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Oxidative carbonylation of phenol to diphenyl carbonate catalyzed by Pd complex with diimine ligands

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Pd complexes with diimine ligands were investigated as novel Pd catalysts for direct synthesis of diphenyl carbonate by oxidative carbonylation of phenol using carbon monoxide and air. Best efficiency was obtained by using a $PdCl_2(ArN{=}CH–)_2$ or $PdCl_2(ArN{=}CMe–)_2/Mn(TMHD)_3/(Ph_3P{=})_2NBr$ system where TOF reached 8.08 and 8.00 mol-DPC/mol-Pd h, respectively. The efficiency was increased with increases in the CO pressure.

Keywords: oxidative carbonylation, phenol, carbon monoxide, palladium, diimine

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]. In recent years, there have been increasing demands for a safer and environmentally favorable process for PCs synthesis. The transesterification process using diphenols and diphenyl carbonate (DPC) has been given more recognition instead of the interfacial polycondensation of diphenols with phosgene, because of advantages such as no toxic phosgene, no solvent, and no salt formation [2]. 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 literature [3–13], the Pd/redox catalyst/ammonium halide system gives the best efficiency. However, the reaction rate of this process is still too low to be an economical process for DPC synthesis. These reports were limited to investigations of simple Pd salt or Pd-supported catalysts (i.e., $PdCl_2$, $PdBr_2$, Pd/charcoal, and so on) and improvements of redox catalyst or ammonium halide. Thus, we have investigated an efficient method for the direct synthesis of DPC from carbon monoxide (CO) and phenol, with the aim to use it eventually for direct synthesis of PC from bisphenol-A and CO [14–17]. In the field of polyolefin synthesis, late transition metal complex catalysts, i.e., Pd– or Ni–diimine complexes and Fe– or Co–2,6-diiminopyridyl complexes have been given more recognition as the next generation catalysts [18–20]. Hence, we investigated the utility of these complexes as catalysts for the oxidative carbonylation of phenol. Here we report a successful synthesis of DPC by the oxidative carbonylation of phenol catalyzed by the Pd–diimine complex with a redox catalyst and an ammonium halide (scheme 1).

2. Experimental

$PdCl_2$–diimine complexes were synthesized by using the diimine ligand and $PdCl_2(COD)$ in CH_2Cl_2 instead of PdClMe(COD) in ether (modified procedure of Brookhart and co-workers [18]). The complex was purified by reprecipitation from the CH_2Cl_2 solution twice by adding hexane. The $PdCl_2$–dipyridyl complexes, the $PdCl_2$–diamine complex, and the $PdCl_2$–diphosphine complex were purchased or synthesized by mixing the corresponding ligands and $PdCl_2(PhCN)_2$ in CH_2Cl_2 (modified procedure of Newkome et al. [21]). $FeCl_2$– or $CoCl_2$–diiminopyridyl complexes were synthesized according to the literature [19,20].

The oxidative carbonylation reaction was performed by mixing phenol (32 mmol), the Pd complex (0.012 mmol), $Mn(TMHD)_3$ (0.024 mmol), and $(Ph_3P{=})_2NBr$ (0.240 mmol) under CO and air, and heating at 100 °C.

3. Results and discussion

Brookhart and co-workers demonstrated that Pd–diimine complexes could efficiently catalyze the synthesis of polyolefins [18]. Presumably this high efficiency can be attributed to the fact that the diimine ligand with aromatic substituents must have made the Pd center electron deficient. If this assumption is correct, then these diimine complexes should be suitable for oxidative carbonylation,

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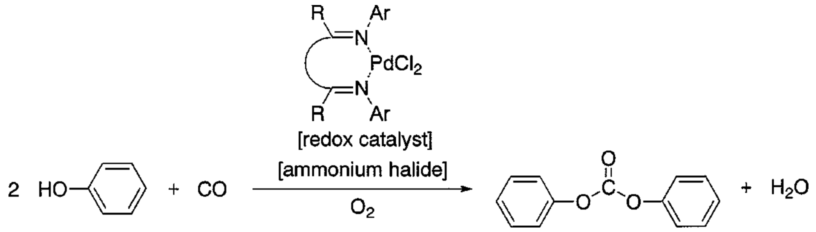
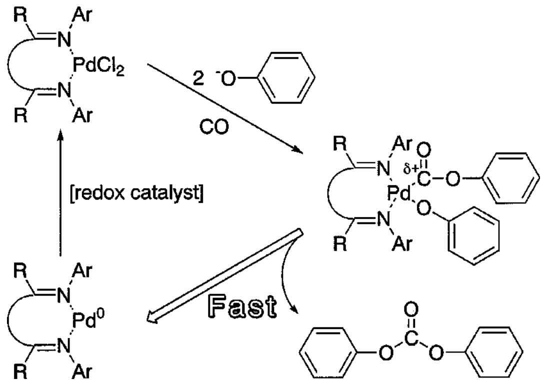


Scheme 1. Oxidative carbonylation of phenol catalyzed by Pd–diimine complex with redox catalyst and ammonium halide.



