

Letter

Oxidative carbonylation of phenol to diphenyl carbonate catalyzed by Pd₂–Sn heterotrinnuclear complex along with Mn redox catalyst without any addition of ammonium halide

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Abstract

Various redox catalysts were investigated for oxidative carbonylation of phenol by using Pd₂–Sn heterotrinnuclear complex, i.e., Pd₂(dpm)₂(SnCl₃)Cl [dpm: bis(diphenylphosphino)methane] under CO and air. The reaction rate was changed by the redox catalyst used. Best results were obtained by using Mn(TMHD)₃ (TMHD: 2,2,6,6-tetramethyl-3,5-heptanedionate). This newly designed catalyst system does not require ammonium halide which is an essential component of conventional catalyst systems. © 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]. Two currently used commercial methods are the interfacial polycondensation of diphenols with phosgene and the transesterification of diphenols with diaryl 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 has been given more recognition because of the advantages like no solvent, no waste water, and no salt formation. But, diaryl carbonates used in transesterification are prepared by the reaction of phosgene and sodium phenolates. On the other hand, dimethyl carbonate (DMC) is readily obtained from oxidative carbonylation of methanol [3]. Thus several patents and reports described the synthesis of PCs using DMC in place of diphenyl carbonate (DPC) [4–6]. However, the reaction of diphenols with

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DMC is thermodynamically unfavorable whereas the reaction of diphenols with DPC is thermodynamically favorable for PC synthesis. So, the DMC method has not so far been shown to be practical for transesterification polymerization to PCs. Therefore, it has been of great interest to prepare DPC directly by Pd-catalyzed oxidative carbonylation of phenol. Among many catalysts reported in patented and published reports [7–14], Pd/redox catalyst/ammonium halide system gives the best efficiency. However, this process 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 carbon monoxide (CO) and phenol without using ammonium halide [15] 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 Pd₂-Sn heterotrinnuclear complex with redox catalyst.

The reaction mechanism of the oxidative carbonylation catalyzed by Pd/redox catalyst/ammonium halide systems has not been made clear. However, it has been reported that the reaction of ammonium halide and phenol produces ammonium phenoxide [13]. Thus, ammonium halide and Pd are supposed to react with phenol and CO, respectively as shown in Scheme 1, and the resulting activated CO and phenolate couple oxidatively to produce DPC.

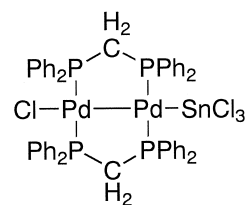
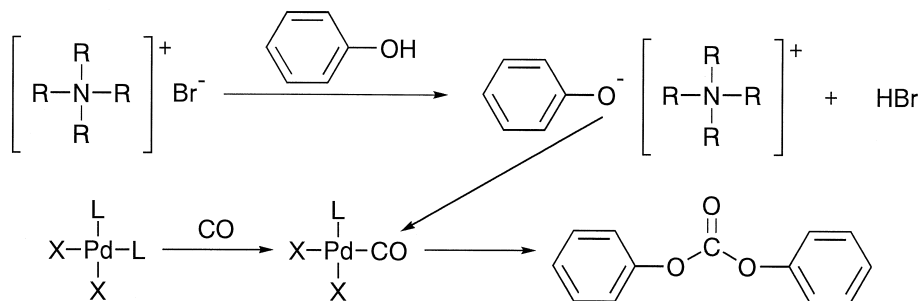


