

DECARBOXYLATION OF ALLYL β -KETO ESTERS TO UNSATURATED KETONES ON POLYMER BOUND PHOSPHINE-PALLADIUM(0) COMPLEXES*

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ABSTRACT

Polystyrylphosphine-Pd(0) and silica supported polysiloxane-phosphine-Pd(0) complexes were synthesized and characterized. Their catalytic properties for the decarboxylation of allyl β -keto esters were investigated. It was found that these complexes have good catalytic activities under mild condition for this decarboxylation in which many novel unsaturated ketones were obtained. The selectivity of this catalytic decarboxylation depends on the polymer ligand and the P/Pd ratio of catalyst. The stabilities of polymer phosphine-Pd(0) complexes catalysts are better than their homogeneous analogue.

INTRODUCTION

The synthesis of ketone from β -keto ester is an important method to get the ketones with novel structure. Usually, three-stepwise reaction, that is, alkylation, hydrolysis and decarboxylation, is necessary. Saegusa^[1] and Tsuji^[2] reported recently that the unsaturated ketones could be obtained from allyl β -keto esters through only one step decarboxylation reaction using homogeneous palladium-phosphine complex catalysts. High yield γ , δ -unsaturated ketones were synthesized by using tetrakis (triphenylphosphine) palladium (0) as catalyst at room temperature. α , β -Unsaturated ketones were prepared by using palladium acetate-1,2-bis (diphenylphosphine) ethane system as catalyst at acetonitrile refluxing temperature. Because it is easy to obtain the allyl β -keto esters^[3-7], the above mentioned catalytic decarboxylation is a very useful method for preparing many novel ketones for which general methods are scarce.

However, palladium (0)-phosphine complexes are very sensitive to air and easily lose their catalytic activities due to absorbing molecular oxygen. Several advantages have been attributed to polymer attached homogeneous catalyst, such as the enhance of catalytic activity and selectivity, no corrosion, ease of separation from the product and stabilization of metal complex^[8,9]. In the present work, we are interested in immobilizing the air sensitive homogeneous Pd(0) complex to polymer and investigate their catalytic properties in catalytic decarboxylation of allyl β -keto ester. The polymer anchored Pd(0) complex catalysts prepared not only possess good catalytic activity but also have the better stability than the homogeneous catalyst.

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EXPERIMENTAL

1. Materials and Equipments

THF and benzene were continuously refluxed and distilled from suspensions or solutions of sodium benzophenone prior to use. The deoxygenated benzene was made by evacuating and filling with N_2 five times.

2% DVB-crosslinked chloromethylated polystyrene (200—400 mesh, Cl 1.25 meq/g) was obtained from Sigma Chemical Co. The silica with specific area of 370 m^2/g was the product of Shenyang Chemical Factory.

$Pd(PPh_3)_4$ was prepared according to the literature method^[10].

Phosphorus and palladium content were analyzed by using spectrophotometric method^[11,12].

IR, ^1H NMR and XPS data were obtained on Perkin-Elmer 683, Cameca-RMN 250 and KRATOS AEI ES-300 instruments respectively. Analytic GLC was performed on a Shang-Fen model 103 gas chromatograph using 3M OV-225 on Shangshi Silyl 102 column.

2. Preparation of Polymeric Phosphine Ligands

The chloromethylpolystyrene (PS-Cl) was treated with $LiPPh_2$ ^[13] in a manner similar to Allum's method^[14] for getting the diphenylphosphinomethylpolystyrene (PSP-1). Silica supported poly- γ -diphenylphosphinopropylsiloxane (SiLp-1) was prepared by treating silica with γ -chloropropyltriethoxysilane (producing SiL-Cl) firstly and then with $LiPPh_2$ according to the same procedure mentioned above.

3. Preparation of Polymer Phosphine Pd(0) Complexes

A typical procedure is as follows: Phosphinated polystyrene (10 g PSP-1 P 7 mmol) was suspended in 150 ml deoxygen benzene containing $Pd(PPh_3)_4$ (4 g, 3.5 mmol). The mixture was stirred under nitrogen and refluxed for 3 days. Filtered and washed with benzene, THF and dried under vacuum. Finally, bright red product, PSP-Pd(0)-1, was obtained.

