

Letter

# Oxidative carbonylation of phenol to diphenyl carbonate catalyzed by Pd–Sn complexes with redox catalyst

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## Abstract

Pd–Sn heterobinuclear complexes were investigated as catalysts for direct synthesis of diphenyl carbonate (DPC) by oxidative carbonylation of phenol using carbon monoxide and oxygen. Pd–Sn heterobinuclear complexes such as  $\text{Pd}_2(\text{dpm})_2(\text{SnCl}_3)\text{Cl}$  and  $\text{Pd}_2(\text{dpm})_2(\text{SnCl}_3)_2$  [dpm: bis(diphenylphosphino)methane] were found to be novel catalysts for the oxidative carbonylation of phenol. This newly designed Pd–Sn complex/redox catalyst system does not require ammonium halides which is an essential component of conventional catalyst systems. © 1999 Elsevier Science B.V. All rights reserved.

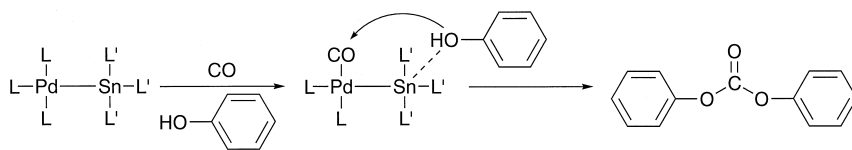
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Diphenyl carbonate (DPC), a starting material for polycarbonate synthesis by transesterification reaction [1] is conventionally synthesized by phosgenation of phenol or transesterification of dimethyl carbonate (DMC) and phenol. A number of routes for producing DPC without using phosgene have been described in the literature [2]. DPC can be prepared mainly by two non-phosgenated approaches, by transesterification of DMC and phenol using Lewis acids [3] and by oxidative carbonylation of phenol using carbon monoxide (CO) and Pd/redox catalyst/ammonium halide systems [4–7]. However, the

transesterification method using DMC as raw material is not a direct method for the preparation of DPC. On the other hand, the oxidative carbonylation method can produce DPC in a single step reaction, but requires a large amount of ammonium halide which causes corrosion of reaction apparatus by halogen ion. Thus, we investigated an efficient method for the direct synthesis of DPC from CO and phenol without using ammonium halide. Here we report oxidative carbonylation of phenol to DPC by a novel, non-ammonium halide catalytic system, i.e., Pd–Sn complexes with redox catalyst.

The reaction mechanism of the oxidative carbonylation catalyzed by Pd/redox catalyst/ammonium halide systems has not been made clear.

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Scheme 1. Reaction of Pd–Sn with CO and phenol.

However, it has been reported that the ammonium halide activates phenol by forming ammonium phenoxide, and the reaction proceeds via oxidative carbonylation of activated phenol catalyzed by Pd. Among Pd/redox catalyst/ammonium halide systems, recently, it was reported in a patent [7] that Pd/Ce(Trop)<sub>4</sub> (Trop: tropolonate)/(Ph<sub>3</sub>P=)<sub>2</sub>NBr [bis(triphenylphosphoranylidene)ammonium bromide] system was effective for oxidative carbonylation of phenol.

We selected Pd–Sn complexes/redox catalyst system instead of Pd/redox catalyst/ammonium halide system, where Pd and Sn are expected to react with CO and phenol as shown in Scheme 1. The selected Pd–Sn complexes

and redox catalyst [Ce(Trop)<sub>4</sub>] were prepared according to the procedure given in literature [7–11]. The oxidative carbonylation reaction was performed by mixing Pd–Sn complex (0.012 mmol), Ce(Trop)<sub>4</sub> (0.011 mmol), and excess amount of phenol (32 mmol) under 0.50 MPa CO and 0.25 MPa air at 100°C for 3 h. Various Pd–Sn complexes were tested for their efficiency as oxidative carbonylation catalyst and in order to study their efficiency clearly, the reaction was carried out for short time using excess amount of phenol.

