

On the mechanism of the hydrogen transfer from $\text{H}_2\text{O}-\text{CO}$ to γ -keto- α -hydroxy carboxylic acids to yield γ -keto acids catalyzed by a $\text{PdCl}_2(\text{PPh}_3)_2$ precursor in combination with hydrochloric acid

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Abstract

The catalytic system $\text{PdCl}_2(\text{PPh}_3)_2-\text{HCl}$ is highly active and selective in the hydrogen transfer reaction from $\text{H}_2\text{O}-\text{CO}$ to $\text{PhCOCH}_2\text{CHOHCOOH}$ which yields the corresponding γ -keto acid $\text{PhCOCH}_2\text{CH}_2\text{COOH}$, with concomitant evolution of CO_2 . An increase of temperature, pressure of carbon monoxide and catalyst concentration have a beneficial effect on the reaction rate, which appears to be of the first order in the substrate and passes through a maximum when varying the concentration of HCl . It is proposed that one important function of HCl is to give rise to chloride $\text{PhCOCH}_2\text{CHClCOOH}$ which interacts with a palladium hydride that takes origin from the decarboxylation of a species having a $\text{Pd}-\text{COOH}$ moiety, which in turn results from the interaction of H_2O and CO on the metal center. The yield passes through a maximum on increasing the concentration of H_2O . This trend is attributed to the fact that, on one hand, H_2O favors the formation of the $\text{Pd}-\text{COOH}$ species, while, on the other hand, it may compete with other reacting molecules for coordination to the metal center. Moreover, H_2O does not favor the formation of the chloride. When employed in relatively high concentration, the catalyst precursor has been recovered as a complex of palladium(0), $\text{Pd}_3(\text{CO})_3(\text{PPh}_3)_3$ or $\text{Pd}(\text{CO})(\text{PPh}_3)_3$, the latter in the presence of PPh_3 . The reduction to palladium(0) takes place only in the presence of H_2O and is likely to occur via the intermediacy of a $\text{Pd}-\text{COOH}$ species, which after CO_2 evolution gives the reduced complex probably via reductive elimination of HCl from the hydride intermediate *trans*- $\text{PdHCl}(\text{PPh}_3)_2$. Moreover, $\text{PhCOCH}=\text{CHCOOH}$ in combination with HCl (equivalent to $\text{PhCOCH}_2\text{CHClCOOH}$) reacts with $\text{Pd}(\text{CO})(\text{PPh}_3)_3$ to give the hydrogenated product $\text{PhCOCH}_2\text{CH}_2\text{COOH}$ and $\text{PdCl}_2(\text{PPh}_3)_2$. On the basis of these results, and knowing that HCl reacts with $\text{Pd}(\text{CO})(\text{PPh}_3)_3$ to give the hydride $\text{PdHCl}(\text{PPh}_3)_2$, it is proposed that the catalytic cycle proceeds through the following steps: (i) H_2O and CO interact with the metal center of the precursor yielding a $\text{Pd}-\text{COOH}$ species, (ii) this gives off CO_2 with formation of a hydride, (iii) this interacts with chloride $\text{PhCOCH}_2\text{CHClCOOH}$ to yield the product $\text{PhCOCH}_2\text{CH}_2\text{COOH}$ and the palladium(II) precursor back to the catalytic cycle.

Keywords: Hydrogen transfer mechanism; Hydroxycarboxylic acids; Keto acids; $\text{PdCl}_2(\text{PPh}_3)_2$ precursor

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1. Introduction

An always renewing interest is shown to carbon monoxide chemistry mainly because of the many applications for the introduction of a carbonyl group into a wide spectrum of organic substrates [1]. An important extension of this methodology is the oxidative carbonylation, for example of alkanols to dialkylcarbonates [2], and the reductive carbonylation of nitro compounds, for example to isocyanates derivatives [3]. Another interesting application is the hydrogenation of organic substrates via hydrogen transfer from the system H_2O-CO which occurs through a mechanism closely related to that of the water gas shift reaction (WGS) [4–7]. In this case carbon monoxide is not incorporated into the organic substrate.

