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Publisher *Taylor & Francis*

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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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To cite this Article Feng, Zhiming , Chen, Bushi and Liu, Hanfan(1987) 'Double Carbonylation of Organohalogen Compounds Catalyzed by Polymer-Bound Palladium Complexes', *Journal of Macromolecular Science, Part A*, 24: 3, 289 – 300

To link to this Article: DOI: 10.1080/00222338708074446

URL: <http://dx.doi.org/10.1080/00222338708074446>

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DOUBLE CARBONYLATION OF ORGANOHALOGEN COMPOUNDS CATALYZED BY POLYMER-BOUND PALLADIUM COMPLEXES

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ABSTRACT

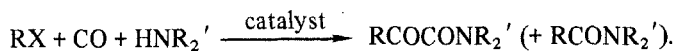
Palladium complex-catalyzed double carbonylation is a recently discovered reaction in organotransition metal chemistry. In this paper, some polymer-bound palladium complexes—polystyrylphosphine-palladium(0) complexes, poly-2-vinylpyridine-palladium(II) complexes, and poly-2-*N*-vinylpyrrolidone-palladium(II) complexes have been prepared and characterized. The complexes were tested as catalysts in the double carbonylation reaction. Among these catalysts, polystyrylphosphine-palladium(0) complexes showed good activity and selectivity, and can be easily recovered and reused. The influence of experimental parameters was investigated as well.

INTRODUCTION

In spite of extensive investigation of palladium complex-catalyzed carbonylation of organic halides, double carbonylation is extremely scarce. Tanaka [1] and Yamamoto [2] recently reported a novel palladium complex-catalyzed

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double carbonylation of organic halides in the presence of carbon monoxide and amines, which gave α -ketoamides in good yields:



Since the reaction route from α -keto acid derivatives to α -amino acids through imine derivatives is well established [3], the above reaction promises to afford a generally applicable route for synthesis of a variety of α -amino acids.

Polymer-supported catalysts [4, 5] are homogeneous analogs of these complexes whose activity and selectivity can be tailored by varying the ligands attached to the metal and by varying the solvents. They possess the ability of stabilizing highly reactive, coordinatively unsaturated metal sites and allow easy catalyst separation from the reaction products as well as repeated recycling. It is of interest to survey the function of polymer-bound homogeneous catalysts in double carbonylation. Here we describe the results of our investigations.

EXPERIMENTAL

1. Materials and Equipment

All solvents and reagents were dried and redistilled under nitrogen prior to use. The deoxygenated benzene was made by evacuating and filling with nitrogen five times. $\text{Pd}(\text{PPh}_3)_4$ was prepared according to the literature method [6].

The phosphorus, nitrogen, and chlorine content was determined in the Laboratory of Microorganic Analysis in our Institute. The palladium content was analyzed by a spectrophotometric method [7].

IR, ^{13}C NMR, XPS, and MS data were obtained with Perkin-Elmer 683, JEOL JNM-FX 100, Kratos AEI ES-300, and Kratos MS-50 instruments, respectively. Analytical GLC was performed with a Shang-Fen Model 103 gas chromatograph using 2M OV-17 columns.

2. Preparation of Polymer Phosphine-Palladium(0) Complexes

2% DVB-crosslinked chloromethylated polystyrene (200-400 mesh; Cl, 1.25 meq/g; designated PS-Cl), purchased from Sigma Chemical Co., was treated with LiPPh_2 [8] in a manner similar to the literature [9] to prepare diphenylphosphinomethylpolystyrene (PSP-1).

Palladium(0) complexes were formed by a typical procedure as follows: phosphinated polystyrene (PSP-1, 10 g; phosphorus content, 7 mmol) was suspended in 150 mL deoxygenated benzene containing $\text{Pd}(\text{PPh}_3)_4$ (4 g, 3.5 mmol).

The mixture was stirred under nitrogen and refluxed for 3 days. It was filtered and washed with benzene and THF consecutively, then dried under vacuum. Finally, a bright red product, PSP-Pd(0)-1, was obtained. If the benzene was not deoxygenated, a dark brown product, PSP-Pd(0)-2, resulted.

3. Preparation of Polymer Pyridine-Palladium(II) Complexes

A copolymer of 2-vinylpyridine, styrene, and divinylbenzene was prepared according to the method reported by Zhu [10]. The resulting resin was ground and passed through a 200 mesh sieve, then extracted with methanol in a Soxhlet apparatus for 8 h and dried under vacuum. Crosslinking of the product (P2VP) amounted to 1%.