As shown in Table 1, Pd<sub>2</sub>(dpm)<sub>2</sub>(SnCl<sub>3</sub>)<sub>2</sub> and Pd<sub>2</sub>(dpm)<sub>2</sub>(SnCl<sub>3</sub>)Cl [dpm: bis(diphenylphosphino)methane] showed good catalytic ac-

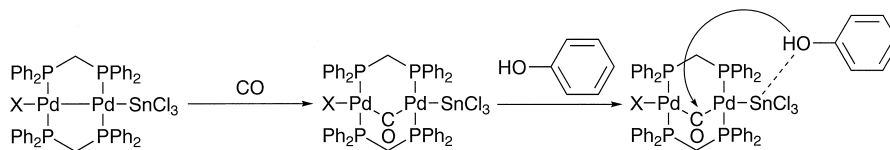
Table 1  
Oxidative carbonylation of phenol catalyzed by Pd–Sn complexes<sup>a</sup>

Run	Pd complex	Redox catalyst	Additive	DPC (mmol)	TOF(DPC <sup>b</sup> /Pd) (mol/mol h)	PS <sup>c</sup> (mmol)	CO <sub>2</sub> (%/CO)
1	Pd <sub>2</sub> (dpm) <sub>2</sub> (SnCl <sub>3</sub> ) <sub>2</sub>	Ce(Trop) <sub>4</sub>	–	0.105	2.91	0.029	0.47
2	Pd <sub>2</sub> (dpm) <sub>2</sub> (SnCl <sub>3</sub> )Cl	Ce(Trop) <sub>4</sub>	–	0.103	2.80	0.024	0.52
3	[Et <sub>4</sub> N][Pd(CO)(SnCl <sub>3</sub> ) <sub>2</sub> Cl]	Ce(Trop) <sub>4</sub>	–	0.002	0.06	0.011	0.46
4	(C <sub>3</sub> H <sub>5</sub> )Pd(PPh <sub>3</sub> )(SnCl <sub>3</sub> )	Ce(Trop) <sub>4</sub>	–	0.001	0.04	0.003	1.54
5	Pd <sub>2</sub> (dpm) <sub>2</sub> (SnCl <sub>3</sub> ) <sub>2</sub>	Ce(Trop) <sub>4</sub>	(Ph <sub>3</sub> P=) <sub>2</sub> NBr	0.010	0.28	0.006	0.07
6	Pd <sub>2</sub> (dpm) <sub>2</sub> (SnCl <sub>3</sub> ) <sub>2</sub>	–	–	0	0	0	0.05
7	Pd <sub>2</sub> (dpm) <sub>2</sub> Cl <sub>2</sub>	Ce(Trop) <sub>4</sub>	–	0.041	1.14	0.010	0.06
8	Pd <sub>2</sub> (dpm) <sub>2</sub> Cl <sub>2</sub>	Ce(Trop) <sub>4</sub>	SnCl <sub>2</sub>	0.005	0.14	0.006	0.62
9	Pd(CO)Cl	Ce(Trop) <sub>4</sub>	–	0.008	0.23	0.002	0.03
10	PdBr <sub>2</sub>	Ce(Trop) <sub>4</sub>	(Ph <sub>3</sub> P=) <sub>2</sub> NBr	0.200	5.53	0.011	0.89

<sup>a</sup>Reaction conditions: 32 mmol phenol, 0.012 mmol (as Pd) Pd complex, 0.011 mmol redox catalyst Ce(Trop)<sub>4</sub> (Trop: tropolonate), 0.240 mmol (Ph<sub>3</sub>P=)<sub>2</sub>NBr [bis(triphenylphosphoranylidene)ammonium bromide] or 0.012 mmol SnCl<sub>2</sub> as additive, 0.50 MPa CO, 0.25 MPa air, 100°C, 3 h. The reaction mixture was analyzed by GC. TOF was based on added Pd and produced DPC.

<sup>b</sup>DPC: diphenyl carbonate.

<sup>c</sup>PS: phenyl salicylate.

