3)_2Br] \quad (5)$$

$$PhCH{=}CHCOCl + [Pd(PPh_3)_4] \longrightarrow [(PhCH{=}CHCO)Pd(PPh_3)_2Cl] \quad (6)$$

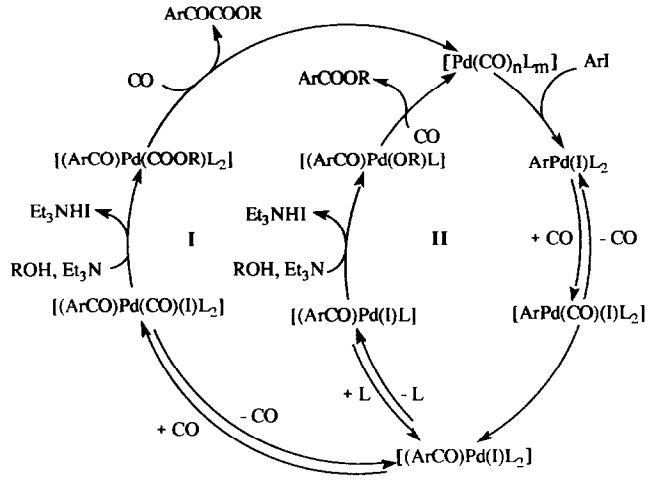
Aroylpalladium(II) complexes may also be prepared in one step by direct oxidative addition of selected acyl halides to Pd^0 species [9]. Thus, chloro-[(*E*)-cinnamoyl]bis(triphenylphosphine)palladium(II) (**2b**) was obtained, for comparative purposes, by reaction of PhCH=CHCOCl with $[Pd(PPh_3)_4]$ (eqn. (6)). As found for similar oxidative addition reactions [10], complex **2b** has a *trans* configuration and the reaction proceeded with retention of the double bond stereochemistry. Spectroscopic data of **2b** are analogous to those of complex **2a**. In particular, the α-(*E*)-CH signal in the ^1H NMR spectrum appears at δ 5.28, only 0.11 ppm downfield from that of complex **2a**, with similar coupling constants ($^3J(H-H) = 16.0$ Hz, $^4J(P-H) = 1.3$ Hz).

In the solid state, both complexes were stable enough to be handled safely in air. In $CDCl_3$ solution, stirring under dinitrogen for one night at room temperature resulted in no change of either the $^{31}P\{^1H\}$ NMR spectrum or of the FTIR spectrum, proving that CO insertion is not reversible under these conditions. The results of the reactions of complexes **1** and **2a** with HCO_2CH_3 in the presence of NEt_3 are summarized in Table 1. In the first set of experiments, we examined the reactivity of the styrylpalladium complex. In the absence of CO, no carbonylation product was observed, and only trace amounts of styrene were obtained when the reaction was carried out at 80°C. Treatment of **1** under elevated CO pressure resulted in the formation of methyl cinnamate in almost quantitative yield; the double carbonylation product, PhCH=CHCOCO$_2$CH$_3$, was not detected.

TABLE 1. Comparison of reactivities of styryl- (**1**), cinnamoyl- (**2a**) and benzoyl- (**3**) palladium complexes towards HCO_2CH_3, NEt_3 and CO [a]

Complex	Temp. (°C)	Reaction time (h)	Pressure (atm)	Products (yield, mol%) [b]
1	25	7	N_2 (1)	No product observed
1	80	4	N_2 (15)	PhCH=CH$_2$ (traces)
1	80	3	CO (135)	*trans*-PhCH=CHCO$_2$CH$_3$ (90) [c]
2a	25	3	N_2 (1)	*trans*-PhCH=CHCO$_2$CH$_3$ (90) [c]
2a	80	3	N_2 (10)	*trans*-PhCH=CHCO$_2$CH$_3$ (90) [c]
3	40	3	N_2 (1)	No product observed

[a] Reaction conditions: Complex (0.12 mmol), NEt_3 (2.9 mmol), HCO_2CH_3 (25 mmol). [b] Calculated on the basis of the complex. [c] Small amounts of *cis*-cinnamate were also produced.



Scheme 1. Mechanism for the palladium-catalysed double (I) and single (II) carbonylation of aryl iodides [3b].

