

Homogeneous mono- and bimetallic palladium based catalysts for the carbonylation of allyl chloride

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Received 25 September 1996; accepted 11 September 1997

Abstract

$\text{PdCl}_2(\text{TPPTS})_2$ [TPPTS = (*m*-C₆H₄SO₃Na)₃P] is used as catalyst in the carbonylation of allyl chloride. This catalyst exhibits very high activity and selectivity in the dilute alcoholic–aqueous NaOH/toluene medium under atmospheric pressure of carbon monoxide at 40°C. Ethanol plays an important role for increasing the catalytic activity and selectivity of $\text{PdCl}_2(\text{TPPTS})_2$. The turnover reaches 2.7×10^4 (mol CO/mol Pd) in 21.5 h when the mole ratio of substrate/catalyst is 3×10^4 . A synergic effect was observed when a second transition metal compound was added to the catalytic system. © 1998 Elsevier Science B.V.

Keywords: Carbonylation; Allyl chloride; Homogeneous bimetallic catalysts

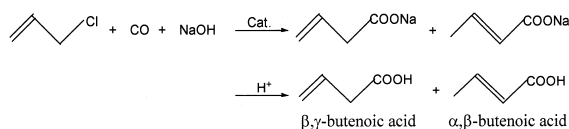
1. Introduction

The carbonylation of allyl halides catalyzed by the transition metal complex offers a valuable tool for the synthesis of β, γ -unsaturated acid [1]. A number of articles using transition metal complexes as catalysts have been published [2–5]. Since allyl halides are susceptible to nucleophilic attack and elimination reactions

under high temperature and pressure, considerable effort has been devoted to conducting the reaction under mild conditions in order to avoid the side reactions [6–9]. Kiji et al. succeeded in the carbonylation of allyl chloride catalyzed by PdCl_2L_2 (L = $\text{Ph}_2\text{P}(m\text{-C}_6\text{H}_4\text{SO}_3\text{Na})$ or Ph_3P) and Na_2PdCl_4 in a two-phase system under atmospheric pressure [6,7]. We have reported the use of polymer supported palladium catalyst to catalyze this reaction [8,9]. Although the catalytic activity and selectivity of the catalyst have been improved, it is still not high enough.

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Recently, we found that $\text{PdCl}_2(\text{TPPTS})_2$ exhibited very high catalytic activity for the carbonylation of allyl chloride in a dilute alcoholic–aqueous $\text{NaOH}/\text{toluene}$ two-phase medium. The addition of a second transition metal compound to the catalytic system influences the catalytic activity and selectivity for β,γ -butenoic acid. The carbonylation can be demonstrated as follows:



2. Experimental

2.1. Materials

The trisodium salt of tri(*m*-sulfonphenyl)-phosphine (TPPTS) was prepared in accordance with the method described in the literature [10]. The sodium salt of tri(sulfonphenyl)-phosphine oxide as an impurity was less than 5%. Water content was about 10%. PdCl_2 was purchased from Johnson Matthey (Pd content 59.89%). $\text{PdCl}_2(\text{PPh}_3)_2$ [11], $\text{PdCl}_2(\text{PhCN})_2$ [12], $\text{Pd}(\text{PPh}_3)_4$ [13] were prepared according to the literature. Water was doubly distilled. Toluene was distilled from Na metal under argon. Carbon monoxide with a purity of 98% (the hydrogen content was 0.02%) was commercially available and directly used.

2.2. Preparation and characterization of $\text{PdCl}_2(\text{TPPTS})_2$

100 mg PdCl_2 and 2 ml of 2 M HCl were added into a Shlenk flask and the mixture was stirred at 50°C until PdCl_2 was dissolved completely. After the flask was cooled to the room temperature and flushed with argon, 0.80 g TPPTS was added into the flask under stirring. The color of the solution was changed from dark red to bright yellow immediately. After 10

min stirring, 15 ml, absolute ethanol was added, a light yellow powder was precipitated and the mixture was stirred for 30 min. The filtered precipitate was washed three times with 30 ml warm 95% ethanol and dried in vacuum. ^{31}P NMR was recorded on a FT-80A spectrometer. Only one peak was observed and the chemical shift was 34.7 ppm, indicating that only one of the steric isomers was obtained and there was no sodium salt of tri(sulfonphenyl)-phosphine oxide. Palladium content was found 7.8% (calculated, 8.0%) determined on Plasma-Spec-I Analyzer (U.S. Leeman Company) [14]. XPS data was obtained with a VGE SCALAB mk-2 X-ray photoelectron spectrometer. The binding energy of $\text{Pd}3\text{d}_{5/2}$ and $\text{P}2\text{p}$ was 338.0 and 131.8 eV respectively. It is analogous to that of $\text{PdCl}_2(\text{PPh}_3)_2$ ($\text{Pd}3\text{d}_{5/2}$, 338.1 ± 0.3 eV; $\text{P}2\text{p}$, 131.7 ± 0.1 eV) [15].