Scheme 2. Expected reaction mechanism of Pd–diimine complex catalyzed oxidative carbonylation of phenol.

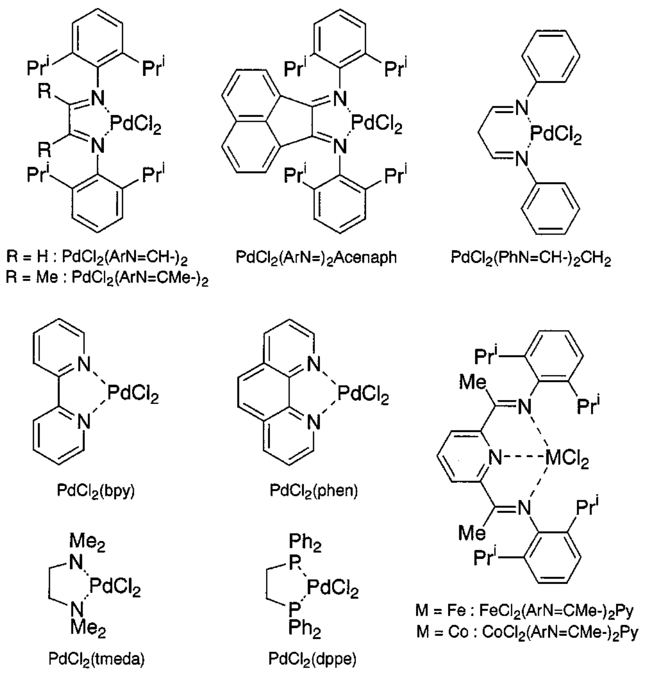


Figure 1. Structure of Pd complexes.

because the electron deficiency of the Pd center can accelerate CO and phenol activation. Thus, in Pd–diimine complexes, CO and phenoxide can bind to the electron deficient Pd complex very rapidly, and the cationicity of the "–CO–" carbon in the intermediate complex "Pd–CO–OPh" is adequate for attack by a phenoxide ion (scheme 2). Thus, a very fast reaction between phenol and CO can be expected to make the Pd–diimine complex an efficient catalyst for the oxidative carbonylation of phenol.

From this consideration, we selected Pd–diimine complexes for the present investigation (figure 1, illustrated with other complexes). We used $PdCl_2$–diimine complexes as Pd–diimine complexes instead of the PdMeCl–diimine complexes reported by Brookhart and co-workers [18] because of their instability against oxygen and moisture present in the reaction mixture. Moreover, recently, Gibson [19] and Brookhart [20] independently reported that Fe– or Co–2,6-diiminopyridyl complexes are efficient for synthesis of polyolefins. So, we examined their efficiency for the oxidative carbonylation of phenol. According to our previous investigations [14–17], we used $Mn(TMHD)_3$ (TMHD: 2,2,6,6-tetramethyl-3,5-heptandionate) as redox catalyst and $(Ph_3P{=})_2NBr$ [bis(triphenylphosphoranylidene)ammonium bromide] as ammonium halide [15] along with the Pd complex. In order to study their efficiency clearly, the reaction was carried out for short time using excess amount of phenol, because no induction period could be found in their reactions.

The results are summarized in table 1. Both the reaction rate and the yields were greatly affected by the difference in the structure of various Pd complexes. Only $PdCl_2(ArN{=}CH{-})_2$ and $PdCl_2(ArN{=}CMe{-})_2$ were found

Table 1
Oxidative carbonylation of phenol catalyzed by Pd–diimine complexes and related complexes.[a]

Run	Pd complex	DPC TOF (DPC/Pd) (mol/mol h)	Yield (%) DPC	PS[b]	CO_2
1	$PdCl_2(ArN{=}CH{-})_2$	8.08	1.81	0.10	4.92
2	$PdCl_2(ArN{=}CMe{-})_2$	8.00	1.80	0.10	5.31
3	$PdCl_2(ArN{=})_2$Acenaph	0.68	0.15	0.01	0.78
4	$PdCl_2(PhN{=}CH{-})_2CH_2$	3.02	0.67	0.03	5.09
5	$PdCl_2$(bpy)	0.68	0.15	0.04	5.04
6	$PdCl_2$(phen)	2.88	0.65	0.02	3.39
7	$PdCl_2$(tmeda)	0.08	0.02	0.02	2.65
8	$PdCl_2$(dppe)	0.60	0.13	0.03	0.50
9	$FeCl_2(ArN{=}CMe{-})_2Py$	0.14	0.03	0.01	0.05
10	$CoCl_2(ArN{=}CMe{-})_2Py$	0.08	0.02	0.01	0.04

[a] Reaction conditions: 32 mmol phenol, 0.012 mmol Pd catalyst, 0.024 mmol $Mn(TMHD)_3$, 0.240 mmol $(Ph_3P{=})_2NBr$, 0.50 MPa CO, 0.25 MPa air, 100 °C, 3 h. The reaction mixture was analyzed by FID-GC (liquid phase) and TCD-GC (gas phase). TOF was based on the amount of charged Pd and produced DPC. DPC and PS yield were based on the amount of charged phenol. CO_2 yield was based on the amount of charged CO.