This last result is in sharp contrast to that previously obtained from iodophenylpalladium(II) complex (**3**) which gave methyl phenylglyoxylate in about 70% yield under similar conditions [7]. A possibility which can be deduced from the comparison of these results is that the aroylpalladium species arising from PhCH=CHBr is more reactive towards alcoholysis than that derived from PhI. It has actually been demonstrated that formation of the double and single carbonylation products from aryl halides occurs in two competitive cycles (Scheme 1) [3b] in which the key intermediate is an aroylpalladium species that can react in two ways. First it could coordinate another CO molecule that, after attack by the alcohol, leads to the (alkoxycarbonyl)aroylpalladium species which can liberate the α-keto ester by reductive elimination (cycle I). Alternatively, direct attack of the alcohol at the aroylpalladium complex could also liberate the ester (cycle II). To examine these two possibilities, we compared the reactivity of cinnamoyl complex **2a** and benzoyl complex **3**. The results (Table 1) were strikingly different; alcoholysis of the former occurred readily and completely at room temperature giving methyl cinnamate in high yield,

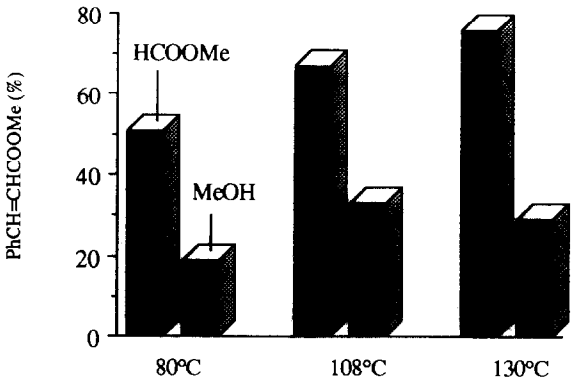


Fig. 2. Influence of temperature on the yield of methyl cinnamate. Reaction conditions: see Fig. 1; HCO_2CH_3 or CH_3OH (320 mmol), P(CO) = 80 atm.

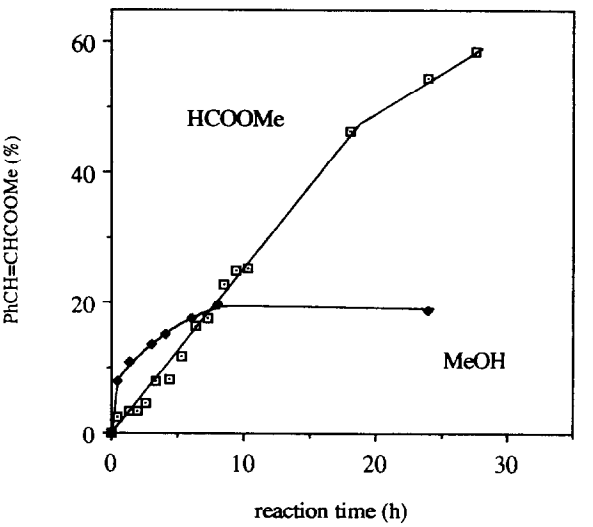


Fig. 3. Time courses of methyl cinnamate production in the methoxycarbonylation reaction of PhCH=CHB. Reaction conditions: see Fig. 2.

whereas the latter remained unreactive at 40°C. It is clear that the alcoholysis rate of **2a** is much higher than that of **3**. Consequently, the coordination of the second CO molecule, the key step for α-keto ester synthesis, is greatly disfavoured in the case of PhCH=CHBr. In our view this could be the main reason for the total inefficiency of the double carbonylation of PhCH=CHBr using methyl formate in our study, and the very low conversions into PhCH=CHCOCO$_2$^{i}Pr obtained with PhCH=CHI and 2-propanol [3c].

2.2. *Catalytic methoxycarbonylation of PhCH=CHBr by HCO_2CH_3*

Despite the relative ineffectiveness of the HCO_2CH_3/[$PdCl_2(PPh_3)_2$] system in the double carbonylation of β-bromostyrene, further investigations were conducted to clarify the mode of methyl cinnamate production as well as the activation pathway of methyl formate. The present catalytic methoxycarbonylation is a relatively slow process, and a moderately high temperature (80°C) is required to perform the reaction at a reasonable rate. The influence of the reaction temperature on methyl cinnamate yield in a catalytic system is illustrated in Fig. 2. When methyl formate is used as solvent, the yield of methyl cinnamate increases with temperature. When CH_2Cl_2 or CH_3OH are used in the place of HCO_2CH_3, a similar reaction-rate enhancement with temperature is seen. However, the yields of methyl cinnamate using HCO_2CH_3 or CH_2Cl_2 as solvent are about twice as high as those obtained with CH_3OH.