Under a nitrogen atmosphere, pyridine-containing polystyrene (P2VP) was suspended in a methanol-water (1:1) solution of palladium chloride, heated to 50–55°C, stirred for 6 h, filtered, washed with water and methanol successively, and dried at room temperature. An orange-yellow complex (P2VP-PdCl₂) was obtained.

4. Preparation of Polymer Pyrrolidone-Palladium(II) Complexes

Silica-supported crosslinked poly-2-*N*-vinylpyrrolidone was prepared by a route similar to the literature [11]. The polymer ligand obtained was a pale-yellow powder with a surface area of 30 m²/g, nitrogen content 3.5% (designated as SiO₂-PNCO).

Polymer ligand (1.0 g) and powdered PdCl₂ · 2H₂O (0.107 g) were suspended in 15 mL ethanol, stirred under nitrogen, heated slowly to 70°C, and refluxed for 8 h. Then it was filtered, washed with water and ethanol, and dried under vacuum at room temperature. A pale-brown complex (SiO₂-PNCO-PdCl₂) was obtained.

5. Catalytic Double Carbonylation of Organohalogen Compounds

A typical procedure was as follows: Polymer catalyst (0.05 mmol Pd), iodo-benzene (3.7 mmol), diethylamine (25 mmol), and *n*-hexadecane (as an inner standard for GLC analysis) were added to a 50-mL glass tube which was placed in a stainless steel autoclave. After evacuation, carbon monoxide (40 atm at

room temperature) was charged to the system, and the mixture was stirred at 85°C. After 3 h the vessel was cooled and the reaction mixture was analyzed by GLC, which showed that *N,N*-diethyl-2-phenylglyoxylamide had been formed in 81% yield along with *N,N*-diethylbenzamide in 6.9% yield. These reaction products were identified by IR, ¹³C NMR, and mass spectrometry after isolation of the products.

RESULTS AND DISCUSSION

1. Characterization of Polymer-Bound Palladium Complexes

The polymer-bound palladium complexes were prepared by a ligand exchange reaction.

The analytical data of polymer-bound palladium complexes are listed in Table 1. The empirical atomic ratio of phosphorus to palladium and nitrogen to palladium is in the 1.9-5.9 range. Because of the steric effect of the polymer chain and the ligand, more than two anchored ligand groups coordinated with one given palladium atom should be highly unfavorable thermodynamically. Even if three or four anchored ligands did coordinate to palladium,

TABLE 1. Analytical Data for Polymer-Bound Palladium Complexes

Complex	Percentage				Empirical atomic ratio		
	P	N	Pd	Cl	P/Pd	N/Pd	Cl/Pd
PSP-Pd(0)-1	2.17		1.28		5.4		
PSP-Pd(0)-10	2.14		2.56		2.5		
PSP-Pd(0)-2	2.17		1.17		5.9		
P4VP-PdCl ₂		5.87	17.50	12.27		2.55	2.10
P2VP-PdCl ₂ -1		7.84	19.17			3.10	
P2VP-PdCl ₂ -2		7.28	25.00			2.20	
P2VP-PdCl ₂ -3		4.71	18.75	14.00		1.90	2.20
SiO ₂ -PNCO-PdCl ₂		2.72	5.60	3.64		3.66	1.94

TABLE 2. IR Spectra of Polymer Ligands and Complexes

Sample	IR absorption band wavenumber, cm^{-1}					
	P-C			P-Pd		
PS-Cl	No absorption peak found					
PSP-1	510 _w	720 _w	1435 _m			
PSP-Pd(0)	510 _s	720 _m	1435 _s	395 _m		
Pd(PPh ₃) ₄	510 _s	525 _m	540 _s	720 _s	1435 _s 1480 _s 1485 _w	410 _m
				Pd-Cl		
	C-C	C-N	C-H	<i>anti</i>	<i>sym</i>	
P2VP	1586 _s	1428 _s	743 _m			
P2VP-PdCl ₂	1600 _s	1432 _s	755 _m	330 _m	320 _m	
			(broader)			
P4VP	1595 _s	1412 _s	818 _m			
P4VP-PdCl ₂	1608 _s	1425 _s	825 _m	352 _w	330 _m	

swelling polymer should cause the dissociation of ligand to generate a more coordinatively unsaturated situation [12]. Therefore, it seemed likely that only up to one or two anchored ligand groups would actually coordinate with palladium even though the P/Pd or N/Pd is greater than two.

