Phosphinated linear polystyrene as a ligand of palladium catalysts for ethoxycarbonylation of 4,4′-dibromobiphenyl

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Phosphinated linear polystyrene was synthesized and used as a ligand of palladium catalysts. It showed high activity for the ethoxycarbonylation of 4,4′-dibromobiphenyl (I) in the presence of triethylamine. The catalysts acted as homogeneous under the reaction conditions (150°C, $p(CO) = 10$ kg/cm^2), and precipitated as solid materials after the reaction. Catalytic performances highly depended on the compositions of the solvent, and the highest activity was achieved in ethanol.

Keywords: polymer ligand; phosphinated linear polystyrene; palladium catalyst; ethoxycarbonylation; 4,4′-dibromobiphenyl; diethyl biphenyl-4,4′-dicarboxylate

1. Introduction

Advanced materials involving biphenyl units have attracted the attention of many researchers because biphenyls are the most promising units for liquid crystals and liquid crystalline polymers. The carbonylation of aryl halides is one of the simplest ways to obtain functionalized biphenyls and it is effectively catalyzed by homogeneous palladium–phosphine complexes [1].

We previously described the selective synthesis of diethyl biphenyl-4,4′-carboxylate (III) and ethyl-4′-bromobiphenyl-4-carboxylate (II) by catalytic ethoxycarbonylation of 4,4′-dibromobiphenyl (I) [2] with the palladium–triphenylphosphine catalysts and bases. In these studies, excess amounts of triphenylphosphine

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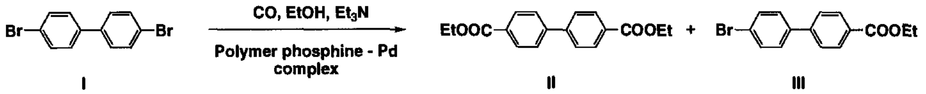
enhanced the catalytic activity and stability of the catalysts. However, it is very difficult to recycle the catalyst without deactivation. To overcome these difficulties, heterogenization of homogeneous catalysts, especially polymer-supported metal complexes, has been investigated over the decades [3,4]. On the other hand, heterogenization of catalysts shows a tendency to decrease activity due to the difficulty in the access to the catalyst metal.

Complex catalysts supported on non-crosslinked linear polystyrene are expected to be highly active because they act like a homogeneous catalyst under appropriate conditions [5–8]. These catalysts are possible to solidify at low temperature or by using other solvents.

In this paper, we report the phosphinated linear polystyrene as an effective ligand of palladium catalysts for synthesis of diethyl biphenyl-4,4′-dicarboxylate by the ethoxycarbonylation of 4,4′-dibromobiphenyl (eq. (1)). These catalysts showed a different behavior with the homogeneous catalyst, especially an interesting solvent effect on catalysis.



(1)

2. Experimental

Diphenylphosphine, 4,4′-dibromobiphenyl (I), and polystyrene (molecular weight is ca. 1200, undecamer) were purchased from Aldrich Japan Co. Ltd., Tokyo, Japan. Chloromethyl methyl ether was obtained from Tokyo Chemical Industry Co., Ltd., Tokyo, Japan. Dichlorobis(benzonitrile)palladium ($Pd(C_6H_5CN)_2Cl_2$) was obtained from Strem Chem. Co. Ltd., MA, USA. Poly-4-(diphenylphosphinomethyl)styrene was synthesized from polystyrene according to the procedures previously described, via chloromethylation with chloromethyl methyl ether [9] and phosphination with diphenylphosphinolithium [10]. Phosphinated polystyrene was purified by repeated reprecipitation from chloroform using methanol. The degree of phosphination was determined 95% by elemental analysis and ^{1}H-NMR spectroscopy. In order to form complexes, the phosphinated polymer was treated with dichlorobis(benzonitrile)palladium in benzene under nitrogen. After complexation for 48 h at room temperature, the solution was concentrated in vacuo and poured into a large amount of methanol and dried. The precipitated complex was washed well with methanol to remove any excess of palladium precursor. The ratio of palladium and phosphino group in the polymer (P/Pd) was controlled by the amount of precursor. The values of P/Pd in the obtained complexes were confirmed by elemental analysis. Complexation of these catalysts was confirmed by ^{31}P NMR spectra [11]. Prepared catalysts are listed in table 1.