Recently, we attempted the carbonylation of γ -keto- α, β -unsaturated acids $ArCOCH=CHCOOH$ and of their HCl and H_2O addition products to the C=C double bond, i.e. $ArCOCH_2CHXCOOH$ ($X = Cl, OH$, respectively). When the reaction was carried out in the presence of H_2O and of a palladium-HCl catalytic system instead of the expected ketomalononic acid derivative $ArCOCH_2CH(COOH)_2$ the reaction selectively yields the γ -keto acid $ArCOCH_2CH_2COOH$ through hydrogen transfer from H_2O-CO with concomitant evolution of CO_2 [8–10].

It was proposed that the reaction occurs through the following steps. The chloride $ArCOCH_2CHClCOOH$, which is formed in situ upon addition of HCl to the C=C double bond, gives oxidative addition to a palladium species in a reduced form with the formation of an intermediate having a Pd-(CH(COOH)CH₂Ar) moiety. Interaction of H_2O and CO with the metal center yields an intermediate having also a carbohydroxy ligand, (HOOC)-Pd-(CH(COOH)CH₂COAr). β -hydride abstraction with concomitant evolution of CO_2 yields the intermediate H-Pd-(CH(COOH)CH₂COAr), which eliminates the final product and gives reduced palladium back to the catalytic cycle.

Alternatively, it was proposed that the product could be formed directly upon protonolysis of the intermediate that is formed in the oxidative addition step with concomitant formation of a Pd^{II} species, which could be reduced by CO in the presence of H_2O , through the intermediacy of a species having Pd-(COOH) moiety. In any case, the essential feature of the proposed mechanisms is the intermediacy of a palladium-carbohydroxy species which is formed.

Under the typical experimental conditions ($110^\circ C$, P_{CO} 30 atm, substrate/PdCl₂(PPh₃)₂ = 500/1, solvent dioxane/aq 36% HCl 16/1 (v/v), [Pd] = 2.5 mol l⁻¹), the yield is practically quantitative and hydrogen transfer to the keto group or to the phenyl ring does not occur. However, extensive decomposition of the precursor to palladium metal occurs.

Hereafter, we will present further evidence on the close relation between this hydrogen transfer reaction and the water-gas shift reaction and some new insights into the mechanism of the catalytic cycle on the basis of the catalyst activity and of elementary reactions possibly involved in the catalytic cycle.

2. Experimental

2.1. Materials

Carbon monoxide, quality N 37, was purchased from S.I.O. Solvents and PPh₃ were of commercial grade. PhCOCH=CHCOOH [16], PhCOCH₂CHXCOOH ($X = OH, Cl$) [17], Pd(CO)(PPh₃)₃ [12] and *trans*-PdCl₂(PPh₃)₂ [18] were prepared as reported in the literature.

2.2. Product identification and analysis

Products were identified by NMR on a Bruker 200 AC spectrometer in CDCl₃ and by IR on a Perkin Elmer model 683 spectrometer. Yields were determined by HPLC on a Perkin Elmer liquid chromatograph, model HPLC series 10, using a C18-SIL-X-10 column of 25 cm; sol-

vent: H₂O 70%, CH₃CN 30% containing 2% CH₃COOH.

2.3. Synthesis of PhCOCH₂CH₂COOH by hydrogen transfer from H₂O–CO to PhCOCH₂CHOHCOOH catalyzed by the system PdCl₂(PPh₃)₂–HCl

In a typical experiment 12 mmol of PhCH₂CHOHCOOH was dissolved in a Pyrex bottle containing 8 ml of dioxane to which 0.5 ml of aqueous 37% HCl together with 0.41 ml of H₂O was added. To the resulting solution 4.5 mg of PdCl₂(PPh₃)₂ was added as catalyst. The bottle was placed in a 75-ml autoclave which was purged with carbon monoxide. The autoclave, provided with a magnetic bar and charged with 30 atm of carbon monoxide, was placed in an oil bath and heated to 90°C in ca. 10 min. This temperature was maintained for 2 h while stirring. Then, after cooling to room temperature, the autoclave was depressurized. The content was analyzed by HPLC.