Typical time courses of methyl cinnamate yield during the [$PdCl_2(PPh_3)_2$]-catalysed reaction of PhCH=CHBr carried out at 80°C in HCO_2CH_3 and CH_3OH are illustrated in Fig. 3. In the early stage of the reaction the system shows a higher reaction rate in CH_3OH than in HCO_2CH_3 (*ca.* 38 *vs.* 6 mol mol^{-1} h^{-1}) but, the reactivity remains almost unchanged throughout the whole reaction time in HCO_2CH_3 whereas it gradually decreases in CH_3OH. These results suggest that CH_3OH induces a deactivation of the catalyst. However, the active species is stable in HCO_2CH_3. Some black palladium deposit is usually obtained with both reactants.

Since alkoxycarbonylations of aryl halides are quite slow processes, it is possible to observe the catalytic species involved in the reaction by means of $^{31}P\{^1H\}$ NMR spectroscopy under the reaction conditions employed [3b]. Fig. 4 shows the result of NMR examination of our catalytic system containing PhCH=CHBr,

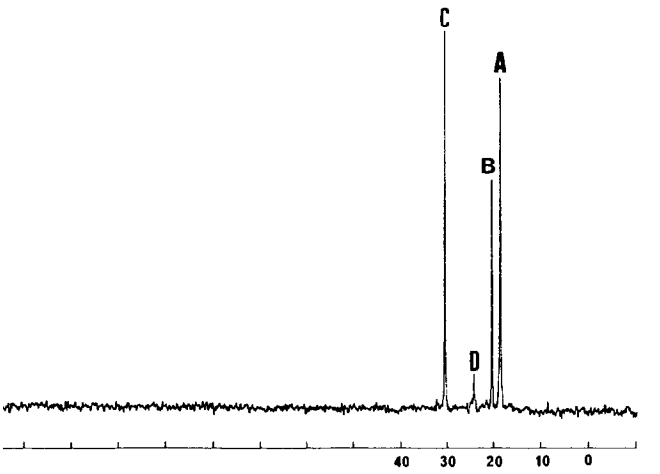


Fig. 4. $^{31}P\{^1H\}$ NMR spectrum of the catalytic system. Reaction conditions: PhCH=CHBr (2.0 mmol), CH_3OH (25 mmol), NEt_3 (2.9 mmol), [$PdCl_2(PPh_3)_2$] (0.085 mmol), $CDCl_3$ (10 mL), 80°C, 3 h; Yield of PhCh=$CHCO_2CH_3$: 56%.

CH_3OH, NEt_3 and $[PdCl_2(PPh_3)_2]$ under 80 atm CO pressure at 80°C.

The spectrum taken after 3 h and shown in this figure shows three principal peaks marked A, B and C. Comparison with authentic samples reveals that $[PdCl_2(PPh_3)_2]$ has been totally converted into *trans*-$[PdCl_2(PPh_3)_2(CO_2CH_3)]$ (A, **4**), *trans*-[(*E*) – {PhCH=CHCO}$Pd(PPh_3)_2Br$] (B, **2a**) and $O{=}PPh_3$ (C) [11*]. When this NMR examination was repeated with HCO_2CH_3 in place of CH_3OH, an analogous spectrum was obtained, indicating that both systems induce the same active species. For the double carbonylation of PhI by HCO_2CH_3, NMR examination indicated the presence of complexes **3** and **4** (*ca.* 80:20 ratio). Therefore, the primary intermediacy of aroylpalladium(II) complexes in simple ester and α-keto ester formation is confirmed.

2.3. Possible involvement of a methoxycarbonylpalladium species

It has been demonstrated that alkoxycarbonylpalladium complexes are key intermediates in the carbonylation of alcohols to alkyl carbonates and oxalate esters [12]. During these processes Pd^0 complexes are produced, indicating that these alkoxycarbonyl species may also be transient intermediates for the reduction of Pd^{II} catalytic precursors into Pd^0 active species. Moser *et al.* studied the role of the methoxycarbonylpalladium complex **4** during carbonylation of bromobenzene to methyl benzoate [13]. Since this complex is stable in the presence of PhBr, NEt_3, and CH_3OH at 90°C, it is not likely to be an active intermediate. In order to determine whether **4** participates in the methoxycarbonylation of PhCH=CHBr, it was synthesized [14] and its reactivity investigated. The results of the stoichiometric reactions of **4** with PhCH=CHBr and PhI are reported in Table 2.

