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Oxidative carbonylation of phenol to diphenyl carbonate catalyzed by Pd dinuclear complex bridged with pyridylphosphine ligand

Hirotoshi Ishii [a,*], Meenakshi Goyal [a], Mitsuru Ueda [b,c], Kazuhiko Takeuchi [c], Michihiko Asai [c]

[a] *Joint Research Center for Precision Polymerization (JRCPP)-Tsukuba, Japan Chemical Innovation Institute (JCII), NIMC, 1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan*
[b] *Department of Organic and Polymeric Materials, Tokyo Institute of Technology, 2-12-1 Ohokayama, Meguro-ku, Tokyo, 152-8552, Japan*
[c] *National Institute of Materials and Chemical Research (NIMC), 1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan*

Abstract

Pd dinuclear complexes bridged with pyridylphosphine ligand such as $Pd_2(Ph_2PPy)_2X_2$ (Ph_2PPy: diphenyl-2-pyridylphosphine, X: Cl, Br, I, OCN, SCN, NO_2, N_3) were investigated as catalysts for direct synthesis of diphenyl carbonate (DPC) by oxidative carbonylation of phenol using carbon monoxide (CO) and air. $Pd_2(Ph_2PPy)_2X_2$/redox catalyst/ammonium halide system were found to be more effective than not only conventional $PdBr_2$/Ce(Trop)$_4$ (Trop: tropolonate)/$(Ph_3P=)_2NBr$ (bis(triphenylphosphoranylidene)ammonium bromide) system but $Pd_2(dpm)_2X_2$ (dpm: bis(diphenylphosphino)methane)/Mn(TMHD)$_3$ (TMHD: 2,2,6,6-tetramethyl-3,5-hepentanedionate)/$(Ph_3P=)_2NBr$ system too. The best efficiency was obtained by using $Pd_2(Ph_2PPy)_2(NO_2)_2$/Ce(TMHD)$_4$/$(Ph_3P=)_2NBr$ system where TOF reached 19.21 (mol-DPC/mol-Pd h). © 1999 Elsevier Science B.V. All rights reserved.
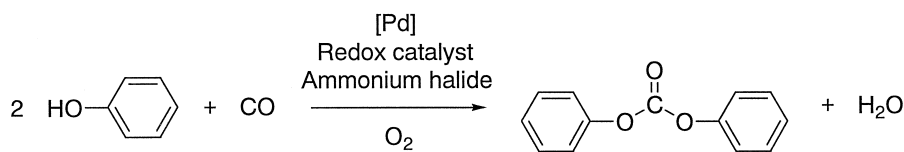
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1. Introduction

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 synthesis routes for producing PCs have been described in the literature [2]. Two currently used commercial methods are the interfacial polycondensation of diphenols with phosgene and the transesterification of diphenols with di-aryl carbonate. The former process is employed almost exclusively for the production of PCs. In recent years, there has been increasing demands 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 in the melt is being given more recognition recently because of the advantages like no solvent, no waste water, and no salt formation. But, diaryl

* Corresponding author. Tel.: +81-298-54-6383; fax: +81-298-55-1206; E-mail: ishihiro@nimc.go.jp

Scheme 1. Oxidative carbonylation of phenol catalyzed by Pd complex.

carbonates used in transesterification are prepared by the reaction of phosgene and sodium phenolates. Therefore, direct synthesis of diphenyl carbonate (DPC) by Pd-catalyzed oxidative carbonylation of phenol has been of great interest. Among many catalysts reported in patented and published reports [3–13], Pd with redox catalyst and ammonium halide gives the best efficiency (Scheme 1). However, the reaction rate of this process is too low to be an economical process for DPC synthesis, and the investigations are limited to simple Pd salts or Pd supported catalysts (i.e., $PdCl_2$, $PdBr_2$, Pd/charcoal, and so on). Thus, we have been investigating an efficient method for the direct synthesis of DPC from carbon monoxide (CO) and phenol [14–16] with an aim to use it eventually for direct synthesis of PC from bisphenol-A and CO. Here we report a successful synthesis of DPC by oxidative carbonylation of phenol using Pd dinuclear complex bridged with pyridylphosphine ligand ($Pd_2(Ph_2PPy)_2X_2$, Ph_2PPy: diphenyl-2-pyridylphosphine, X: Cl, Br, I, OCN, SCN, NO_2, N_3) along with a redox catalyst and an ammonium halide. The results obtained were compared with those obtained with $Pd_2(dpm)_2(OCN)_2$ catalyst which was the best from $Pd_2(dpm)_2X_2$ series (dpm: bis(diphenylphosphino)methane, X: Cl, Br, I, OCN, SCN, NO_2, N_3) reported separately elsewhere [16].