The catalysts PSP-Pd(0)-2 (with different Pd content from PSP-Pd(0)-1) and SiLp-Pd(0) were prepared by the same procedure mentioned above. If benzene was not deoxygenated, a dark brown product PSP-Pd(0)-3 was obtained.

4. Catalytic Decarboxylation of Allyl β -Keto Ester

The following is a representative procedure: A mixture of 2m mol allyl β -keto ester and 0.2 g (0.02 mg-atom Pd) PSP-Pd(0)-1 and 5 ml THF were added into a 50 ml round-bottomed flask equipped with condenser and a magnetic stirrer. This mixture was stirred at refluxing temperature under nitrogen and analyzed periodically by using GLC.

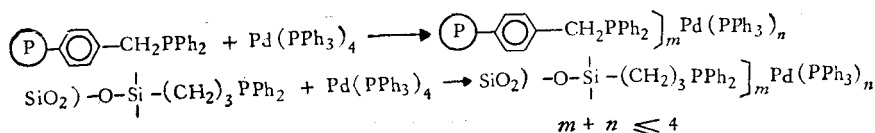
RESULTS AND DISCUSSION

1. Characterization of Polymer Phosphine-Pd(0) Complexes

The polymer phosphine-Pd(0) complexes were prepared by the ligand exchange reaction

(Scheme 1).

Scheme 1



The analytical data of polymer phosphine Pd(0) catalysts were listed in Table 1. The atomic ratio of phosphorus to palladium is 2.5–5.9. Because of the steric effect of polymer chain and ligand, more than two anchored phosphines coordinate with one palladium atom

Table 1 Phosphorus and palladium analysis

Catalyst	P(%)	Pd(%)	P/Pd	Color
PSP-Pd(0)-1	2.17	1.28	5.4	bright red
PSP-Pd(0)-2	2.14	2.56	2.5	dark red
PSP-Pd(0)-3	2.17	1.17	5.9	dark Brown
SiLp-Pd(0)	1.8	1.65	4.5	dark red

should become highly thermodynamic unfavourable. Even if three or four anchored phosphines did coordinate to palladium, swelling polymer should cause the dissociation of phosphine to generate a more coordinatively unsaturated situation^[15]. Therefore, it seemed likely that only up to two anchored phosphines would actually coordinate with palladium even though the $\text{P/Pd} > 2$. In other word, in Scheme 1, m should be 1 or 2. On the other hand, XPS analysis showed that there still is small amount of PPh_3 coordinating with palladium in polymer complexes that means n should be 0,1,2 or 3.

The formation of polymer phosphine-Pd(0) complexes were evidently elucidated by IR and XPS data. Comparing IR spectra of polymeric ligand, polymer catalyst and homogeneous analogue (Table 2), three bands of 510cm^{-1} , 720cm^{-1} ; 1435cm^{-1} which are supposed to be P—C bond absorption were not found in the spectra of polymer (PS—Cl) but observed in that of

Table 2 IR spectra of polymer ligands and catalysts

Sample	$\nu_{\text{P-C}}$ (cm^{-1})	$\nu_{\text{P-Pd}}$ (cm^{-1})
PS-Cl	/	/
PSP-I	510_w 720_w 1435_m	/
PSP-Pd(0)	510_s 720_m 1435_s	395_m
SiLp-Pd(0)	540_s 690_s 720_s 1435_s 1480_w 1590_w	to be covered
$\text{Pd}(\text{PPh}_3)_4$	510_s 525_m 540_s 720_s 1435_s 1480_s 1485_w	410_m

polymer ligand. As we had expected, the intensity of these peaks increase in the spectra of polymer complexes. It is worthy to note, one new band at 395cm^{-1} of P-Pd absorption appeared in the spectra of polymer complexes. This band is in the near position with that of Pd(PPh_3)₄. Above results were consistent with that observed from other polymer palladium complex^[16] and indicated that the polymer phosphine palladium complexes had formed.