Complex **4** was found to be less reactive than aroylpalladium(II) species (Table 1), and a temperature of 80°C was necessary to obtain significant amounts of esters. Furthermore, under these conditions, all reactions of **4** with PhCH=CHBr went to completion, whereas only partial conversions of **4** were observed with PhI. This last result is consistent with that of Stille who observed a 25% yield of $PhCO_2CH_3$ from **4** after 12 h at 60°C [2b]. In the presence of CO, PhCH=CHBr led only to methyl cinnamate, but PhI yielded both benzoate and phenylglyoxylate esters. To the best of our knowledge, the production of an α-keto ester from such methoxycarbonyl species has not been reported.

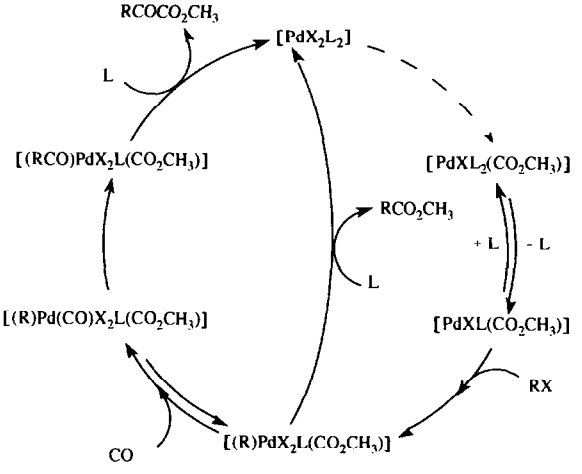
* Reference number with asterisk indicates a note in the list of references.

TABLE 2. Reactivity of $PdCl(PPh_3)_2(CO_2CH_3)$ (**4**) towards organic halides, NEt_3 and CO [a]

Organic halide	Temp. (°C)	Pressure (atm)	Reaction time (h)	Products (Yield, mol %) [b]
PhCH=CHBr	25	N_2 (1)	120	$PhCH{=}CHCO_2CH_3$ (traces)
PhCH=CHBr	80	N_2 (15)	3	$PhCH{=}CHCO_2CH_3$ (95%) [c]
PhCH=CHBr	80	CO (110)	3	$PhCH{=}CHCO_2CH_3$ (~100%) [c]
PhI	80	N_2 (15)	3	$PhCO_2CH_3$ (20%)
PhI	80	CO (110)	3	$PhCO_2CH_3$ (21%), $PhCOCO_2CH_3$ (13%)

[a] Reaction conditions: Complex **4** (0.16 mmol), RX (0.36 mmol), NEt_3 (0.65 mmol), CH_2Cl_2 (1 ml). [b] Calculated on the basis of **4**. [c] *trans* isomer.

The classical catalytic reaction mechanism (Scheme 1) involves formation of the aroyl species prior to that of the methoxycarbonyl moiety, whereas the reverse is true in this case. A possible mechanism for the complex **4** - organic halide reaction is outlined in Scheme 2. Oxidative addition of the organic halide to complex **4** would give a palladium(IV) intermediate. This can react *via* two pathways: (i) CO coordination, CO insertion into the Pd–C(aryl) bond, and reductive elimination to give the α-keto ester, and regenerated $[PdX_2(PPh_3)_2]$ (X = hal) and (ii) direct reductive elimination to give the ester, and regenerated $[PdX_2(PPh_3)_2]$. In this mechanism involving a palladium(IV) intermediate, our results indicate that with PhCH=CHBr reductive elimination of methyl cinnamate occurs more rapidly than CO coordination and/or insertion and therefore that pathway (ii) dominates. In



Scheme 2. Proposed mechanism for simple ester and α-keto ester formation from organic halides and $[PdCl(PPh_3)_2(CO_2CH_3)]$ (L = PPh_3, X = hal).

contrast, with PhI the two pathways compete more equally.

