

Letter

Oxidative carbonylation of phenol to diphenyl carbonate catalyzed by Pd dinuclear complex

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Abstract

Pd dinuclear complexes were investigated as catalysts for direct synthesis of diphenyl carbonate (DPC) by oxidative carbonylation of phenol using carbon monoxide and air. Pd dinuclear complexes such as Pd₂(dpm)₂X₂ [dpm: bis(diphenylphosphino)methane, X: Cl, Br, I, OCN, SCN, N₂O, N₃] were found to be novel catalysts for the oxidative carbonylation of phenol. Pd₂(dpm)₂(OCN)₂/Mn(TMHD)₃/(Ph₃P=)₂NBr system was more effective than conventional Pd mononuclear catalyst. © 1999 Elsevier Science B.V. All rights reserved.

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Polycarbonates (PCs) are excellent engineering thermoplastics and substitutes for metals and glass because of their good impact strength, heat resistance and transparency [1]. A number of synthetic routes for producing PCs have been described in the literature [2]. In recent years there has been increasing demand for a safer and environmentally favorable process for PCs synthesis, such as the process not requiring any solvent and toxic phosgene [2]. Therefore, the transesterification process which uses diphenyl

carbonate (DPC) as carbonyl source has been given more recognition, and the research on direct synthesis of DPC by Pd catalyzed oxidative carbonylation of phenol has been pursued with great interest. Among many catalysts reported in patented and published literature, Pd/redox catalyst/ammonium halide system [3–11] required a large amount of ammonium

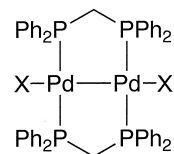


Fig. 1. Structure of Pd₂(dpm)₂X₂ (X: Cl, Br, I, OCN, NO₂, N₃, SCN).

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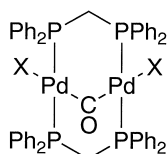


Fig. 2. Structure of $\text{Pd}_2(\mu\text{-CO})(\text{dpm})_2\text{X}_2$ (X: Cl, Br, I, OCN, NO_2 , N_3 , SCN).

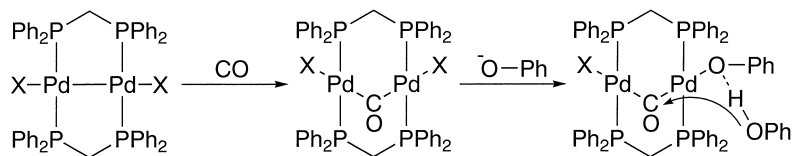
halide, which causes corrosion of reaction apparatus by halogen ion. Recently, we have tried to develop an efficient catalyst system for the direct synthesis of DPC from carbon monoxide (CO) and phenol without using halogenated catalyst system with an aim to use it eventually for direct synthesis of PC from bisphenol-A and CO, and we found that the $\text{Pd}_2(\text{dpm})_2(\text{SnCl}_3)\text{Cl}$ [dpm: bis(diphenylphosphino)methane]/redox catalyst system gives good efficiency [12,13]. In these investigations, we realized that the Sn free complex, i.e., $\text{Pd}_2(\text{dpm})_2\text{Cl}_2$ /redox catalyst system gives moderate efficiency. Thus, we investigated Pd dinuclear complexes [$\text{Pd}_2(\text{dpm})_2\text{X}_2$ (X: Cl, Br, I, OCN, SCN, N_2O , N_3)] in detail. Here we report a synthesis of DPC by oxidative carbonylation of phenol using Pd dinuclear complexes with redox catalyst along with or without using ammonium halide.

The reaction mechanism of the oxidative carbonylation catalyzed by Pd/redox reagent/ammonium halide systems has not been made clear. However, it has been reported that the reaction of ammonium halide and phenol produces ammonium phenoxide [9]. Thus, ammonium halide and Pd are supposed to react with phenol and CO, and the resulting activated CO and phenolate couple oxidatively to produce DPC.

We selected $\text{Pd}_2(\text{dpm})_2\text{X}_2$ (X: Cl, Br, I, OCN, SCN, N_2O , N_3) [14] (Fig. 1) for the catalytic system. These Pd dinuclear complexes react with CO to form $\text{Pd}_2(\text{dpm})_2(\mu\text{-CO})\text{X}_2$ (Fig. 2) [14]. Moreover, nucleophilic attack of phenol at one Pd center may occur. Thus, the CO and phenol both will be bound to the Pd catalyst, that is, the substrate and the reagent are both parts of the same molecule. Thus, we can expect a very fast reaction between phenol and CO (Scheme 1).