2.3. Catalytic reaction

A typical procedure was conducted as follows: catalyst, sodium hydroxide and phase transfer agent (if it was used) were added into a 50 ml three necked, jacketed bottle closed with self-sealing silicon rubber cap, connected to the vacuum, carbon monoxide lines and constant pressure gas burette. The temperature of the circulating water passing through the jacket was maintained by a thermostat. After the atmosphere was replaced with carbon monoxide, water, toluene and aqueous solution of $\text{PdCl}_2(\text{TPPTS})_2$ were added successively. After the mixture was stirred vigorously for 15 min, allyl chloride was added. The course of the reaction was monitored by the carbon monoxide uptake measured by the constant pressure gas burette. After the reaction, the aqueous layer was acidified with excess hydrochloric acid and then used for the analysis of butenoic acids by HPLC (Shimadzu LC-5A, 4.6 mm i.d. \times 25 cm Zorbax ODS column; mobile phase, (v/v) $\text{MeOH}/\text{H}_2\text{O} = 1:1$) and the analysis of allyl alcohol by GC (2 m DEGS column) using external standard method.

3. Results and discussion

3.1. Carbonylation of allyl chloride catalyzed by PdCl₂(TPPTS)₂

3.1.1. Effect of solvents

Table 1 summarizes the results of solvent effect on the carbonylation of allyl chloride catalyzed by PdCl₂(TPPTS)₂ in aq. NaOH/toluene two phase medium under atmospheric pressure. If pure water is used as solvent, the reaction rate is very low and the selectivity for β,γ -butenoic acid is poor. The main byproducts are allyl alcohol and propene. It is found that the addition of ethanol to the reaction system accelerates the reaction rate significantly. When the reaction is carried out in a dilute alcoholic–aqueous solution, the catalytic activity is increased remarkably and the side reactions can be mostly avoided. The catalytic activity of PdCl₂(TPPTS)₂ increases with increasing ethanol concentration in the aqueous phase. However, high concentration of ethanol causes the formation of allyl ethyl ether. If absolute alcohol is used as solvent, the reaction rate is still high; but the reaction between allyl chloride and alcohol with the formation of allyl ethyl ether and the reaction between CO and NaOH with the formation of sodium formate are serious. It seems that a 23% alcoholic–aqueous solution is preferable. The average turnover fre-

quency (TOF_{av} mol allyl chloride converted/mol Pd per min) reaches 30.9 min⁻¹ when a 23% alcoholic–aqueous solution is used as solvent. To our knowledge, this result is much higher than those reported in the literature so far. In addition, the catalytic activity of PdCl₂(TPPTS)₂ is very stable during the carbonylation of allyl chloride. When the mole ratio of substrate/catalyst is 3×10^4 , the turnover (mol CO/mol Pd) reaches 2.7×10^4 in 21.5 h under atmospheric pressure of carbon monoxide at 40°C.

Some studies [16,17] have demonstrated that the co-solvent such as ethanol can increase the transfer phenomenon between water and organic solvent in the hydrogenation and hydroformylation catalyzed by water soluble rhodium–phosphine complexes. In the case of the carbonylation of allyl chloride catalyzed by PdCl₂(TPPTS)₂ in H₂O/toluene two-phase medium, the addition of ethanol to the reaction system leads to a very high reaction rate which may be related to the higher solubility of allyl chloride in alcoholic–aqueous medium.

3.1.2. Effect of bases

Various bases were tested for the reaction, and the results are presented in Table 2. Strong bases such as NaOH and KOH are effective. NaOAc is ineffective. It is noteworthy that when Ca(OH)₂ is used as the base, the selectivity for

Table 1
Effect of ethanol concentration in the aqueous phase on the carbonylation of allyl chloride catalyzed by PdCl₂(TPPTS)₂

Ethanol (%) ^a	Time (min)	TOF _{av} (min ⁻¹) ^b	Yield (%)		
			butenoic acid ($\beta,\gamma/\alpha,\beta$) ^c	allyl alcohol	allyl ethyl ether
0	245	10.2	90 (6)	3.5	0
9	180	13.9	93 (13)	1.6	trace
23	81	30.9	94 (21)	1.1	trace
33	63	39.7	95 (21)	1.0	1.7
100 ^d	90	27.8	57 (18)	0	43

Reaction conditions: 40°C; 0.1 MPa; Pd. 5.07×10^{-3} mmol; allyl chloride/Pd = 2500 (mole ratio); NaOH, 25 mmol; solvent, water, 10 ml, toluene, 10 ml.