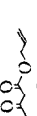
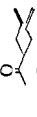
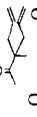
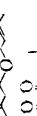
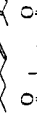
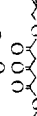
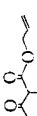
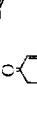
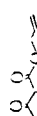
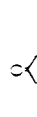
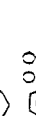
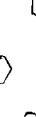
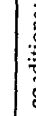
X-ray photoelectrospectroscopy (XPS) study on polymer catalysts supported the formation of polymer palladium complexes and a zero oxidation state for palladium (Table 3). The

Table 3 XPS data

Sample	Binding energies (eV)				
	P _{2p}	Pd _{3d_{5/2}}	Si _{2p}	O _{1s}	Cl _{2p}
PPh ₃	130.8				
Pd(PPh ₃) ₄	131.8	337.2			
PS-Cl					201.1
PSP-I	130.5				
PSP-Pd(0)-1	132.6	336.8			
PSP-Pd(0)-3	132.8	336.8		532.6	
SiL-Cl			103.9	533.4	201.1
SiLp-I	130.8		103.8	533.4	
SiLp-Pd(0)	132.8	336.2	103.7	533.4	
PdCl ₂		338.3			199.2
Pd metal		335.5			

P_{2p} binding energies of polymer phosphine ligands are almost the same with triphenylphosphine, this is understandable because the bonding groups with phosphorus atoms both in polymer phosphine and triphenylphosphine are all the carbon atoms. It is more important that the P_{2p} binding energies increased 2.1—2.3 eV after ligand exchange reaction of polymer ligand with tetrakis (triphenylphosphine) palladium(0). These shifts evidently demonstrated that the phosphorus atom donated electrons to palladium while the coordination bond formed. On the other hand, the P_{2p} spectra of polymer complexes showed broader peaks with 3.0—3.4 eV energy widths at half-maximum intensity which are broader about 0.8—1.2 eV than that of P_{2p} of triphenylphosphine. This perhaps shows the phosphines coordinated with palladium in polymer complex to be composed of two species, the major anchored phosphines and a little triphenylphosphine. It is not surprising that no great difference was found in Pd_{3d_{5/2}} binding energies between polymer complexes and Pd(PPh₃)₄, because ligand exchange reaction did not change the coordination situation markedly. However, this data gave a good evidence for a Pd(0) complex but not a palladium metal. PSP-Pd(0)-3 was prepared in undeoxygenated benzene. A lower O_{1s} and a little higher P_{2p} binding energy were observed. That seems to be some P=O in this catalyst.

Table 4 Catalytic decarboxylation of allyl β -keto esters by PSP-Pd(0)-1*

Entry	β -keto ester	Product	Time (h)	Conversion** (%)	Yield of decarboxylation (%)
1			2	95.7	76.7
2			24	86.5	68.3
3			24	80.2	67.9
4			24	100	70.2
5			4	100	77.2
6			2	100	95.2
7			3	—	80.2
8			24	—	60.3
9			24	—	75.8

* Reaction conditions: Substrate 2m mol, Pd 0.02 mg-atom, 5 ml THF, 65°C, 1 atm.

** Conversion of allyl % is total conversion percentage of allyl groups both in decarboxylation and allyl substitution reactions.

2. Catalytic Properties

Polymer phosphine Pd(0) complex catalysts PSP-Pd(0)-1,2,3 and SiLp-Pd(0) were used for catalytic decarboxylation of allyl acetoacetate. No great difference in catalytic activity was found among these catalysts except PSP-Pd(0)-3 which gave a lower catalytic activity. Then PSP-Pd(0)-1 was used to catalyze the decarboxylation of a series of allyl β -keto esters. Table 4 summarized the results. It is seen that the polymer phosphine Pd(0) complex catalyst has good catalytic activity for catalytic decarboxylation of allyl β -keto ester to produce C—C bond coupling products of α -allyl ketones or α,β -enones under mild condition and this catalytic decarboxylation provided an excellent procedure for synthesis of unsaturated ketones. It was found that the reaction rates were going slower for those of β -keto esters with substitute on α -methyl or methylene and allyl group (entries 2—4,8). If the keto group was displaced by electron withdrawing group such as—CN (entry 9), the decarboxylation still took place in the same condition. It was valuable to note that entries 3 and 4 gave all the same products of decarboxylation. This evidently indicated that an intermediate of π -allyl-Pd complex formed during the reaction and the mechanism of decarboxylation of allyl β -keto esters catalyzed by polymer phosphine Pd(0) complex catalysts is similar to that of homogeneous catalysis^[17]. Because these polymer phosphine Pd(0) complex catalysts are also catalysts of allyl alkylation of nucleophile^[18] and β -keto esters are just good nucleophiles, therefore, as we found, a side reaction of allylation on methylene carbon of β -keto esters occurred accompanied with the decarboxylation. But fortunately, this side reaction sometime gave many rare and valuable ketones with two double carbon bonds for which the general method is scarce (entries 1—5, 8,9).