From a catalytic point of view, our kinetic measurements during methoxy-carbonylation of PhCH=CHBr with both HCO_2CH_3 and CH_3OH show that complex **4** induces an initial reaction rate that is similar to that of $[PdCl_2(PPh_3)_2]$, 42 and 8 mol mol^{-1} h^{-1} respectively compared with 38 and 6 mol mol^{-1} h^{-1} for the latter. An analogous trend was observed for double carbonylation of PhI. However, $^{31}P\{^1H\}$ NMR examination of the catalytic system established that complex **4** is not stable, and that it was rapidly converted into the corresponding aroyl complex **3**. Thus, these results indicate that this methoxycarbonylpalladium(II) species may be a plausible intermediate for simple ester and α-keto ester formation. However, **4** is above all an intermediate during the reduction of $[PdCl_2(PPh_3)_2]$ to Pd^0 species that leads to classical aroylpalladium(II) complexes which are the essential active species.

2.4. Activation pathway of methyl formate

Since the yield of methyl cinnamate was markedly decreased in CH_3OH, it appeared essential to investigate the influence of this reactant. Therefore, we have carried out competitive methoxycarbonylation of PhCH=CHBr using equimolar amounts of HCO_2CH_3 and CD_3OD. However, interpretation of this experiment (GC/MS) was impossible because of the rapid base-catalysed transesterification equilibrium between these two reactants. Nevertheless, once again the yield of methyl cinnamate observed at the end of this reaction (20% yield, 98% selectivity $ArCO_2CH_3 : ArCO_2CD_3 \sim 25:75$) was comparable with yields obtained in pure CH_3OH (Figs. 2 and 3). We have therefore examined the influence of CH_3OH concentration in HCO_2CH_3. For that purpose, pure HCO_2CH_3 was obtained by distillation of commercial product over acetic anhydride (final CH_3OH content < 0.1%) [15*]. Figure 5 shows that the yield of methyl cinnamate is drastically influenced by the CH_3OH content. The maximum yield is obtained for a 3–5% content, a stoichiometric ratio with respect to the methoxycarbonylation reaction. Above this content, the yield rapidly decreases and stabilizes around 35%. Lower CH_3OH contents limit the formation of methyl cinnamate, and only minute amounts (*ca.* 2%) were obtained from pure HCO_2CH_3.

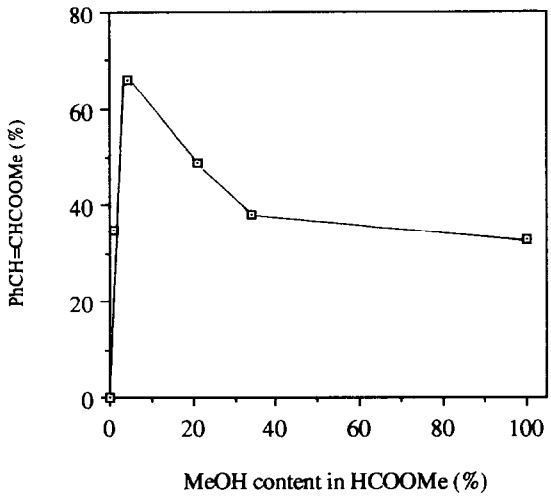


Fig. 5. Influence of the methanol concentration on methyl cinnamate production during methoxycarbonylation of PhCH=CHBn. Reaction conditions: see Fig. 2; $HCO_2CH_3 + CH_3OH$ (320 mmol).

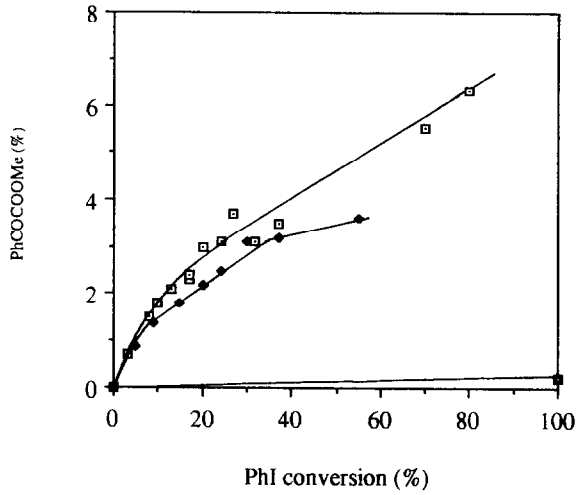


Fig. 6. Influence of the methanol concentration on methyl cinnamate production during double carbonylation of PhI. Reaction conditions: PhI (27 mmol), NEt_3 (50 mmol), $[PdCl_2(PPh_3)_2]$ (0.15 mmol), CH_2Cl_2 (20 mL) or HCO_2CH_3 (400 mmol), 80°C, P(CO) = 105 atm. □ (i), ◇ (ii), ■ (iii).