The formation of polymer phosphine-palladium(0) complexes were elucidated by IR and XPS data. Table 2 shows that three bands (at 510, 720, and 1435 cm^{-1}) which are assigned to P-C bond absorption were not found in the spectra of chloromethylated polymer (PS-Cl) but observed in those of polymer ligands. As we had expected, the intensity of these peaks increased in the spectra of polymer complexes. One new band of P-Pd absorption (at 395 cm^{-1}) appeared in the spectra of polymer complexes. This band is near the position of that of Pd(PPh₃)₄. The above results are consistent with those observed from other polymer-palladium complexes [13] and indicate that polymer phosphine-palladium complexes had formed.

An x-ray photoelectrospectroscopy (XPS) study on polymer phosphine-containing catalysts supported the formation of polymer-palladium complexes, and the central atom palladium appeared to be in a zero oxidation state (Table

TABLE 3. XPS Data for Polymer-Bound Palladium Complexes and Related Substances

Compound	Binding energy, ^a eV					
	Pd _{3d 3/2}	Pd _{3d 5/2}	Cl _{2p}	P _{2p}	N _{1s}	O _{1s}
PPh ₃				130.8		
Pd(PPh ₃) ₄		337.2		131.8		
PS-Cl			201.1			
PSP-1				130.5		
PSP-Pd(0)-1		336.8		132.6		
PSP-Pd(0)-2		336.8		132.8		532.6
PSP-Pd(0)-4		336.3		132.1		
Pd (metal)	341.2	335.7				
PdCl ₂	343.6	338.3	199.1			
P4VP-PdCl ₂	344.5	338.8	199.4			
P2VP-PdCl ₂ -5	344.1	338.8	199.0		401.3	
SiO ₂ -PNCO-PdCl ₂	343.8	338.4	199.3		400.6	533.7

^aThe binding energy values are referred to C_{1s} (285.0 eV) or Si_{2p} (103.4 eV).

3). The P_{2p} binding energies of polymer phosphine ligands are almost the same as that of triphenylphosphine. This is expected because the phosphorus atoms are bonded to the same kinds of carbon atoms in polymer phosphine and triphenylphosphine. A more important fact is that the P_{2p} binding energies increased by 2.1-2.3 eV after the ligand exchange reaction of polymer ligand with tetrakis(triphenylphosphine)palladium. These shifts demonstrate that the phosphorus atom donates electrons to palladium when the coordination bond is formed. On the other hand, the P_{2p} spectra of polymer complexes show broader peaks with 3.0-3.4 eV energy widths at half-height, which are broader by about 0.8-1.2 eV than that of P_{2p} of triphenylphosphine. This implies that the phosphine coordinated with palladium in the polymer complex is

composed of two species, anchored phosphine and triphosphine. It is not surprising that no great difference was found in $\text{Pd}_{3d\ 5/2}$ binding energies between polymer complexes and $\text{Pd}(\text{PPh}_3)_4$ because ligand exchange does not change the coordination situation markedly. However, the data are good evidence for the presence of a palladium(0) complex rather than a palladium metal state. PSP-Pd(0)-2 was prepared in undeoxygenated benzene. In its XPS spectra, a small O_{1s} band with lower binding energy value was observed. The appearance of the new band may be due to the formation of a $\text{P}=\text{O}$ bond (oxidation of the phosphine by the residual oxygen in the system) during the course of catalyst preparation.

Comparison of the IR spectra of complexed pyridine polymers to those of the corresponding free ligands (Table 2) shows that some vibrations of C—C stretching, C—N stretching, and C—H deformation have shifted to higher frequencies. This is consistent with reports for the coordination systems of pyridine derivatives or homopolymers in the literatures [14-16]. The IR spectra of the polymer-pyridine complexes contain two bands not found in the spectra of the polymer ligand. These bands appeared at 352 and 330 cm^{-1} for P4VP-PdCl₂, and at 330 and 320 cm^{-1} for P2VP-PdCl₂. The terminal Pd—Cl stretching band in several complexes of pyridine derivatives appeared in the same region [17, 18]. As measured by XPS, the Pd_{3d} and Cl_{2p} binding energies of the polymer-bound pyridine-palladium complexes are slightly higher than those of palladium chloride (Table 3), in good agreement with literatures results [19, 20]. According to elemental analysis, IR, and XPS, the oxidation state of palladium in the polymer-pyridine complexes seems to be divalent.

Because of the low concentration of the polymer ligand in the case of silica-supported crosslinked poly-2-*N*-vinylpyrrolidone, good IR spectra were not obtained, but the XPS data agreed with those of literature [20]. From the results of elemental analysis and XPS, it is likely that the oxidation state of palladium in polymer-pyrrolidone complex is divalent.