A mixture of α,β -unsaturated ketone and γ,δ -unsaturated ketone was obtained from the decarboxylation of allyl cyclohexan-2-one carboxylate catalyzed by polymer phosphine Pd(0) complex catalyst (entry 7). Solvent effect was not serious (Table 5), but the experimental

Table 5 PSP-Pd(0)-1 catalyzed decarboxylation of allyl cyclohexen-2-one carboxylate in different solvent*

Solvent	Time (h)	Yield (%)	Selectivity**
Methanol	3	62.8	2.0
Toluene	2	62.3	2.6
THF	2	80.2	3.0
Cyclohexane	2	73.8	4.8
Acetonitrile	1	61.4	5.9
Acetone	2	78.9	6.9

* Reaction conditions are the same with Table 4.

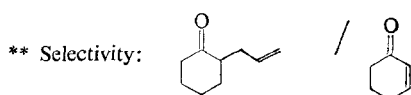
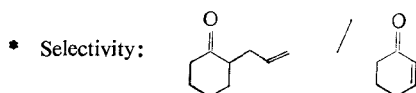


Table 6 Catalytic decarboxylation of allyl cyclohexan-2-one carboxylate*

Catalyst	P/Pd	Selectivity**
Pd(PPh ₃) ₄	0	100
PSP-Pd(0)-2	2.5	20
PSP-Pd(0)-1	5.4	3
SiLp-Pd(0)	4.5	0.5



** Reaction conditions are the same with Table 4.

results of Table 6 indicated that the selectivity depends on the catalyst markedly. The catalyst with higher P/Pd ratio is favourable for the formation of α, β -unsaturated ketone. In other word, polymer complex with chelate structure is the best for the production of α, β -enone, because chelate units in polymer complex will increase with the increase of P/Pd ratio. However, γ, δ -unsaturated ketone (α -allyl ketone) is always main product by using PSP-Pd(0)-1 or 2 as catalyst; but if SiLp-Pd(0) is used the α, β -unsaturated ketone is main product. It is supposed that the carbon chain in silica supported poly- γ -diphenylphosphinopropylsiloxane is more flexible than that of phosphinated polystyrene so that more favourable for the formation of polymer palladium chelate.

Polymer phosphine Pd(0) catalysts used in our work are air stable. No appreciable change in catalytic activity was observed after a half year storage in air. They could be recovered and reused easily by a simple filtration. But the leaching of palladium and losing in catalytic activity were observed during the recycles (Fig. 1). Anyway, the polymer phosphine Pd(0) catalysts improved the stability of homogeneous analogue which only could be used once and lose its catalytic activity easily even during the storage

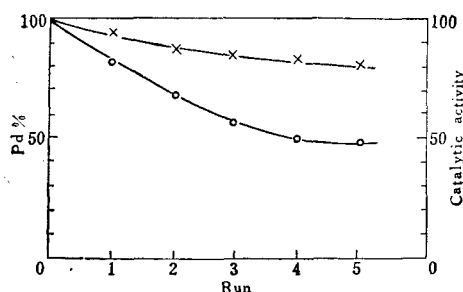


Fig. 1 Reusing the catalyst PSP-Pd(0)-2 in decarboxylation of allyl cyclohexan-2-one carboxylate

— x — Pd content; — o — Catalytic activity

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