2. Results and discussion

Oxidative carbonylation of phenol was carried out using various complexes $Pd_2(Ph_2\text{-}PPy)_2X_2$ series as carbonylation catalyst. Other components of the catalyst system involved a redox catalyst, i.e., $Mn(TMHD)_3$ or $Ce(TMHD)_4$ (TMHD: 2,2,6,6-tetramethyl-3,5-hepentane-dionate) which is effective for the catalytic system found by us [15] and an ammonium halide, i.e., $(Ph_3P=)_2NBr$ (bis(triphenylphosphoranylidene)ammonium bromide). To compare the reactivities clearly, reaction was carried out with excess amount of phenol, low CO and air pressure, and short reaction time. The oxidative carbonylation reaction was performed by mixing phenol (32 mmol), $Pd_2(Ph_2PPy)_2X_2$ (0.006 mmol, 0.012 mmol on the basis of Pd), $Mn(TMHD)_3$ (0.024 mmol) or $Ce(TMHD)_4$ (0.011 mmol), and $(Ph_3P=)_2NBr$ (0.240 mmol) under 0.50 MPa CO and 0.25 MPa air at 100°C for 3 h. Various $Pd_2(Ph_2PPy)_2X_2$ complexes [1] were tested for oxidative carbonylation, and their reactivities were compared with that of $Pd_2(dpm)_2(OCN)_2$ [16].

The results given in Table 1 show that most of the $Pd_2(Ph_2PPy)_2X_2$ complexes were more efficient than $Pd_2(dpm)_2(OCN)_2$. Both the reaction rate and the yield were greatly affected by X. In the presence of $Mn(TMHD)_3$ as redox catalyst, the yield of DPC increased in the following order: OCN > N_3 = NO_2 = Cl > Br > I = SCN. On the other hand, in the presence of $Ce(TMHD)_4$, the yield of DPC increased in the following order: NO_2 > Cl > Br > N_3 > OCN > I > SCN. Best results were obtained by using $Pd_2(Ph_2PPy)_2(NO_2)_2$ and $Ce(TMHD)_4$ along with $(Ph_3P=)_2NBr$, where TOF reached

Table 1
Oxidative carbonylation of phenol catalyzed by $Pd_2(Ph_2PPy)_2X_2$[a]

Run	Pd catalyst	Redox catalyst	DPC[b] TOF (DPC/Pd) (mol/mol h)	DPC[b] yield (%)	PS[c] yield (%)	CO_2 yield (%)
1	$Pd_2(Ph_2PPy)_2Cl_2$	$Mn(TMHD)_3$	10.34	2.33	0.08	5.94
2	$Pd_2(Ph_2PPy)_2Cl_2$	$Ce(TMHD)_4$	17.55	3.97	0.08	1.71
3	$Pd_2(Ph_2PPy)_2Br_2$	$Mn(TMHD)_3$	8.92	2.01	0.08	5.03
4	$Pd_2(Ph_2PPy)_2Br_2$	$Ce(TMHD)_4$	15.51	3.48	0.08	1.76
5	$Pd_2(Ph_2PPy)_2I_2$	$Mn(TMHD)_3$	2.90	0.65	0.05	3.47
6	$Pd_2(Ph_2PPy)_2I_2$	$Ce(TMHD)_4$	3.83	0.87	0.03	1.01
7	$Pd_2(Ph_2PPy)_2(SCN)_2$	$Mn(TMHD)_3$	2.32	0.52	0.01	0.51
8	$Pd_2(Ph_2PPy)_2(SCN)_2$	$Ce(TMHD)_4$	1.29	0.29	0.05	0.24
9	$Pd_2(Ph_2PPy)_2(OCN)_2$	$Mn(TMHD)_3$	17.40	3.88	0.02	4.43
10	$Pd_2(Ph_2PPy)_2(OCN)_2$	$Ce(TMHD)_4$	12.53	2.79	0.02	0.92
11	$Pd_2(Ph_2PPy)_2(N_3)_2$	$Mn(TMHD)_3$	10.59	2.35	0.02	3.12
12	$Pd_2(Ph_2PPy)_2(N_3)_2$	$Ce(TMHD)_4$	14.62	3.25	0.04	1.01
13	$Pd_2(Ph_2PPy)_2(NO_2)_2$	$Mn(TMHD)_3$	10.35	2.32	0.03	4.40
14	$Pd_2(Ph_2PPy)_2(NO_2)_2$	$Ce(TMHD)_4$	19.21	4.33	0.04	1.88
15	$Pd_2(dpm)_2(OCN)_2$	$Mn(TMHD)_3$	7.66	1.70	0.01	0.72