These results indicate that CH_3OH, either initially present or smoothly produced by decarbonylation of HCO_2CH_3 [16], is the main source of the alkoxy function in methyl cinnamate. Thus, compared to pure CH_3OH, HCO_2CH_3 induces a lower CH_3OH concentration in the reaction medium and this enhances the stability of the catalytically active species. In addition, since the selectivity for formation of the double carbonylation product should increase with lower CH_3OH concentration, this could also explain the better results observed during the double carbonylation of PhI with HCO_2CH_3. In order to check this, we have reexamined the last reaction by using different experimental procedures and CH_3OH concentrations. The results are illustrated in Fig. 6. Maximal methyl phenylglyoxylate selectivities were obtained by procedure (i) injecting either HCO_2CH_3 containing 3–4% MeOH or a dilute solution of CH_3OH in CH_2Cl_2 (1/14 v/v) into the reaction medium. When the total amount of HCO_2CH_3

was initially introduced in the reactor, procedure (ii), selectivities for the α-keto ester slowly decreased. In contrast, with an excess of CH_3OH present at the start of the reaction, procedure (iii), the α-keto ester selectivity was found to decrease strikingly.

3. Conclusions

Methyl formate as carbonylation agent of β-bromostyrene does not give double carbonylation products, even under high CO pressure, in contrast to our previous report with iodobenzene as substrate. This difference in behaviour between vinyl and aryl halides is probably due to the alcoholysis rate of the intermediate (bromo)cinnamoyPd^{II} species which is much higher than that of its homologous benzoyliodoPd^{II} species.

Nevertheless, on account of a better stability of the catalytic species, increased yields of methyl cinnamate are obtained by monocarbonylation of β-bromostyrene with methyl formate than with methanol as solvent. Moreover, our study of the reactivity of the chloro (methoxycarbonyl)palladium complex observed together with classical catalytic species by NMR examination of the reaction medium, shows that this complex can react directly with β-bromostyrene or iodobenzene to give methyl cinnamate or a mixture of benzoate and phenylglyoxylate methyl esters. Its participation in the carbonylation catalytic cycle cannot be excluded. However, in a methyl formate medium, with a palladium complex present, the formation of the methoxycarbonylpalladium complex does not seem to result from direct activation of HCO_2CH_3 by oxidative addition to the metal. On the contrary, all experimental results indicate that the carbonylation reaction of halides in methyl formate proceeds *via* CH_3OH that is either initially present or produced by decarbonylation of formate.

4. Experimental details

All manipulations were conducted under dinitrogen using Schlenk techniques. Solvents, aryl halides, methanol, and methyl formate were dried, distilled, and deoxygenated prior to use. Tetrakis(triphenylphosphine)palladium was used as purchased from Strem. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded in $CDCl_3$ solutions on a Bruker AM 400 spectrometer. $^{31}P\{^1H\}$ NMR spectra were measured at room temperature on a WP 80 spectrometer using H_3PO_4 as an external reference. IR spectra were recorded on a Nicolet 60SX FT-IR spectrometer in CsI pellets or $CHCl_3$ solutions. FAB/MS data of palladium complexes were obtained in 80/20 *v/v* 3-nitrobenzyl alcohol/1,3,5-trichlorobenzene solutions by using a CONCEPT II H-H spectrometer (Kratos Analytical Ltd). *Trans*-[(*E*){PhCH=CH}Pd(PPh_3)$_2$Br] (**1**) [8] and *trans*-[PdCl(PPh_3)$_2$-(CO_2CH_3)] (**4**) [14] were prepared as previously described.

