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Oxidative carbonylation of phenol to diphenyl carbonate catalyzed by Pd–carbene complexes

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Abstract

Various Pd–carbene complexes with bis(heterocyclic carbene) ligands were prepared and was investigated their catalytic activity for oxidative carbonylation of phenol with carbon monoxide to diphenyl carbonate (DPC). The catalyst system was composed of Pd complex, inorganic redox cocatalyst, organic redox cocatalyst, organic salt, and molecular sieve. The Pd–carbene complex systems $PdBr_2$(c1-^{t}Bu)/Ce(TMHD)$_4$ (TMHD: 2,2,6,6-tetramethyl-3,5-heptanedionate)/^{n}Bu$_4$NBr/hydroquinone showed approximately a double activity compared to a conventional $PdBr_2$ catalytic system without the use of ligands.
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Keywords: Palladium; Heterocyclic carbene; Oxidative carbonylation; Polycarbonate; Diphenyl carbonate

1. Introduction

Diphenyl carbonate (DPC), which is used as a starting material for polycarbonate, is conventionally synthesized from phosgene and phenol. In recent years, the need has arisen for a method that does not require the use of highly toxic phosgene because of increasing demands for a safer and environmentally benign process for DPC synthesis [1]. Direct oxidative carbonylation of phenol with carbon monoxide is the most promising candidate among non-phosgenated approaches, but no effective catalytic system has been reported yet [2–8]. Palladium is used frequently as an active center for this reaction. Various catalytic systems were reported such as palladium salt with heteropolyacid [9], heterogeneous reaction on palladium carbon [10], etc. [11,12]. Recently, we have found that simple palladium salts (i.e. $PdCl_2$, $PdBr_2$, $Pd(OAc)_2$) in combination with redox cocatalysts and ammonium salt give moderate efficiency, as shown in Scheme 1 [13,14]. We have also demonstrated that a palladium complex such as Pd-2,2′-bipyridyl complex works more effectively than typical palladium salts, with the substituents of bipyridyl ligands sterically influencing the activity of the catalyst system to a great extent [15–20].

Heterocyclic carbene ligands have been shown to be alternatives for the widely used phosphine ligands in transition metal complex-catalyzed homogeneous reactions [21–27]. The great interest in carbene complexes has stimulated research on their application to catalytic reactions such as olefin metathesis

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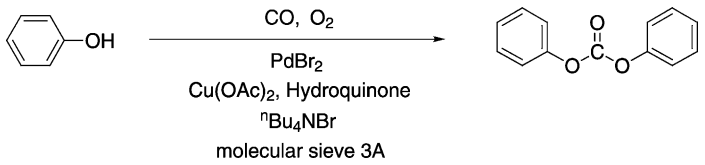


Scheme 1. Oxidative carbonylation of phenol catalyzed by Pd complex with redox catalyst and organic salt.

[21–23], Heck reaction [24], Suzuki coupling [25,26], and copolymerizations of carbon monoxide with ethylene [27]. Stable carbene ligands can be also expected to prolong the life of catalysts, because strong coordination bonds between transition metals and heterocyclic carbene ligands prevent the dissociation of complexes [28]. Hence, it is interesting to investigate the utility of Pd–carbene complexes as catalysts for oxidative carbonylation of phenol. Here, we report the successful synthesis of DPC from phenol by oxidative carbonylation with a novel Pd–carbene complex system.

2. Experiments

2.1. Materials

Phenol was purified by vacuum distillation prior to use. Dichloromethane was distilled and stored over molecular sieve 3 Å. All other reagents were obtained from commercial sources and used as received. Molecular sieve 3 Å was activated in vacuo at 250 °C for 12 h before use. 1-Substituented-imidazoles (R: ^{n}Bu, ^{t}Bu, ^{c}Hex, and Mesityl) were prepared according to the method reported in the literature [29]. 1,1′-Disubstituented-3,3′-methylenediimidazolium dibromide (R: Me, ^{t}Bu, and Mesityl) was prepared according to the literature [27,30]. {1,1′-Disubstituented-3,3′-methylenediimidazolin-2,2′-diylidene}palladium (II) dibromide ($PdBr_2$(c1-R)) (R: Me, ^{t}Bu, and Mesityl) was also prepared according to the literature [27,30].