2. Catalytic Reaction

As shown in Table 4, poly-pyridine-palladium complexes showed lower activity and stability than those of poly-phosphine-palladium complexes. During the reaction, a palladium mirror was formed on the wall of the glass tube when poly-pyridine-palladium complexes with different N/Pd ratios were used as catalysts. The yield of the reaction was around 50%. This is believed to be related to the fact that the coordination bond of N→Pd formed in the poly-pyridine-palladium complexes is not strong enough. With a large excess of diethylamine, leaching of the metal from the polymer catalysts oc-

TABLE 4. Double Carbonylation of Iodobenzene in the Presence of Polymer-Bound Catalysts^a

Catalyst	Ligand/Pd	Pd, mmol	Time, h	Yield, %		Remarks
				PhCONEt ₂	PhCOCONEt ₂	
P2VP-PdCl ₂	1.8	0.082	3	2.0	53	Pd mirror appeared
P2VP-PdCl ₂ -2	2.2	0.05	5	2.0	53	Pd mirror appeared
P2VP-PdCl ₂ -7	7.5	0.09	5	18.5	55.5	Pd mirror appeared
SiO ₂ -NCO-PdCl ₂		0.05	4	0	Trace	
PSP-Pd(0)-1	5.4	0.05	3	15.8	84.5	No Pd mirror appeared
PSP-Pd(0)-2	5.9	0.05	3	12	81	No Pd mirror appeared

^aReaction conditions: PhI, 3.7 mmol; HNEt₂, 25 mmol; CO, 40 kg/cm²; temperature, 85°C.

TABLE 5. Double Carbonylation of Halobenzene^a

Substrate	Time, h	Yield, %			Remark
		PhCOEt ₂	PhCOCOEt ₂	Total	
PhI	3	12	81	93	
PhBr	5	4.5	Trace	4.5	Unknown peak appeared
PhCl	4.5	0	0	0	

^aReaction conditions: catalyst, PSP-Pd(0)-2; 0.05 mmol Pd, others as in Table 4.

curred; this caused the formation of a palladium mirror and lowered the catalytic activity. However, this kind of catalyst still possesses a good selectivity. When the catalyst P2VP-PdCl₂-7 (N/Pd = 7) was used in the reaction, the amount of by-product benzamide increased, i.e., the selectivity evidently deteriorated. Poly-phosphine-palladium complex was the best catalyst; it afforded α -ketoamide from iodobenzene in good yield and selectivity under mild condition. It also possessed good stability, for no palladium mirror formed during the reaction and it could be reused several times. The poly-pyrrolidone-palladium complexes were inactive in the carbonylation reaction, possibly because position hindrance of the ring of pyrrolidone or the chelation of the neighboring nitrogen and oxygen atoms blocked the insertion of carbon monoxide.

With poly-phosphine-palladium(0) complexes as catalysts, double carbonylation took place in good yield and selectivity when iodobenzene was employed. Under the same condition, bromobenzene caused extensive monocarbonylation to give benzamide as a main product in lower yield (4.5% PhCOEt₂) with trace amounts of α -ketoamide. In the case of chlorobenzene, carbonylation did not occur (Table 5).

Diethylamine was a stronger base, it took part in the reaction, and it was used as a solvent as well as a hydrogen halide remover. There was no obvious effect of the amount of amine on the selectivity of the double carbonylation. With a large excess of diethylamine or lower iodobenzene-to-amine ratio, the activity and selectivity of the double carbonylation became worse (see Table 6). One needs to find the appropriate amount of amine to optimize the reaction condition and to prevent the metal from leaching out.

TABLE 6. Influence of the Amount of Amine on the Double Carbonylation Reaction

PhI:amine, molar ratio	Yield, ^a %			Selectivity, ^c %
	PhCOEt ₂	PhCOCOEt ₂	Total	
1:14.5	9.0	60	69	87
1:10.5	10.8	76.5	87.3	88
1:6.7	12	81	93	87
1:5.2	8.0	58	66	89
1:2.0	15	28	43.5	65.5

PhI:amine, molar ratio	Yield, ^b %			Selectivity, ^c %
	PhCOEt ₂	PhCOCOEt ₂	Total	
1:14.5	12.7	57.8	70.5	82
1:10.5	9.0	71	80	89
1:6.7	9.7	86.5	96.2	90
1:3.0	6.2	65	71.2	91
1:2.0	5.5	43	49.4	89

^aReaction conditions: time, 3 h, otherwise as in Table 5.

^bReaction conditions: CO pressure, 30 kg/cm²; temperature, 100°C; time, 5 h; otherwise as in Footnote a.