^aEthanol concentration, [EtOH/(EtOH + H₂O)] \times 100% (V/V%).

^bAverage turnover frequency, mol allyl chloride converted/mol Pd min.

^cThe value in the parentheses is the mole ratio of β,γ -butenoic acid to α,β -butenoic acid.

^d10 ml absolute ethanol was used as solvent. 0.6 mmol sodium formate was produced during the reaction.

Table 2
Effect of base on the carbonylation of allyl chloride catalyzed by PdCl₂(TPPTS)₂

Base	Time (min)	Conversion (%)	Yield (%) ^a	
			butenoic acid (β,γ/α,β)	allyl alcohol
NaOH	81	100	94 (21)	1.1
KOH	90	100	86 (17)	1.6
Ca(OH) ₂	160	50	46 (32)	1.7

Reaction conditions: base, 25 mmol; ethanol concentration, 23%; the others are the same as those in Table 1.

^aUnder these reaction conditions, only a trace amount of allyl ethyl ether has been observed by GC analysis.

Table 3
Comparison of various homogeneous palladium catalysts for the carbonylation of allyl chloride

Catalyst	Ethanol (%)	Time (min)	TOF _{av} (min ⁻¹)	Yield (%)	
				butenoic acid (β,γ/α,β) ^c	allyl alcohol
Na ₂ PdCl ₄	0	200	3.25	5 (1)	21.0
	23	220	11.4	97 (13)	2.3
PdCl ₂ (TPPTS) ₂	0	245	10.2	90 (6)	3.5
	23	81	30.9	94 (21)	1.1
Pd(PPh ₃) ₄	0	320	2.3	27 (6)	1.9
	23	320	7.8	94 (9)	1.9
PdCl ₂ (PPh ₃) ₂	0	250	3.5	31 (2)	2.1
	23	250	2.0	16 (2)	2.4
PdCl ₂ (PhCN) ₂	23	250	10.0	95 (13)	2.3

Reaction conditions: the same as those in Table 1.

β,γ-butenic acid is very high. Kiji et al. [6] have reported that α,β-butenic acid is not a direct product of the carbonylation. It is the product of the base catalyzed isomerization of β,γ-butenic acid and the ratio of β,γ/α,β depends on the concentration of NaOH. The results in Table 2 indicate that the degree of isomerization of β,γ-butenic acid varies with different basicity of the base as well.

3.1.3. Comparison of various homogeneous palladium catalysts

Five catalysts have been tested. Among which, Na₂PdCl₄ and PdCl₂(TPPTS)₂ are water soluble while the others are soluble in toluene. It can be seen from Table 3 that among the homogeneous palladium catalysts investigated, PdCl₂(TPPTS)₂ exhibits the highest catalytic activity and selectivity. In the case of Na₂PdCl₄ and Pd(PPh₃)₄, the presence of ethanol also greatly accelerates the reaction rate, but in the case of PdCl₂(PPh₃)₂, the catalytic activity decreases.

The kinetic curves using various homogeneous palladium catalysts are shown in Fig. 1. The course of the reaction was monitored by the

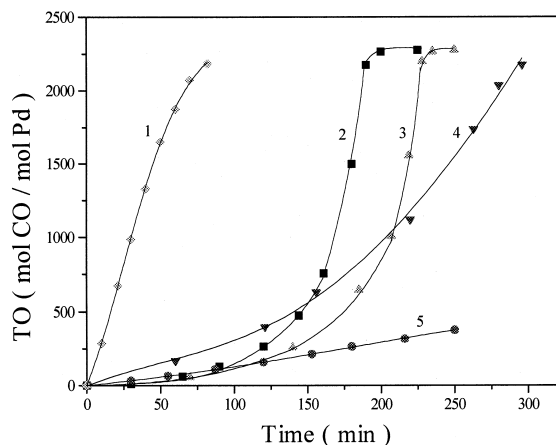


Fig. 1. Kinetic curves of the carbonylation of allyl chloride catalyzed by homogeneous palladium catalysts. Catalyst: 1 = PdCl₂(TPPTS)₂; 2 = Na₂PdCl₄; 3 = PdCl₂(PhCN)₂; 4 = Pd(PPh₃)₄; 5 = PdCl₂(PPh₃)₂. Reaction conditions: ethanol concentration, 23%; the others are the same as those in Table 1.