The oxidative carbonylation reaction was performed by mixing phenol (32 mmol), $\text{Pd}_2(\text{dpm})_2\text{X}_2$ (X: Cl, Br, I, OCN, SCN, N_2O , N_3 ; 0.006 mmol), $\text{Mn}(\text{TMHD})_3$ (TMHD: 2,2,6,6-tetramethyl-3,5-heptandionate) as redox catalyst (0.024 mmol), and $(\text{Ph}_3\text{P}=\text{N})\text{Br}$ [bis(triphenylphosphoranylidene)ammonium bromide] (0 or 0.240 mmol) as phenol activator under 0.50 MPa CO and 0.25 MPa air at 100°C for 3 h. The results are summarized in Table 1.

Both the reaction rate and the yield were greatly affected by anion of Pd dinuclear complex and presence of $(\text{Ph}_3\text{P}=\text{N})\text{Br}$. For example, in the presence of $(\text{Ph}_3\text{P}=\text{N})\text{Br}$, the yield of DPC increased in the following order: OCN > Cl > NO_2 > Br > N_3 > I. In the absence of $(\text{Ph}_3\text{P}=\text{N})\text{Br}$, the yield of DPC increased in the following order: Cl = Br > NO_2 = N_3 > OCN > I. On using $\text{Pd}_2(\text{dpm})_2(\text{SCN})_2$, the reaction did not occur. We presumed that the orders are affected by basicity of reaction medium and cationicity of $(\mu\text{-CO})$ is affected by *trans* effect of X in the intermediate shown in Scheme 1. In the presence of $\text{Pd}_2(\text{dpm})_2\text{Cl}_2$ and $\text{Pd}_2(\text{dpm})_2\text{Br}_2$, the reaction rates were not so much affected by the presence of $(\text{Ph}_3\text{P}=\text{N})\text{Br}$. On



Scheme 1. Reaction of $\text{Pd}_2(\text{dpm})_2\text{X}_2$ with CO and phenol (X: Cl, Br, I, OCN, NO_2 , N_3 , SCN).

Table 1
Oxidative carbonylation of phenol catalyzed by Pd dinuclear complexes^a

Run	Pd complex	Additive	DPC		PS	CO ₂
			TOF (DPC/Pd) (mol/mol h)	yield (%)	yield (%)	yield (%)
1	Pd ₂ (dpm) ₂ Cl ₂	–	5.75	1.28	0.06	0.73
2	Pd ₂ (dpm) ₂ Cl ₂	(Ph ₃ P=) ₂ NBr	6.87	1.55	0.02	1.04
3	Pd ₂ (dpm) ₂ Br ₂	–	5.89	1.30	0.05	1.28
4	Pd ₂ (dpm) ₂ Br ₂	(Ph ₃ P=) ₂ NBr	4.35	0.97	0.01	0.51
5	Pd ₂ (dpm) ₂ I ₂	–	0.42	0.09	0.01	1.15
6	Pd ₂ (dpm) ₂ I ₂	(Ph ₃ P=) ₂ NBr	2.48	0.56	0.01	1.52
7	Pd ₂ (dpm) ₂ (OCN) ₂	–	1.63	0.36	0.08	0.25
8	Pd ₂ (dpm) ₂ (OCN) ₂	(Ph ₃ P=) ₂ NBr	7.66	1.70	0.01	0.72
9	Pd ₂ (dpm) ₂ (NO ₂) ₂	–	2.22	0.50	0.10	0.77
10	Pd ₂ (dpm) ₂ (NO ₂) ₂	(Ph ₃ P=) ₂ NBr	6.35	1.41	0.02	1.92
11	Pd ₂ (dpm) ₂ (N ₃) ₂	–	2.19	0.49	0.07	0.36
12	Pd ₂ (dpm) ₂ (N ₃) ₂	(Ph ₃ P=) ₂ NBr	3.90	0.87	trace	0.42
13	Pd ₂ (dpm) ₂ (SCN) ₂	–	0	0	trace	0.21
14	Pd ₂ (dpm) ₂ (SCN) ₂	(Ph ₃ P=) ₂ NBr	0.04	0.01	0	0.17
15	PdBr ₂ ^b	–	2.02	0.45	0.08	2.64
16	PdBr ₂ ^b	(Ph ₃ P=) ₂ NBr	1.14	0.25	0.02	1.86

^aReaction conditions: 32 mmol phenol, 0.006 mmol Pd₂(dpm)₂X₂ (X: Cl, Br, I, OCN, NO₂, N₃, SCN), 0.024 mmol Mn(TMHD)₃ as redox catalyst, 0 or 0.240 mmol (Ph₃P=)₂NBr, 0.50 MPa CO, 0.25 MPa air, 100°C, 3 h. Reaction mixture was analyzed by GC. TOF was based on charged Pd and produced DPC. DPC yield and PS yield were based on charged phenol. CO₂ yield was based on charged CO.