[a] Reaction conditions: 32 mmol phenol, 0.012 mmol (on the basis of Pd) Pd catalyst, 0.024 mmol $Mn(TMHD)_3$ or 0.011 mmol $Ce(TMHD)_4$ as redox catalyst, 0.50 MPa CO, 0.25 MPa air, 100°C, 3h, reaction mixture was analyzed by FID-GC (liquid phase) and TCD-GC (gas phase). DPC and PS yield were based on the amount of charged phenol. CO_2 yield was based on the amount of charged CO.
[b] DPC: diphenyl carbonate.
[c] PS: phenyl salicylate.
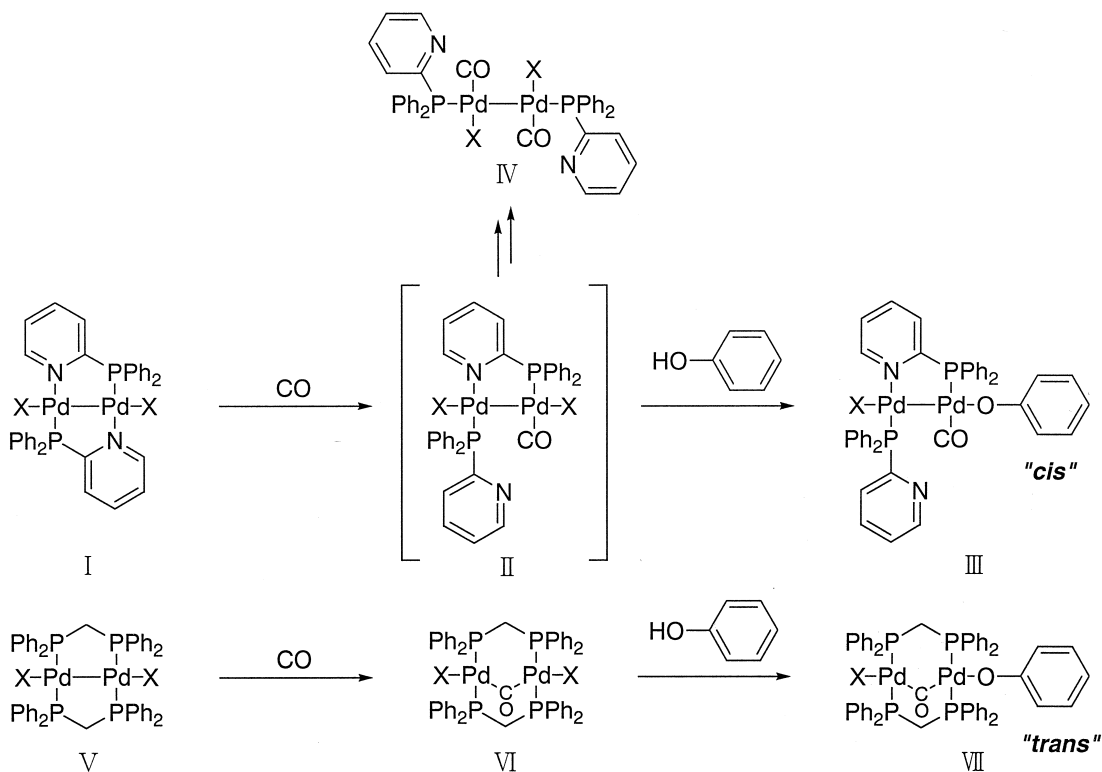
Scheme 2. Reaction of Pd dinuclear complexes with CO and phenol.

19.21 (mol-DPC/mol-Pd h). This value is much higher than 5.53 (mol-DPC/mol-Pd h) obtained by conventional Pd mononuclear catalyst system, i.e., $PdBr_2/Ce(Trop)_4$ (Trop: tropolonate)/ $(Ph_3P=)_2NBr$ under the similar reaction conditions [3]. In these oxidative carbonylation reactions, the selectivity for DPC based on charged phenol was up to 90%, and small amount of phenyl salicylate (PS), carbon dioxide (CO_2), and trace amount of about 10 co-products including phenoxyphenols and biphenols were detected by GC.

The reaction mechanism of the oxidative carbonylation of phenol to produced DPC is not very well studied yet. In carbonylation reactions catalyzed by Pd complex, coupling reaction of CO and alkoxide ion (RO^-) to produce RO–CO–Pd intermediate can occur through two possible path ways. One pathway involves ''direct attack'' of RO^- to coordinated CO on Pd center, and the other one includes ''stepwise attack'' of RO^- to coordinated CO on Pd center (First RO^- gets coordinated to Pd center to which CO is already coordinated and then coupling of the coordinated RO^- and coordinated CO on Pd center takes place). Pd catalyzed carbonylation of alkyl or aryl halide (R'–X) and alcohol with CO to give esters is reported to proceed by a ''stepwise attack'' mechanism in the step of producing R'–CO–Pd intermediate [17].