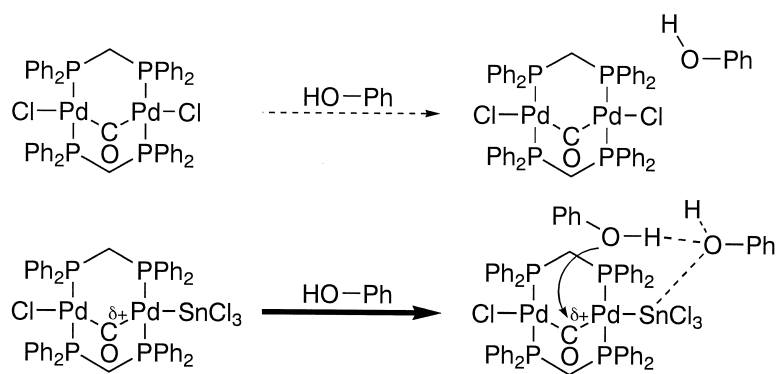
Fig. 1. Structure of Pd₂(dpm)₂(SnCl₃)Cl.

We had selected Pd₂(dpm)₂(SnCl₃)Cl [dpm: bis(diphenylphosphino)methane] (Fig. 1) [16] for the non-ammonium halide catalytic system [15]. This Pd₂-Sn heterotrinnuclear complex reacts with CO to form Pd₂(dpm)₂(μ-CO)(SnCl₃)Cl [16]. It seems that the (μ-CO) of Pd₂(dpm)₂(μ-CO)(SnCl₃)Cl is more reactive than that of Pd₂(dpm)₂(μ-CO)Cl₂ because of cationicity of the Pd moiety. Moreover, Sn moiety activates phenol by a Lewis acid–base interaction. Thus, the CO and the phenol both are bound to the Pd catalyst, that is, the substrate and the reagent are both parts of the same molecule. So, we can expect a very fast reaction between phenol and CO (Scheme 2).

The oxidative carbonylation reaction was performed by mixing phenol (32 mmol), Pd₂(dpm)₂(SnCl₃)Cl (0.006 mmol) and redox catalyst (0.011 mmol), under 0.50 MPa CO and 0.25 MPa air at 100°C for 3 h. Various redox catalysts were tested for their efficiency and in order to study their efficiency clearly, the reaction was carried out for short time using excess



Scheme 1. Reaction of Pd with CO and ammonium halide with phenol.

Scheme 2. Reactivity of $\text{Pd}_2(\text{dpm})_2(\mu\text{-CO})\text{Cl}_2$ and $\text{Pd}_2(\text{dpm})_2(\mu\text{-CO})(\text{SnCl}_3)\text{Cl}$.

amount of phenol. The results are summarized in Table 1.

Both the reaction rate and the yield were greatly affected by metals, oxidation state of metals and ligands of redox catalyst. For example, Mn shows better catalytic efficiency than Ce and Fe, and Mn^{3+} is more active than

Mn^{2+} . Among the Mn^{3+} based redox catalyst, the yield of DPC increased in the following order: $\text{Mn}(\text{TMHD})_3 > \text{Mn}(\text{Trop})_3 > \text{Mn}(\text{acac})_3 > \text{Mn}(\text{F6-acac})_3$ (TMHD: 2,2,6,6-tetramethyl-3,5-heptanedionate, Trop: tropolonate, acac: acetylacetonate, F6-acac: 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate). Best results were

Table 1
Oxidative carbonylation of phenol catalyzed by $\text{Pd}_2\text{-Sn}$ with redox catalysts^a