The ethoxycarbonylation was carried out by the following procedures. The sub-

Table 1
Phosphinated polystyrene–palladium complexes

Catalyst No.	P/Pd ratio [a] (meq./mmol)	
	calculated	found [b]
PC1	1.0	0.8
PC2	2.0	2.2
PC3	5.0	4.6
PC4	10.0	9.3

[a] Phosphine moiety (mmol eq.)/ $Pd(C_6H_5CN)_2Cl_2$ (mmol) ratio as used for the complexation.
[b] Determined by elemental analysis.

strate I (5 mmol), the catalyst (0.1 mmol as palladium), triethylamine (12 mmol), ethanol (40 ml) were placed in a 100 ml stainless-steel autoclave equipped with a magnetic stirrer. After purging air with nitrogen, 10 kg/cm^2 of carbon monoxide was introduced. Then the autoclave was heated up to 150°C and kept there 5 h. After cooling the equipment and purging excess carbon monoxide, the product was collected and washed with ethanol. The palladium complex was solidified onto the autoclave wall. The product was analyzed by gas chromatograph using an Ultra-1 capillary column (12 m × 0.25 mm × 0.2 μm; Hewlett-Packard) as previously reported [2].

3. Results and discussion

Ethoxycarbonylation of I smoothly proceeded with the phosphinated polymer–palladium catalyst. The effects of the reaction conditions on catalytic performances were first investigated. The results at various temperatures using the catalyst (P/Pd = 2) are summarized in table 2. The carbonylation occurred above 130°C. At 150°C, catalytic activity was high and the yield of III was achieved over 70%. Palladium complexes were found as solid materials on the reactor wall after

Table 2
Temperature effect on ethoxycarbonylation of I [a]

Reaction temperature (°C)	Conversion (%)	Selectivity (%)	
		II	III
100	2.5	–	–
130	19	69	3
150	96	16	74
180	99	7	51

[a] Reaction conditions: I: 5.0 mmol; catalyst PC-3: 0.1 mmol as Pd; Et_3N: 12 mmol; EtOH: 40 ml; reaction time: 5 h; CO pressure: 10 kg/cm^2.

the reaction. However, the reaction, when carried out above 180°C, resulted in the decrease of the yield of III owing to decomposition of the palladium complex and formation of by-products [#1].

Table 3 summarizes the effect of the P/Pd ratio in the catalyst on the ethoxycarbonylation of I. The increase of the P/Pd ratio enhanced the activity and the selectivity of III, similar to the case of the palladium–triphenylphosphine catalyst described previously [2]. Since phosphinated polystyrene does not have a high coordination ability, as is the case of triphenylphosphine, the palladium complex with excess phosphine ligand is necessary to get stability in the presence of the reducing agent such as carbon monoxide and ethanol. This behavior of the polymer catalyst showed that the stability of the complex was an important factor for catalytic performance.

The effect of carbon monoxide pressure on the ethoxycarbonylation of I is summarized in table 4. Catalytic activity had a tendency to decrease with increasing CO pressure, however, the effect of CO pressure was not significant. In the case of homogeneous palladium–triphenylphosphine catalyst, CO pressure largely affected the catalytic activity [2].

The solvent effect on the ethoxycarbonylation of I is shown in table 5. Benzene, toluene, hexane, tetrahydrofuran, and pyridine were used as co-solvents with ethanol. Although these co-solvents were considered to increase the solubility of phosphinated polymer catalyst, they inhibited the ethoxycarbonylation. The conversions in the presence of these co-solvents were as low as 20–60%. The ethoxycarbonylation of I in pure ethanol solvent smoothly proceeded to give III as the principal product with the yield of 74%.

Fig. 1 summarizes the effect of the volume ratio between benzene and ethanol on the catalytic ethoxycarbonylation of I. Phosphinated polymer palladium catalysts and homogeneous triphenylphosphine–palladium catalyst showed quite different features regarding the activity changes which depended on the solvents. The polymer ligand catalyst showed the highest activity in pure ethanol solvent. When the solvent was mixed with benzene, the catalytic activity decreased drastically. On

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[#1] By-products contained biphenyl, 4-bromobiphenyl and unidentified compounds.