When using a larger amount of catalyst (35–70 mg, together with an equimolecular amount of PPh₃) in acetonitrile, the precursor was recovered as the palladium(0) complex Pd(CO)(PPh₃)₃.

2.4. Reduction of PdCl₂(PPh₃)₂ to palladium(0) complexes by carbon monoxide in the presence of water

In a Pyrex bottle, 200 mg of PdCl₂(PPh₃)₂ together with 82 mg of PPh₃ was added to 7 ml of acetonitrile–water (5/2, v/v). The bottle was placed in an autoclave, which was purged with carbon monoxide. The mixture was heated at 70°C for 2 under 50 atm of carbon monoxide. After cooling and depressurising, the autoclave was opened. A whitish precipitate was observed at the bottom of the bottle. The solid was collected on a filter, washed and dried under vacuum. The solid was identified by IR as Pd(CO)(PPh₃)₃ (211 mg, 8%). Practically the same result was obtained when the solvent was

a mixture of 5 ml of acetonitrile and 2 ml of aqueous 1.4 M HCl.

When PdCl₂(PPh₃)₂ was treated as just described, except for the absence of water, there was no reduction to any palladium(0) complex, and the starting complex was recovered as such.

2.5. Oxidation of Pd(CO)(PPh₃)₃ with HCl to PdCl₂(PPh₃)₂

In a Pyrex bottle, 100 mg of Pd(CO)(PPh₃)₃ was added under an atmosphere of carbon monoxide to 7 ml of acetonitrile where dry HCl was previously dissolved (1 mol l⁻¹). The resulting mixture was pressurized in an autoclave with 50 atm of carbon monoxide and heated at 70°C for 2 h. After cooling and depressurizing the yellow solid was collected on a filter, washed and dried. It was identified by IR as *trans*-PdCl₂(PPh₃)₂ (yield practically quantitative).

When the same treatment was repeated also in the presence of 1 ml of aqueous 1 M HCl the starting complex was recovered as such.

2.6. Reaction of Pd(CO)(PPh₃)₃ with PhCOCH=CHCOOH in the presence of HCl

In a Pyrex bottle, 19 mg of PhCOCH=CHCOOH (0.1 mmol) was added under CO atmosphere to 2 ml of CH₃CN where

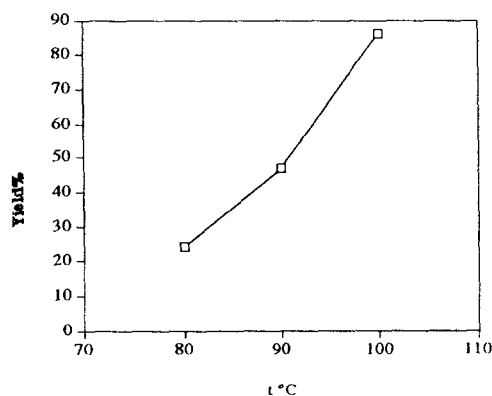
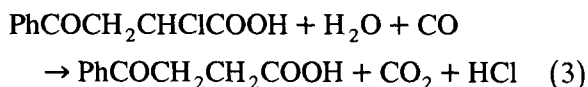
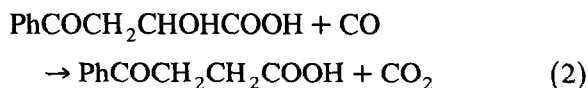
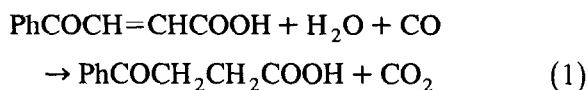