[b] PS: phenyl salicylate.

Table 2
Oxidative carbonylation of phenol catalyzed by $PdCl_2(ArN{=}CH–)_2$ and $PdCl_2(ArN{=}CMe–)_2$.[a]

Run	Pd complex	Pressure (MPa) CO	Pressure (MPa) Air	CO conq.[b] (%)	Time (h)	DPC TOF (DPC/Pd) (mol/mol h)	DPC yield (%)
1	$PdCl_2(ArN{=}CH–)_2$	0.50	0.25	66.7	3	8.08	1.81
2	$PdCl_2(ArN{=}CH–)_2$	0.60	0.15	80.0	3	3.05	0.68
3	$PdCl_2(ArN{=}CH–)_2$	1.00	0.25	80.0	3	12.90	2.89
4	$PdCl_2(ArN{=}CMe–)_2$	0.50	0.25	66.7	3	8.00	1.80
5	$PdCl_2(ArN{=}CMe–)_2$	1.00	0.25	80.0	3	10.35	2.30
6	$PdCl_2(ArN{=}CMe–)_2$	6.00	0.30 (O_2)[c]	80.0[d]	24	2.98	5.38

[a] Reaction conditions: 32 mmol phenol, 0.012 mmol Pd catalyst, 0.024 mmol $Mn(TMHD)_3$, 0.240 mmol $(Ph_3P{=})_2NBr$, 100 °C. The reaction mixture was analyzed by FID-GC (liquid phase). TOF was based on the amount of charged Pd and produced DPC. DPC yield was based on the amount of charged phenol.

[b] CO conq. = (CO press.)/[(CO press.) + (air press.)].

[c] Pure O_2 was used instead of air.

[d] Calculated using 1.50 MPa air instead of 0.30 MPa O_2.

to be efficient. The efficiencies of $PdCl_2(PhN{=}CH–)_2CH_2$ and $PdCl_2(ArN{=})_2$Acenaph were lower than those of $PdCl_2(ArN{=}CH–)_2$ and $PdCl_2(ArN{=}CMe–)_2$. Although the reason for this behavior has not been made clear, in the case of $PdCl_2(ArN{=}CH–)_2$ and $PdCl_2(ArN{=}CMe–)_2$, we assumed that the bite angle and the flexibility of the C–C bond between a pair of imine substituents of the ligand are suitable for maintaining their high electron deficiency to obtain high efficiency, owing to their relatively stable intermediate. On the other hand, the Fe and Co versions of the $PdCl_2$–diimine complex, i.e., Fe– and Co–2,6-diiminopyridyl complexes [$FeCl_2(ArN{=}CMe–)_2Py$ and $CoCl_2(ArN{=}CMe–)_2Py$] did not catalyze the reaction at all. Best results were obtained by using $PdCl_2(ArN{=}CH–)_2$ or $PdCl_2(ArN{=}CMe–)_2$, $Mn(TMHD)_3$, and $(Ph_3P{=})_2NBr$ where TOF reached to 8.08 or 8.00 mol-DPC/mol-Pd h, respectively. This value is superior to 5.53 mol-DPC/mol-Pd h obtained by a conventional Pd salt catalyst system, i.e., $PdBr_2/Ce(Trop)_4$ (Trop: tropolonate)/$(Ph_3P{=})_2NBr$ under 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 ten co-products including phenoxyphenols and biphenols were detected by GC.

To give higher efficiency and yield, some optimization studies on $PdCl_2(ArN{=}CH–)_2$ and $PdCl_2(ArN{=}CMe–)_2$ were performed. As shown in table 2, under high CO pressure, it was found that the TOFs of $PdCl_2(ArN{=}CH–)_2$ and $PdCl_2(ArN{=}CMe–)_2$ reached to 12.90 and 10.35 mol-DPC/mol-Pd h, respectively (runs 3 and 5). Moreover, the DPC yield was increased to 5.38% (based on the amount of charged phenol) with increases in the reaction time (run 6). We expected to obtain higher efficiency and yield from more detailed optimization studies of the $PdCl_2(ArN{=}CH–)_2$ system and the $PdCl_2(ArN{=}CMe–)_2$ system.

4. Conclusions

In summary, a facile synthesis of diphenyl carbonate, which involves oxidative carbonylation of phenol in the presence of a $PdCl_2$–diimine complex [$PdCl_2(ArN{=}CH–)_2$ or $PdCl_2(ArN{=}CMe–)_2$] along with redox catalyst and ammonium halide, has been developed. The reaction catalyzed by $PdCl_2(ArN{=}CH–)_2$ proceeded smoothly in the presence of CO and air at 100 °C and the TOF reached to 8.08 mol/mol-Pd h. In comparison to the most efficient conventional catalyst system, our $PdCl_2(ArN{=}CH–)_2$/$Mn(TMHD)_3$/$(Ph_3P{=})_2NBr$ system gives higher TOF. The TOF was increased to 12.90 mol/mol-Pd h with increases in the high CO pressure. The DPC yield using the $PdCl_2(ArN{=}CH–)_2$ system reached to 5.38%. 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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