Table 3
Effect of P/Pd ratio of polymer supported palladium complexes on ethoxycarbonylation of I [a]

Catalyst	P/Pd	Conversion (%)	Selectivity (%)	
			II	III
PC1	1	35	69	25
PC2	2	76	41	54
PC3	5	96	16	74
PC4	10	100	0.2	96

[a] Reaction conditions: I: 5.0 mmol; catalyst PC1–PC4: 0.1 mmol as Pd; Et_3N: 12 mmol; EtOH: 40 ml; reaction time: 5 h; reaction temperature: 150°C; CO pressure: 10 kg/cm^2.

Table 4
Effect of pressure of carbon monoxide on ethoxycarbonylation of I [a]

CO pressure (kg/cm^2)	Conversion (%)	Selectivity (%)	
		II	III
5	99	7	80
10	96	16	74
30	97	12	87
50	84	25	73

[a] Reaction conditions: I: 5.0 mmol; catalyst PC3: 0.1 mmol as Pd; Et_3N: 12 mmol; EtOH: 40 ml; reaction time: 5 h; reaction temperature: 150°C.

the other hand, the activity of homogeneous triphenylphosphine–palladium catalyst was not largely affected by the composition of solvent. Furthermore, contrary to polymer ligand catalysts, the activity was gradually increased by mixing benzene with ethanol.

It is interesting that the polymer ligand catalysts showed different features than homogeneous catalysts concerning the solvent effect. We have not fully understood the characteristic features of our catalysts. One possibility is that the conformation of polymer catalysts vary in between pure ethanol and mixed solvent with benzene. It is considered that these conformational variations affected the environment around the catalyst sites, accessibility of reactant to catalyst and the activity of the catalyst.

The non-crosslinked polymer ligand catalysts like our system, act as homogeneous catalysts under the reaction conditions [4]. The catalysts were easily separated as solid materials by cooling after the reaction due to the low solubility of the polymer complex. Recovered catalysts had relatively high activities and could be recycled several times.

Table 5
Effect of reaction solvent on ethoxycarbonylation of I [a]

Solvent	(ml/ml)	Conversion (%)	Selectivity (%)	
			II	III
EtOH	40	96	16	74
THF/EtOH	20/20	23	63	31
benzene/EtOH	20/20	30	57	37
pyridine/EtOH	20/20	61	40	57
toluene/EtOH	20/20	65	41	54
hexane/EtOH	20/20	41	71	25

[a] Reaction conditions: I: 5.0 mmol; catalyst PC3: 0.1 mmol as Pd; Et_3N: 12 mmol; reaction time: 5 h; CO pressure: 10 kg/cm^2; reaction temperature: 150°C.

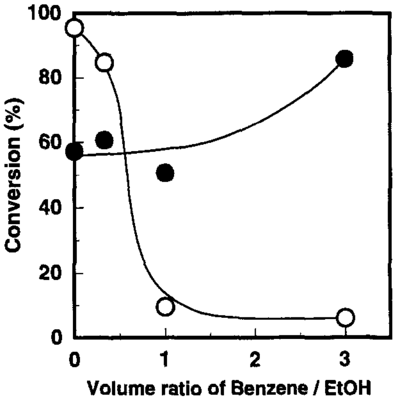

Fig. 1. The effect of solvent composition consisting of benzene and ethanol on the catalytic activity of ethoxycarbonylation of I. (○) Pd catalyst with polymer phosphine ligand (PC3), 0.1 mmol as Pd. (●) $PdCl_2(PPh_3)_2$, 0.05 mmol. Reaction conditions: I: 5.0 mmol; Et_3N: 12 mmol; solvent: total 40 ml; reaction temperature: 150°C; reaction time: 5 h; CO pressure: 10 kg/cm^2.

4. Conclusion

In summary, the palladium catalysts complexed with phosphinated non-cross-linked linear polystyrene were active for ethoxycarbonylation of 4,4′-dibromobiphenyl to produce diethyl biphenyl-4,4′-dicarboxylate in excellent yield. Ethanol was the best solvent for high catalytic activity and the solvent effect on activity was different from that of homogeneous catalysts. The catalyst was easily separated as solid material from ethanol after reaction, and it was possible to recycle.

Further details of the reaction mechanism, solvent effects and recycling of the catalyst are under investigation.

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