Fig. 1. Run conditions: PhCOCH₂CHOHCOOH 12 mmol, H₂O 44 mmol, HCl 6 mmol, PdCl₂(PPh₃)₂ 6.4 · 10⁻³ mmol in 8 ml dioxane (V_{tot} = 11 ml); P_{CO} = 30 atm at room temperature; reaction time 2 h.

dry HCl was previously dissolved (1 mol l^{-1}). 92 mg of $\text{Pd}(\text{CO})(\text{PPh}_3)_3$ (0.1 mmol) was added at room temperature under carbon monoxide. The mixture was stirred for 2 h under CO pressure. There was formation of a yellow solid identified by IR as *trans*- $\text{PdCl}_2(\text{PPh}_3)_2$ (65 mg, 93% yield). The solution, analyzed by HPLC, showed the presence of $\text{PhCOCH}_2\text{CH}_2\text{COOH}$ (60% yield).

3. Results and discussion

The hydrogen transfer reactions studied are schematized in Eqs. 1–3:



In order to make the study of the effect of the reaction variables on the yield possible, experiments were carried out at a typical temperature of 90°C at which decomposition of the catalyst precursor to the metal is not observed, in the presence of a low concentration of catalyst and for a reaction time that results in a yield which is significantly lower than 100%. In the pres-

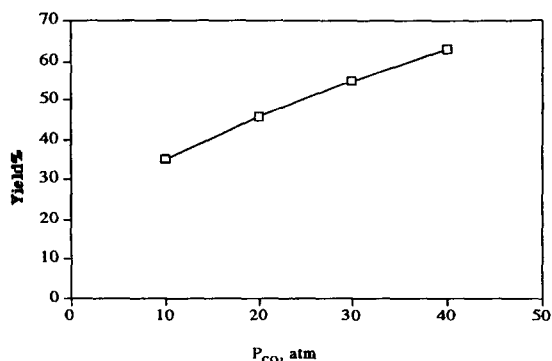


Fig. 2. Run conditions: $\text{PhCOCH}_2\text{CHOHCOOH}$ 12 mmol, H_2O 44 mmol, HCl 6 mmol, $\text{PdCl}_2(\text{PPh}_3)_2$ $6.4 \cdot 10^{-3}$ mmol in 8 ml dioxane ($V_{\text{tot}} = 11$ ml); temperature 90°C ; reaction time 2 h.

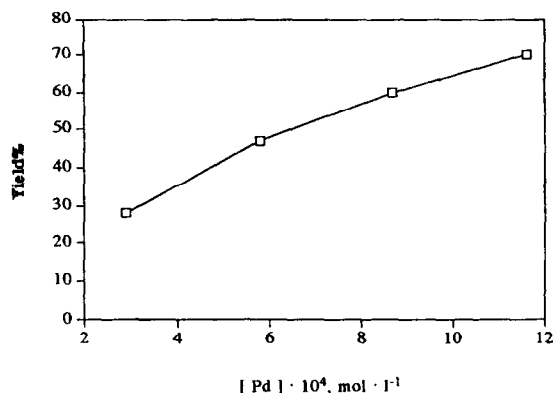


Fig. 3. Run conditions: $\text{PhCOCH}_2\text{CHOHCOOH}$ 12 mmol, H_2O 44 mmol, HCl 6 mmol in 8 ml dioxane; $P_{\text{CO}} = 30$ atm at room temperature; temperature 90°C ; reaction time 2 h.

ence of H_2O and HCl, the substrates employed in reactions (1–3) yield comparable results because they interconvert. The results reported here refer to reaction (2), since we observed that $\text{PhCOCH}_2\text{CHOHCOOH}$ gives slightly lower yields.

An increase in temperature, pressure of carbon monoxide, and catalyst concentration have a beneficial effect on the yield as represented in Figs. 1–3.