Scheme 2. Reaction of Pd<sub>2</sub>(dpm)<sub>2</sub>(SnCl<sub>3</sub>)<sub>2</sub>X with CO and phenol (X–: Cl– or Cl<sub>3</sub>Sn–).

tivity, giving TOF (turn over frequency) of 2.91 and 2.80 mol-DPC/mol-Pd h, respectively (run 1, 2) as compared to 5.53 mol-DPC/mol-Pd h obtained by conventional Pd catalyst with ammonium halide [7] (run 10). In these reactions, the main co-products were phenyl salicylate (PS) and carbon dioxide ( $\text{CO}_2$ ). In the presence of ammonium halide  $[(\text{Ph}_3\text{P}=\text{O})_2\text{NBr}]$ ,  $\text{Pd}_2(\text{dpm})_2(\text{SnCl}_3)_2$  lost its catalytic activity (run 5).  $\text{Pd}_2(\text{dpm})_2\text{Cl}_2$  (run 7) was found to be more efficient than  $\text{Pd}(\text{CO})\text{Cl}$  (run 9), though both are  $\text{Pd}^+$  complex.  $\text{Pd}_2(\text{dpm})_2(\text{SnCl}_3)_2$  (run 1) was more efficient than  $\text{Pd}_2(\text{dpm})_2\text{Cl}_2$  (run 7) or  $\text{Pd}_2(\text{dpm})_2\text{Cl}_2$  with  $\text{SnCl}_2$  (run 8). Further investigation revealed that  $\text{Ce}(\text{Trop})_4$  was must for DPC formation (run 6). From these results, it is presumed that  $-\text{SnCl}_3$  activates phenol as Lewis acid, and  $[\text{Pd}-\text{Pd}-\text{SnCl}_3]$  structure is essential for DPC production in the absence of ammonium halide. Furthermore, on the basis of these observations, it can be assumed that the phenol activated by  $-\text{SnCl}_3$  reacted with the  $[\text{Pd}-(\text{CO})-\text{Pd}]$  intermediate [8,9] as shown in Scheme 2. Main co-product PS might have been produced through rearrangement of DPC and the other main co-product  $\text{CO}_2$  may be an outcome of direct oxidation of CO.

In summary, we designed a novel catalyst system for the synthesis of DPC by oxidative carbonylation of phenol, which does not require ammonium halides. To improve the efficiency of this catalyst system, a detailed optimization

study including investigation for more suitable redox catalysts and reaction condition is in progress.

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## References

- [1] Y. Kim, K.Y. Choi, T.A. Chamberlin, *Ind. Eng. Chem. Res.* 31 (1992) 2118.
- [2] Y. Ono, *Pure Appl. Chem.* 68 (1996) 367.
- [3] Z. Fu, Y. Ono, *J. Mol. Catal. A: Chem.* 118 (1997) 293.
- [4] J.E. Hallgren, R.O. Matthews, *J. Organomet. Chem.* 175 (1979) 135.
- [5] J.E. Hallgren, G.M. Lucas, R.O. Matthews, *J. Organomet. Chem.* 204 (1981) 135.
- [6] J.E. Hallgren, G.M. Lucas, *J. Organomet. Chem.* 212 (1981) 135.
- [7] Y. Okago, H. Hayashi, H. Miyagi, K. Kujira, M. Takagi, N. Suzuki, *Jpn. Kokai Tokkyo Koho*, JP 96 193, 056, 1996.
- [8] L.S. Benner, A.L. Balch, *J. Am. Chem. Soc.* 100 (1978) 6099.
- [9] M.M. Olmstead, L.S. Benner, H. Hope, A.S. Balch, *Inorg. Chim. Acta* 32 (1979) 193.
- [10] J.V. Kingston, G.R. Scollary, *J. Chem. Soc., Chem. Commun.* (1970) 362.
- [11] R. Mason, G.B. Robertson, P.O. Whimp, *J. Chem. Soc., Chem. Commun.* (1968) 1655.