2.2. Synthesis of 1,1′-diethyl-3,3′-methylenediimidazolium dibromide

A stirred toluene solution (30 ml) of 1-ethylimidazole (4.4 ml, 46 mmol) and CH_2Br_2 (1.4 ml, 20 mmol) was heated at 120 °C for 1 day to yield white powder of the product, which was collected, washed with THF, and dried in vacuo. Yield: 5.36 g (80%); ^{1}H-NMR (600 MHz, d_6-DMSO): d 1.43 (6H, t, J = 1.80 Hz, –CH_3), 4.25 (4H, q, J = 7.20 Hz, N–CH_2), 6.76 (2H, s, N–CH_2–N), 7.94 (2H, br s, CH(imid)), 8.14 (2H, br s, CH(imid)), 9.70 (2H, s, N–CH–N); ^{13}C-NMR (d_6-DMSO): d 14.8 (–CH_3), 45.0 (N–CH_2), 58.1 (N–CH_2–N), 122.3 (CH(imid)), 123.0 (CH(imid)), 137.4 (N–CH–N).

2.3. Synthesis of 1,1′-di-n-butyl-3,3′-methylenediimidazolium dibromide

This compound was prepared by the same method as described above by using 1-butylimidazole (2.9 ml, 22 mmol) and CH_2Br_2 (0.7 ml, 10 mmol). Yield: 3.60 g (42%); ^{1}H-NMR (600 MHz, d_6-DMSO): d 0.89 (6H, t, J = 7.20 Hz, –CH_3), 1.27 (4H, m, –CH_2–CH_3), 1.78 (4H, m, CH_2–CH_2–CH_2), 4.22 (4H, t, J = 7.20 Hz, N–CH_2), 6.74 (2H, s, N–CH_2–N), 7.92 (2H, br s, CH(imid)), 8.12 (2H, br s, CH(imid)), 9.66 (2H, s, N–CH–N); ^{13}C-NMR (d_6-DMSO): d 13.2 (–CH_3), 18.7 (–CH_2–CH_3), 30.9 (CH_2–CH_2–CH_2), 49.0 (N–CH_2), 57.7 (N–CH_2–N), 122.0 (CH(imid)), 123.0 (CH(imid)), 137.5 (N–CH–N).

2.4. Synthesis of 1,1′-dicyclohexyl-3,3′-methylenediimidazolium dibromide

This compound was prepared by the same method as described above by using 1-cyclohexylimidazole (2.9 ml, 22 mmol) and CH_2Br_2 (0.7 ml, 10 mmol). Yield: 1.74 g (74%); ^{1}H-NMR (600 MHz, D_2O): d 1.14 (2H, m, 4-CH of ax-^{c}Hex), 1.33 (4H, m, 2-CH of ax-^{c}Hex), 1.59 (6H, m, 4-CH of eq-^{c}Hex), 3-CH of eq-^{c}Hex), 1.78 (4H, m, 3-CH of ax-^{c}Hex), 2.06 (4H, m, 2-CH of eq-^{c}Hex), 4.24 (2H, m, N–CH

of ^{c}Hex), 6.54 (2H, s, N–CH_2–N), 7.60 (2H, br s, CH(imid)), 7.65 (2H, br s, CH(imid)) (remaining N–CH–N imid proton exchanged with D); ^{13}C-NMR (d_6-DMSO): d 24.3 (3-CH_2, 4-CH_2 (^{c}Hex)), 32.1 (2-CH_2 (^{c}Hex)), 57.7 (N–CH_2–N), 59.0 (1-CH (^{c}Hex)), 121.4 (CH(imid)), 122.2 (CH(imid)), 136.4 (N–CH–N).

2.5. Synthesis of 1,1′-diphenyl-3,3′-methylenediimidazolium dibromide

This compound was prepared by the same method as described above by using 1-phenylimidazole (1.93 g, 13 mmol) and CH_2Br_2 (0.35 ml, 5 mmol). Yield: 1.33 g (44%); ^{1}H-NMR (600 MHz, D_2O): d 6.83 (2H, s, N–CH_2–N), 7.53–7.57 (10H, m, ArH), 7.92 (2H, br s, CH(imid)), 7.95 (2H, br s, CH(imid)) (remaining N–CH–N imid proton exchanged with D); ^{13}C-NMR (d_6-DMSO): d 58.3 (N–CH_2–N), 121.5 (*o*-CH of phenyl), 121.9 (CH(imid)), 123.0 (CH(imid)), 130.2 (*m*-CH of phenyl), 130.3 (*p*-CH of phenyl), 134.5 (N–C of phenyl), 137.3 (N–CH–N).