The yield is practically independent of the concentration of the substrate, thus indicating that the reaction rate is practically first order in the substrate (Fig. 4). Moreover, the yield is practically not influenced also when PPh_3 is

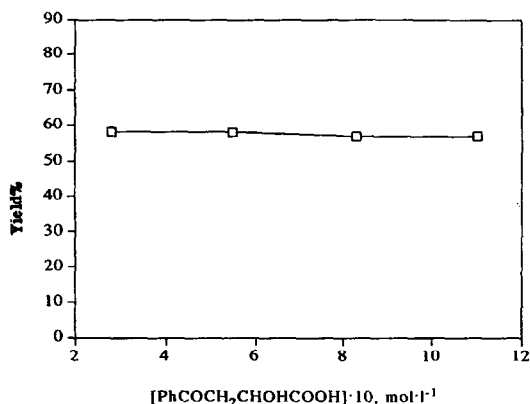


Fig. 4. Run conditions: H_2O 71 mmol, HCl 6 mmol, $\text{PdCl}_2(\text{PPh}_3)_2$ $6.4 \cdot 10^{-3}$ mmol in dioxane ($V_{\text{tot}} = 11$ ml); $P_{\text{CO}} = 30$ atm at room temperature; temperature 90°C ; reaction time 2 h.

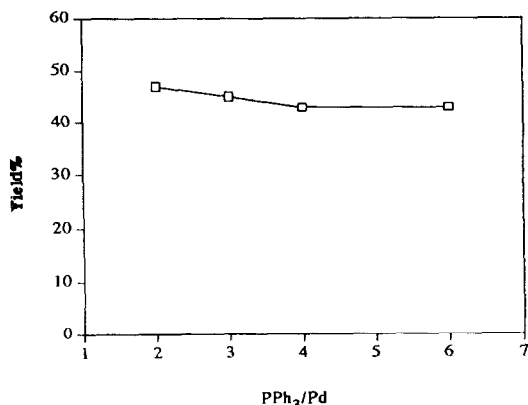


Fig. 5. Run conditions: PhCOCH₂CHOHCOOH 12 mmol, H₂O 44 mmol, HCl 6 mmol, PdCl₂(PPh₃)₂ 6.4 · 10⁻³ mmol in 8 ml dioxane; P_{CO} = 30 atm at room temperature; temperature 90°C; reaction time 2 h.

added to the catalyst precursor (Fig. 5), thus indicating that this ligand does not compete significantly with other reacting molecules for the coordination with the central metal atom.

The reaction rate is significantly influenced by the presence of H₂O and HCl. The effect of the concentration of H₂O is shown in Fig. 6. The yield increases on increasing the concentration of H₂O in the range 0–6 mol l⁻¹, after which a further increase in H₂O concentration results in a decrease in yield. This trend can be attributed to the fact that on one hand H₂O is a

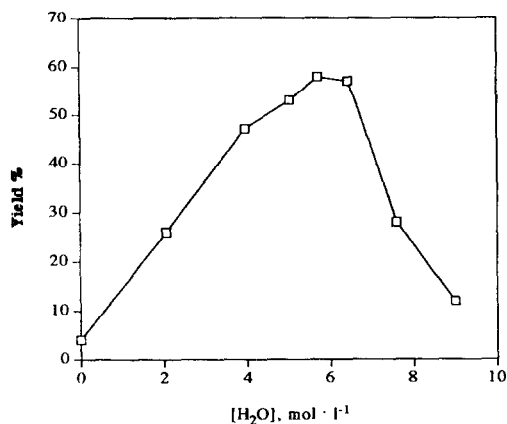


Fig. 6. Run conditions: PhCOCH₂CHOHCOOH 12 mmol, HCl 6 mmol, PdCl₂(PPh₃)₂ 6.4 · 10⁻³ mmol in dioxane (V_{tot} = 11 ml); P_{CO} = 30 atm at room temperature; temperature 90°C; reaction time 2 h.

reactant, even though this does not appear in reaction (2), where PhCOCH₂CHOHCOOH is equivalent to PhCOCH=CHCOOH and H₂O in the ratio 1/1, on the other hand H₂O may compete with other reacting molecules for coordination to the metal center and, probably more important, does not favor the formation of the γ -keto chloride (equilibrium (4)), which is proposed to interact with a hydride of palladium(II) in the step yielding the product (see the proposed catalytic cycle, step 10):



Quite interestingly a similar trend has been found in the Pd/C–HCl catalyzed hydrogen transfer from H₂O–CO to ArCHOHCOOH that yields ArCH₂COOH with concomitant evolution of CO₂ [11].