4.1. Synthesis of *trans*-[{(*E*)-PhCH=CHCO}Pd(PPh_3)$_2$-Br] (2a)

To a Schlenk tube containing *trans*-[{(*E*)-PhCH=CH}Pd(PPh_3)$_2$Br] (100 mg, 0.123 mmol) was added 5 ml of CH_2Cl_2. CO was bubbled through the solution. The solution changed immediately from pale yellow to orange yellow. After bubbling had been maintained for 1 h, the CO gas was purged with dinitrogen and the solvent was removed under reduced pressure. The resulting orange powder was washed with Et_2O (3 × 10 ml) and dried in vacuo. Yield: 90%. Anal. Found: C, 63.19; H, 4.83. $C_{45}H_{37}BrOP_2Pd$ calcd: C, 64.19; H, 4.43% ^1H NMR δ 5.39 (dt, 1H, CHCO, ^3J(H–H) = 16.0 Hz, ^4J(P–H) = 1.2 Hz), 7.61 (d, 1H, ArCH), 7.2–7.5 et 7.7–7.9 (m, H aro). $^{13}C\{^1H\}$ NMR δ 145.8 (s, CH), 231.3 (t, CO, ^2J(C–P) = 3 Hz). $^{31}P\{^1H\}$ NMR δ 19.3 (s). IR (CsI, cm^{-1}) 1638 (vs, ν(C=O)), 1482, 1436 (vs, ν(C=C)PPh_3), 521, 511, 494 (vs, ν PPh_3). FAB/MS: 630 (Pd(PPh_3)$_2$, 711 (Pd(PPh_3)$_2$Br), 733 ((PhCH=CH)Pd(PPh_3)$_2$), 761 ((PhCH=CHCO)Pd(PPh_3)$_2$).

4.2. Synthesis of *trans*-[(*E*)-{PhCH=CHCO}Pd(PPh_3)$_2$-Cl] (2b)

To a solution of [Pd(PPh_3)$_4$] (277 mg, 0.24 mmol) in benzene (20 ml) was added a solution of PhCH=CHCOCl (200 mg, 1.20 mmol) in benzene (10 ml). After stirring 20 h at room temperature, benzene (*ca.* 25 ml) was removed under reduced pressure and pentane (20 ml) was added to the concentrate. The resulting yellowish precipitate was filtered, washed with Et_2O (6 × 10 ml), and dried *in vacuo*. Yield: 90%. Anal. Found: C, 67.57; H, 4.79. $C_{45}H_{37}ClOP_2Pd$ calcd: C, 67.76; H, 4.68%. ^1H NMR δ 5.28 (dt, 1H, CHCO, ^3J(H–H) = 16.0 Hz, ^4J(P–H = 1.3 Hz), 7.48 (d, 1H, ArCH), 7.1–7.4 et 7.6–7.8 (m, 37 H, H aro). $^{13}C\{^1H\}$ NMR δ 145.5 (s, CH), 230.8 (t, CO, ^2J(C–P) = 3 Hz). $^{31}P\{^1H\}$ NMR δ 19.2 (s). IR (CsI, cm^{-1}) 1642 (vs, ν(C=O), 1482, 1436 (vs, ν(C=C) PPh_3), 519, 509 (vs, ν PPh_3). FAB/MS: 630 (Pd(PPh_3)$_2$, 665 (Pd(PPh_3)$_2$Cl), 761 ((PhCH=CHCO)Pd(PPh_3)$_2$).

4.3. Catalytic methoxycarbonylation of PhCH=CHBr

As a typical procedure, PhCH=CHBr (7.8 mmol), NEt_3 (11.5 mmol), HCO_2CH_3 (320 mmol) and CH_2Cl_2 (20 ml) were added to a 100 ml stainless-steel autoclave containing $PdCl_2(PPh_3)_2$ (0.031 mmol) under nitrogen atmosphere. The vessel was charged with carbon monoxide (80 atm at room temperature) and magneti-

cally stirred at 80°C for 24 h. After the vessel had been cooled, and the CO gas purged, the mixture was analysed by means of GLC (0.12 mm × 25 m CPSil 5 capillary column). The GLC analysis revealed the formation of $PhCH{=}CHCO_2CH_3$ (52%) with 52% conversion of PhCH=CHBr.

4.4. Stoichiometric reactions of trans-[PdCl(PPh$_3$)$_2$-(CO$_2$CH$_3$)] (4) with organic halides

To a 50 ml stainless-steel autoclave containing *trans*-$[PdCl(PPh_3)_2(CO_2CH_3)]$ (0.16 mmol) were added ArX (0.36 mmol), NEt_3 (0.65 mmol), and CH_2Cl_2 (1 ml) under nitrogen atmosphere. CO (110 atm) or N_2 (15 atm) was then introduced at room temperature and the system was magnetically stirred at 80°C for 3 h. After the vessel had been cooled, the reaction solution was analysed by means of GLC, and sometimes by $^{31}P\{^1H\}$ NMR spectroscopy.

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