From the literature [18,19], it is known that $Pd_2(Ph_2PPy)_2X_2$ and $Pd_2(dpm)_2X_2$ have different reactivities toward CO (Scheme 2). It is reported that CO is coordinated to Pd center where 2-pyridyl moiety (Py) has been coordinated in $Pd_2(Ph_2PPy)_2X_2$ and coordination site of the phosphine and X were exchanged [18]. On the basis of this structure, it can be assumed that during the reaction of $Pd_2(Ph_2PPy)_2X_2$ and CO, mono-CO-coordinated intermediate (Scheme 2, II) will be produced. Furthermore, if it is presumed that the oxidative carbonylation of phenol is taking place through ''stepwise attack'', phenoxide ion (PhO^-) will exchange with X of intermediate II resulting in intermedi-ate III with CO and PhO^- coordinated to Pd center in *cis* position. Because of close vicinity of activated CO and PhO^- in intermediate III, they can easily couple to form DPC, thus a very fast reaction between phenol and CO can be expected.

On the other hand, in the reaction of $Pd_2(dpm)_2X_2$, CO is inserted into a Pd–Pd bond [19] and PhO^- will exchange with X at ''*trans*'' position of CO–Pd bond (Scheme 2, VII). ''*Trans*'' stereochemistry of activated CO and PhO^- of $Pd_2(dpm)_2X_2$ complex will make the reaction comparatively slower. These assumptions are in complete agreement with the experiment results thereby supporting the proposed reaction mechanism involving ''stepwise attack''.

3. Conclusions

In summary, a facile synthesis of diphenyl carbonate, which involves oxidative carbonylation of phenol in the presence of Pd dinuclear complex bridged with pyridylphosphine ligand $[Pd_2(Ph_2PPy)_2X_2]$ and redox catalyst along with ammonium halide, has been developed. Reactions proceeded smoothly in the presence of CO and air at 100°C and the TOF reached 19.21 (mol-DPC/mol-Pd h). In comparison to the most efficient direct DPC syntheses reported in literatures, our $Pd_2(Ph_2PPy)_2X_2$ complex/ redox catalyst/ammonium halide system is simple and gives the higher 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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References

[1] D. Freitag, U. Grico, P.R. Muller, W. Nouvertne, Polycarbonate, in: H.F. Mark (Ed.), Encyclopedia of Polymer Science and Engineering, Vol. 11, Wiley, New York, 1987, p. 649.

[2] Y. Ono, Pure Appl. Chem. 68 (1996) 367.

[3] Y. Okago, H. Hayashi, H. Miyagi, K. Kujira, M. Takagi, N. Suzuki, Jpn. Kokai Tokkyo Koho, JP 96 193,056 (1996).

[4] J.A. King, Jr., T.E. Kraft, G.R. Faller, US. Pat., US 5,142,086 (1992).

[5] H. Kezuka, F. Okuda, Eur. Pat., EP 503,581 (1992).

[6] T. C-T. Chang, Eur. Pat., EP 350,697 (1990).

[7] T. C-T. Chang,. Eur. Pat., EP 350,700 (1990).

[8] J.E. Hallgren, US. Pat., US 4,201,721 (1980).

[9] J.E. Hallgren, G.M. Lucas, J. Organomet. Chem. 212 (1981) 135.

[10] M. Takagi, H. Miyagi, T. Yoneyama, Y. Ohgomori, J. Mol. Catal. A: Chem. 129 (1998) L1.

[11] M. Goyal, R. Nagahata, J. Sugiyama, M. Asai, M. Ueda, K. Takeuchi, Catal. Lett. 54 (1998) 29.

[12] M. Goyal, R. Nagahata, J. Sugiyama, M. Asai, M. Ueda, K. Takeuchi, J. Mol. Catal. A: Chem. 137 (1999) 147.

[13] A. Vavasori, L. Toniolo, J. Mol. Catal. A: Chem. 139 (1999) 109.

[14] H. Ishii, M. Ueda, K. Takeuchi, M. Asai, J. Mol. Catal. A: Chem. 138 (1999) 311.

[15] H. Ishii, M. Ueda, K. Takeuchi, M. Asai, J. Mol. Catal. A: Chem. 144 (1999) 369.

[16] H. Ishii, M. Ueda, K. Takeuchi, M. Asai, J. Mol. Catal. A: Chem. 144 (1999) 477.

[17] A. Schoenberg, I. Bartoletti, R.F. Heck, J. Org. Chem. 39 (1974) 3318.

[18] A. Maisonnat, J.P. Farr, A.L. Balch, Inorg. Chim. Acta 53 (1981) L217.

[19] L.S. Benner, A.L. Balch, J. Am. Chem. Soc. 100 (1978) 6099.