We have also found that the yield passes through a maximum with the variation of the concentration of HCl as shown in Fig. 7. It should be underlined that there is no catalytic activity when the reaction is carried out without HCl. Thus, even though HCl is not a reactant, it must play a key role in the catalytic cycle. We proposed that an important function of HCl is to give rise to chloride PhCOCH₂CHClCOOH which interacts with a palladium hydride that

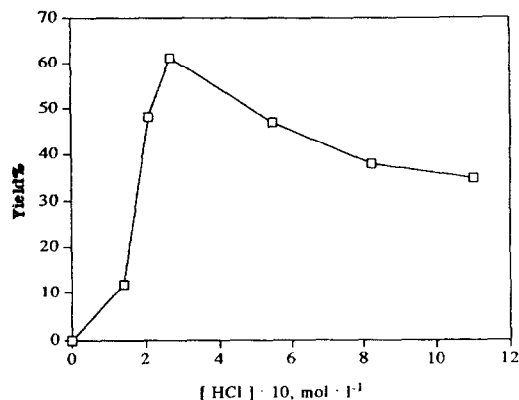
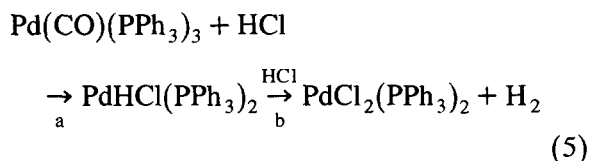


Fig. 7. Run conditions: PhCOCH₂CHOHCOOH 12 mmol, H₂O 44 mmol, PdCl₂(PPh₃)₂ 6.4 · 10⁻³ mmol in dioxane (V_{tot} = 11 ml); P_{CO} = 30 atm at room temperature; temperature 90°C; reaction time 2 h.

takes origin from the decarboxylation of a Pd-COOH species, which in turn is formed from the interaction of H₂O and CO on the metal center (see the proposed catalytic cycle).

It is worth noting that in the Pd/C-HCl catalyzed hydrogen transfer from H₂O-CO to ArCHOHCOOH that yields ArCH₂COOH it has been found that the effect of the concentration of H₂O and of HCl has a trend similar to the one shown in Figs. 6 and 7 [11].

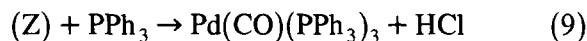
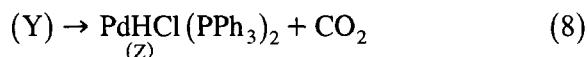
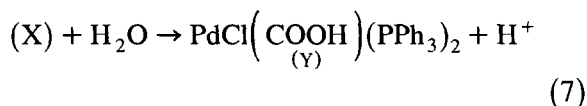
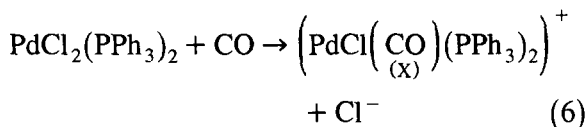
The catalyst is also very efficient in acetonitrile as solvent. Moreover, when employing the catalyst in higher concentration, for example 5–10 mmol l⁻¹ and in the presence of an equimolecular amount of PPh₃, it has been partially recovered as a complex of palladium(0), Pd(CO)(PPh₃)₃ [12]¹, even when catalysis is carried out in the presence of relatively large amounts of HCl. This is rather remarkable because it has been reported that Pd(CO)(PPh₃)₃ reacts at low temperature with an equimolecular amount of dry HCl to give a hydride-chloride and with an excess of HCl and at room temperature to give a dichloride [13]:



Moreover, we have found that PdCl₂(PPh₃)₂ is not reduced by CO in the absence of H₂O and that Pd(CO)(PPh₃)₃ is not reoxidized to PdCl₂(PPh₃)₂ when treated even with a relatively large excess of HCl in the presence of CO and of H₂O. Thus H₂O plays a key role in keeping palladium in a low oxidation state.