Table 4
Carbonylation of allyl chloride catalyzed by PdCl₂(TPPTS)₂-ML_n

Catalyst	Time (min)	TOF _{av} (min ⁻¹)	Yield (%)	
			butenoic acid (β,γ/α,β)	allyl alcohol
CuCl ₂ ^a	80	—	0	1.0
Co ₂ (CO) ₈ ^a	80	—	0	1.6
NiCl ₂ ^a	240	—	0	1.9
Co(OAc) ₂ ^a	330	—	0	3.8
PdCl ₂ (TPPTS) ₂	81	30.9	94 (21)	1.1
PdCl ₂ (TPPTS) ₂ -RuCl ₃	73	34.2	96 (19)	0.9
PdCl ₂ (TPPTS) ₂ -Co(OAc) ₂	71	35.2	92 (13)	1.1
PdCl ₂ (TPPTS) ₂ -SnCl ₂	85	29.4	92 (16)	1.3
PdCl ₂ (TPPTS) ₂ -NiCl ₂	68	36.8	95 (15)	1.0
PdCl ₂ (TPPTS) ₂ -CuCl ₂	56	44.6	87 (19)	3.4
PdCl ₂ (TPPTS) ₂ -Co ₂ (CO) ₈	60	41.7	92 (17)	1.3

Reaction conditions: Pd, 5.07×10^{-3} mmol; ethanol concentration, 23%; M/Pd = 1 (mole ratio); the others are the same as those in Table 1.

^a0.02 mmol ML_n was used.

carbon monoxide uptake and the turnover (TO) represents mol CO uptake per mol Pd at the time indicated in the figure. Since the side reactions, such as hydrolysis and hydrodechlorination of allyl chloride, do not consume carbon monoxide, so the conversion of allyl chloride is higher than that calculated from the consumption of CO.

3.2. Carbonylation of allyl chloride catalyzed by the palladium based bimetallic catalysts

In order to improve the catalytic properties of the monometallic catalyst, much attentions have been focused on the homogeneous bimetallic catalysts [18–25]. Several metal compounds

such as NiCl₂, RuCl₃, CuCl₂ or Co₂(CO)₈ were added as the second component to PdCl₂(TPPTS)₂ and the synergic effects with respect to catalytic activity and selectivity were studied. The results in Table 4 demonstrate that in most cases, a second metal compound added accelerates the reaction rate. No reaction takes place when these second metal compounds are used alone even if a large amount of these compounds is used. The synergic effect of the above mentioned second metal compounds with Na₂PdCl₄ catalyst has also been studied. No obvious synergic effect was observed.

Table 5 gives the catalytic behaviors of PdCl₂(TPPTS)₂-CuCl₂ and PdCl₂(TPPTS)₂-Co₂(CO)₈ in different M/Pd ratios. Although

Table 5
PdCl₂(TPPTS)₂ catalyzed carbonylation of allyl chloride in the presence of CuCl₂ or Co₂(CO)₈

M/Pd	Mole ratio	Time (min)	TOF _{av} (min ⁻¹)	Yield (%)	
				butenoic acid (β,γ/α,β)	allyl alcohol
Cu/Pd	0	81	30.9	94 (21)	1.1
	0.25	60	41.7	90 (18)	2.3
	1	56	44.6	87 (19)	3.4
	4	43	58.1	68 (22)	7.7
	8	42	59.5	62 (22)	11.9
Co/Pd	1	60	41.7	92 (17)	1.3
	8	66	37.9	91 (26)	0.6
	10	69	36.2	91 (20)	1.6

Reaction conditions: ethanol concentration, 23%; M/Pd = 1; the others are the same as those in Table 1.

the reaction rate is accelerated with the increase of the Cu/Pd ratio, the selectivity for butenoic acid decreases and large amount of byproducts such as propene and allyl alcohol are produced. Propene may be produced by the hydrodehalogenation of allyl chloride catalyzed by palladium catalyst. It is considered that except small amount of H₂ in CO, the reactive hydrogen may be generated by the water gas shift reaction. Co/Pd ratio does not give obvious effect on the activity.

Acknowledgements

The authors would like to thank the National Natural Science Foundation of China and the Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences for the financial support.

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