Run	Redox catalyst	DPC		PS	CO ₂
		TOF (DPC/Pd) (mol/mol h)	Yield (%)	Yield (%)	Yield (%)
1	$\text{Mn}(\text{TMHD})_3^b$	7.66	1.70	0.07	0.77
2	$\text{Mn}(\text{Trop})_3^b$	3.14	0.70	0.13	1.79
3	$\text{Mn}(\text{TMHD})_3$	4.46	1.00	0.06	0.58
4	$\text{Mn}(\text{Trop})_3$	3.53	0.80	0.12	1.95
5	$\text{Mn}(\text{acac})_3$	2.62	0.59	0.05	1.39
6	$\text{Mn}(\text{F6-acac})_3$	0	0	0	0.06
7	$\text{Mn}(\text{Trop})_2$	2.80	0.62	0.07	1.67
8	$\text{Mn}(\text{acac})_2$	0.52	0.12	0.02	0.77
9	$\text{Ce}(\text{Trop})_4$	2.80	0.64	0.15	0.52
10	$\text{Ce}(\text{TMHD})_4$	2.45	0.55	0.08	0.25
11	$\text{Ce}(\text{acac})_3 \cdot 3\text{H}_2\text{O}$	0.74	0.16	0.02	0.24
12	$\text{Ce}(\text{F3-acac})_3$	0.22	0.05	0.03	0.41
13	$\text{Fe}(\text{acac})_3$	0.19	0.04	0.05	0.53
14	$\text{Fe}(\text{F3-acac})_3$	0	0	0	0.17
15	$\text{Mn}(\text{TMHD})_3^c$	0.45	0.10	0	0.46
16	$\text{Mn}(\text{TMHD})_3^d$	6.46	0.96	0.04	0.71

^aReaction conditions: 32 mmol phenol, 0.006 mmol $\text{Pd}_2(\text{dpm})_2(\text{SnCl}_3)\text{Cl}$, 0.011 mmol 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 and PS yields were based on charged phenol. CO₂ yield was based on charged CO.

^b0.024 mmol redox catalyst.

^c0.024 mmol redox catalyst with 0.240 mmol $(\text{Ph}_3\text{P}=\text{N})_2\text{NBr}$ [bis(triphenylphosphoranylidene)ammonium bromide].

^d0.024 mmol redox catalyst, 2 h.

obtained by using $\text{Mn}(\text{TMHD})_3$ as the redox catalyst, where TOF (turn over frequency) reached 7.66 (mol-DPC/mol-Pd h). This value is superior to that obtained by Pd/redox catalyst/ammonium halide system [7] under the employed reaction conditions.¹ Using $\text{Pd}_2(\text{dpm})_2(\text{SnCl}_3)\text{Cl}$ with $\text{Mn}(\text{TMHD})_3$ as catalyst when reaction time was decreased from 3 to 2 h, no substantial difference in TOF was observed. So we consider that the catalytic activity is not lost in 3 h. As we mentioned in the former report [15], $\text{Pd}_2(\text{dpm})_2(\text{SnCl}_3)\text{Cl}$ was more effective than $\text{Pd}_2(\text{dpm})_2\text{Cl}_2$ with SnCl_2 in the oxidative carbonylation. From these results, we assumed that [Pd–Pd–Sn] structure was essential for high reactivity. In these reactions, the main coproducts were phenyl salicylate (PS) and carbon dioxide (CO_2). Furthermore, in the presence of ammonium halide [$(\text{Ph}_3\text{P}=\text{N})_2\text{NBr}$: bis(triphenylphosphoranylidene)ammonium bromide], $\text{Pd}_2(\text{dpm})_2(\text{SnCl}_3)\text{Cl}/\text{Mn}(\text{TMHD})_3$ system lost its catalytic activity. Presumably ammonium halide adduct to acidic Sn center prevents the activation of phenol.

In summary, a facile synthesis of diphenyl carbonate, which involves oxidative carbonylation of phenol in the presence of $\text{Pd}_2\text{–Sn}$ heterotrinnuclear complex [$\text{Pd}_2(\text{dpm})_2(\text{SnCl}_3)\text{Cl}$] and redox catalyst [$\text{Mn}(\text{TMHD})_3$], 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 $\text{Pd}_2\text{–Sn}$ heterotrinnuclear com-

plex/redox catalyst system is simple and 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), PdBr_2 (0.012 mmol), $\text{Ce}(\text{Trop})_4$ (0.011 mmol) and $(\text{Ph}_3\text{P}=\text{N})_2\text{NBr}$ [bis(triphenylphosphoranylidene)ammonium bromide] (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.