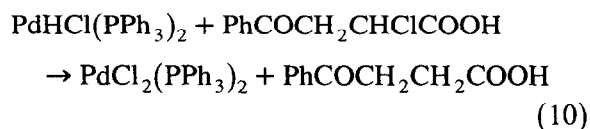
The reduction of the precursor probably occurs through the intermediacy of a palladium-carbohydroxy species (Y) which is formed

through the interaction of CO with H₂O on the metal center:



If, in the presence of CO and H₂O, hydride (Z) reacted with HCl as in reaction (5b), Eqs. (5–8) would compose a catalytic cycle for the WGSR. This mechanism retraces the one proposed for the WGSR catalyzed by Pd(CF₃COO)₂(PPh₃)₂ in aqueous trifluoroacetic acid [14,15].

However, the WGSR reaction does not take place to an appreciable extent under the conditions in which PdCl₂(PPh₃)₂ catalyzes reactions (1–3). Instead, we have found that, when to an acetonitrile solution of PhCOCH=CHCOOH and of HCl an equimolecular amount of the complex of palladium(0) Pd(CO)(PPh₃)₃ is added under CO atmosphere, there is formation of the hydrogenated product PhCOCH₂CH₂COOH in ca. 30% yield, and of PdCl₂(PPh₃)₂ (practically quantitative). This result suggests that under these conditions the palladium(0) complex reacts with HCl to give the hydrido chloride that in part reacts further with HCl to give the dichloride as schematized in (5b), and in part it reacts with chloride PhCOCH₂CHClCOOH to give the hydrogenated product and PdCl₂(PPh₃)₂:



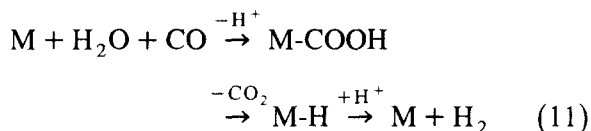
Reactions (6–8) and (10) compose a catalytic cycle which is proposed to be operative for reactions (1–3). Reaction (10) can be viewed as

¹ In the absence of added PPh₃ the complex of palladium(II) is reduced by CO-H₂O to the palladium(0) complex Pd₃(CO)₃(PPh₃)₃ [12].

the result of a hydride transfer from Pd(II) to chloride PhCOCH₂CHClCOOH similar to the one that occurs with HCl in reaction (5b).

The trend shown in Fig. 7 may be related to equilibrium (7). An increase of the concentration of HCl increases the concentration of chloride PhCOCH₂CHClCOOH, and hence the rate of the formation of the product (step 10), however, it opposes equilibrium (7). When NaOH is used in place of HCl, the precursor is readily reduced to palladium(0), however, the catalytic activity falls to zero. Thus, even though NaOH is likely to favor the formation of a species such as (Y), through nucleophilic attack of OH⁻ to carbonyl (X)², it favors also the reductive elimination of HCl from intermediate (Z), with formation of a palladium(0) complex which is inactive unless HCl is present. Thus another important function of HCl is to increase the concentration of the hydride–chloride (Z).

Thus this mechanism is basically related to that of the WGS catalyzed by transition metal complexes. In this case the metal-hydride that is formed upon decarboxylation of a M-COOH moiety interacts with a proton with evolution of hydrogen:



In the present case there is no hydrogen evolution, even in the presence of relatively

high concentration of HCl. This fact suggests that the interaction of the hydride with the organic chloride is much faster than with hydrochloric acid.

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² Since the palladium system described here is highly active in the presence of an acid such as HCl, it appears that CO activation through coordination is sufficient to facilitate the nucleophilic attack by water as schematized in step (7).