^cFor α -ketoamide.

Lower temperature did not favor α -ketoamide formation, but caused a decrease in the reaction rate. When the reaction was conducted at 100°C for 3 h, 99% conversion with a selectivity of 90% α -ketoamide was obtained. At 60°C for 4 h, conversion is lowered to 61% with worse selectivity (72% α -ketoamide, Table 7).

The double carbonylation reaction rate increased with increasing CO pressure from 10 to 20 atm, then declined to a constant for higher pressures, while the selectivity was nearly independent of CO pressure (Table 8).

TABLE 7. Influence of Temperature on the Double Carbonylation Reaction^a

Temperature, °C	Yield, %			Selectivity, ^b %
	PhCONEt ₂	PhCOCONEt ₂	Total	
60	16.7	44.5	61.2	72
70	20.2	72	92.2	78
85	12	81	93	87
100	9	90	99	90

^aReaction conditions as in Table 5; reaction time, 3 h except 4 h at 60°C.

^bFor α -ketoamide.

TABLE 8. Influence of Carbon Monoxide Pressure on the Double Carbonylation Reaction^a

CO pressure, kg/cm ₂	Yield, %			Selectivity, ^b %
	PhCONEt ₂	PhCOCONEt ₂	Total	
40	9	90	99	90.9
30	10	87	97	89.7
20	8.2	89	97.2	91.6
10	7.6	49	56.6	86.6

^aReaction conditions: temperature, 100°C, otherwise as in Table 6 Footnote a.

^bFor α -ketoamide.

REFERENCES

- [1] T. Kobayashi and M. Tanaka, *J. Organomet. Chem.*, 233, C64 (1982).
- [2] (a) F. Ozawa, H. Soyama, T. Yamamoto, and A. Yamamoto, *Tetrahedron Lett.*, 23, 3383 (1982). (b) F. Ozawa, T. Sugimoto, Y. Yuasa, M. Santra, T. Yamamoto, and A. Yamamoto, *Organometallics*, 3, 683

- (1984). (c) F. Ozawa, T. Sugimoto, T. Yamamoto, and A. Yamamoto, *Ibid.*, 3, 692 (1984).
- [3] D. Valentine Jr. and J. W. Scott, *Synthesis*, p. 329 (1978), and references cited therein.
- [4] Y.-Y. Jiang, *Huaxue Shiji (Chemical Reagents, China)*, p. 691 (1980).
- [5] C. U. Pittman Jr., in *Comprehensive Organometallic Chemistry*, Vol. 8 (G. Wilkinson, F. G. A. Stone, and E. W. Abel, eds.), Pergamon, Oxford, 1982, p. 553.
- [6] D. R. Coulson, *Inorg. Synth.*, 13, 121 (1972).
- [7] G. H. Ayres and J. H. Alsop, *Anal. Chem.*, 31, 1135 (1959).
- [8] M. D. Fryzuk and B. Bosnich, *J. Am. Chem. Soc.*, 99, 6262 (1977).
- [9] K. G. Allum, R. D. Hancock, I. V. Howell, S. McKenzie, R. C. Pitkethly, and P. I. Robinson, *J. Organomet. Chem.*, 87, 203 (1975).
- [10] X.-C. Zhu, Research Report of the Institute of Chemistry, Academia Sinica, 1966.
- [11] Y.-J. Li and Y.-Y. Jiang, *Gaofenzi Tongxun (Polymer Communications, China)*, p. 53 (1984).
- [12] C. U. Pittman Jr. and Q. Ng, *J. Organomet. Chem.*, 153, 85 (1978).
- [13] J. Lahaye and R. Lagarde, *J. Catal.*, 60, 270 (1979).
- [14] M. Goodgame and P. J. Hayward, *J. Chem. Soc., A*, p. 632 (1966).
- [15] S. Tadashi and M. Fujinao, *Bull. Chem. Soc. Jpn.*, 41, 2440 (1968).
- [16] J. Roda, *Makromol. Chem.*, 178, 203 (1977).
- [17] M. Pfeffer, P. Braunstein, and J. Dehand, *Spectrochim. Acta, Part A*, 30, 331 (1974).
- [18] J. R. Durig, B. R. Mitchell, D. W. Sink, J. N. Willis Jr., and A. S. Wilson, *Ibid.*, 23, 1121 (1967).
- [19] P. Brant, J. H. Enemark, and A. L. Balch, *J. Organomet. Chem.*, 114, 99 (1976).
- [20] M. Terasawa, K. Kaneda, T. Imanaka, and S. Teranishi, *J. Catal.*, 51, 406 (1978).