^b0.012 mmol PdBr₂.

the other hand, in case of other Pd dinuclear complexes, the reaction rates were greatly improved by (Ph₃P=)₂NBr. From these results, we assumed that Cl and Br which play an important role in the regeneration of reduced Pd [15] are essential in this oxidative carbonyl-

ation reaction. Best results were obtained by using Pd₂(dpm)₂(OCN)₂ in the presence of (Ph₃P=)₂NBr where TOF reached 7.66 (mol-DPC/mol-Pd h). This value is superior to that obtained by conventional Pd/redox catalyst/ammonium halide [3] under the employed reac-

Table 2
Oxidative carbonylation of phenol catalyzed by Pd₂(dpm)₂Cl₂ and related complexes^a

Run	Pd complex	Additive	DPC		PS	CO ₂
			TOF (DPC/Pd) (mol/mol h)	yield (%)	yield (%)	yield (%)
1	Pd ₂ (dpm) ₂ Cl ₂	–	5.75	1.28	0.06	0.73
2	Pd ₂ (dba) ₃ CHCl ₃ + Pd(PhCN) ₂ Cl ₂ ^b	dpm ^c	3.81	0.85	0.07	0.45
3	Pd ₂ (dba) ₃ CHCl ₃ + Pd(PhCN) ₂ Cl ₂ ^b	–	2.01	0.45	0.10	0.27
4	PdBr ₂ ^d	–	2.02	0.45	0.08	2.64

^aReaction conditions: 32 mmol phenol, 0.006 mmol Pd₂(dpm)₂Cl₂, 0.024 mmol Mn(TMHD)₃ as redox catalyst, 0.50 MPa CO, 0.25 MPa air, 100°C, 3 h. Reaction mixture was analyzed by GC. TOF was based on charged Pd and produced DPC. DPC yield and PS yield were based on charged phenol. CO₂ yield was based on charged CO.

^b0.003 mmol Pd₂(dba)₃CHCl₃ and 0.006 mmol Pd(PhCN)₂Cl₂.

^c0.012 mmol dpm.

^d0.012 mmol PdBr₂.

tion conditions¹ or obtained by PdBr₂/Mn(TMHD)₃/(Ph₃P=)₂NBr and PdBr₂/Mn(TMHD)₃ (Table 1). In these oxidative carbonylation reactions, the main coproducts were phenylsalicylate (PS) and carbon dioxide (CO₂). When a mixture of raw materials of Pd₂(dpm)₂-Cl₂ [Pd₂(dba)₃CHCl₃ (dba: dibenzylideneacetone), Pd(PhCN)₂Cl₂ (PhCN: benzonitrile), and dpm] [14] was used, the rate of reaction was found to be lower than that obtained by using Pd₂(dpm)₂Cl₂. Moreover, when this reaction was carried out in the absence of dpm, further reduction in the reaction rate was observed, and this reaction rate was same as obtained with PdBr₂ (Table 2). From these results, we consider that the Pd dinuclear complexes retain their dipalladium structure during the reaction (Scheme 1).

In summary, a facile synthesis of DPC, which involves oxidative carbonylation of phenol in the presence of Pd dinuclear complex [Pd₂(dpm)₂(OCN)₂]/redox catalyst/ammonium halide system, has been developed. Reactions proceeded smoothly in the presence of CO and air at 100°C and the TOF reached 7.66 (mol-DPC/mol-Pd h). In comparison to the most efficient direct DPC syntheses reported, our Pd dinuclear complex/redox catalyst/ammonium halide system gives the best TOF. To improve the catalytic efficiency as oxidative carbonylation catalyst, a more detailed optimization study

and direct synthesis of polycarbonate are in progress.

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¹ Reaction by Pd/redox catalyst/ammonium halide: mixing of phenol (32 mmol), PdBr₂ (0.012 mmol), Ce(Trop)₄ (Trop: tropolonate, 0.011 mmol) and (Ph₃P=)₂NBr (0.240 mmol), under 0.50 MPa CO and 0.25 MPa air at 100°C for 3 h yielded DPC (TOF: 5.53 mol-DPC/mol-Pd h, 1.23%) and coproducts.