2.6. Synthesis of {1,1′-diethyl-3,3′-methylenediimidazolin-2,2′-diylidene}palladium(II) dibromide ($PdBr_2$(c1-Et))

A stirred solution (10 ml) of 1,1′-diethyl-3,3′-methylenediimidadolium dibromide (0.37 g, 1.0 mmol) and $Pd(OAc)_2$ (0.22 g, 1.0 mmol) in DMSO was heated at 50 °C for 1 h, and then heated at 110 °C for 20 min. The remaining DMSO was then removed in vacuo at 80 °C, and the remaining solid was washed with dichloromethane to give the product. The product was recrystallized from acetonitrile to give white needles. Yield: 232 mg (49%); ^{1}H-NMR (600 MHz, d_6-DMSO): d 1.34 (6H, t, $J = 6.60$ Hz, –CH_3), 4.22 (2H, q, N–CH_2), 4.63 (2H, br, N–CH_2), 6.26 (2H, s, N–CH_2–N), 7.40 (2H, br s, CH(imid)), 7.58 (2H, br s, CH(imid)); ^{13}C-NMR (d_6-DMSO): d 16.3 (–CH_3), 45.5 (N–CH_2), 62.5 (N–CH_2–N), 121.5 (CH(imid)), 158.3 (carbene); ESI-MS: calc. for $^{12}C_{13}{}^{1}H_{19}{}^{79}Br^{14}N_5{}^{108}Pd$ *m/z* 431.98, obs. 432.02; $C_{11}H_{16}Br_2N_4Pd$: calc.: C, 28.08; H, 3.43; N, 11.91; found: C, 28.37; H, 3.06; N, 11.58%.

2.7. Synthesis of {1,1′-di-n-butyl-3,3′-methylenediimidazolin-2,2′-diylidene}palladium(II) dibromide ($PdBr_2$(c1-^{n}Bu))

$PdBr_2$(c1-^{n}Bu) was prepared by the same method as described above by using 1,1′-di-*n*-butyl-3,3′-methylenediimidadolium dibromide (0.42 g, 1 mmol) and $Pd(OAc)_2$ (0.22 g, 1 mmol). The product was recrystallized from acetonitrile to give pale yellow plates. Yield: 189 mg (36%); ^{1}H-NMR (600 MHz, d_6-DMSO): d 0.87 (6H, t, $J = 7.20$ Hz, –CH_3), 1.17 (4H, m, CH_2–CH_3), 1.74 (4H, br s, CH_2–CH_2–CH_2), 4.01 (2H, t, $J = 6.60$ Hz, N–CH_2), 4.81 (2H, br s, N–CH_2), 6.26 (2H, s, N–CH_2–N), 7.38 (2H, br s, CH(imid)), 7.57 (2H, br s, CH(imid)); ^{13}C-NMR (d_6-DMSO): d 13.5 (–CH_3), 19.1 (CH_2–CH_3), 32.6 (CH_2–CH_2–CH_2), 50.0 (N–CH_2), 62.5 (N–CH_2–N), 121.3 (CH(imid)), 122.0 (CH(imid)), 158.4 (carbene); ESI-MS: calc. for $^{12}C_{15}{}^{1}H_{24}{}^{79}Br^{14}N_4{}^{108}Pd$ *m/z* 447.02, obs. 447.05; $C_{15}H_{24}Br_2N_4Pd$: calc.: C, 34.21; H, 4.59; N, 10.64; found: C, 34.19; H, 4.42; N, 10.42%.

2.8. Synthesis of {1,1′-dicyclohexyl-3,3′-methylenediimidazolin-2,2′-diylidene} palladium(II) dibromide ($PdBr_2$(c1-^{c}Hex))

$PdBr_2$(c1-^{c}Hex) was prepared by the same method as described above by using 1,1′-dicyclohexyl-3,3′-methylenediimidadolium dibromide (0.47 g, 1 mmol) and $Pd(OAc)_2$ (0.22 g, 1 mmol). The product was recrystallized from acetonitrile to give pale yellow needles. Yield: 130 mg (23%); ^{1}H-NMR (600 MHz, d_6-DMSO): d 1.14–1.20 (2H, m, 4-CH of ax-^{c}Hex), 1.29–1.39 (4H, m, 2-CH of ax-^{c}Hex), 1.51 (2H, m, 2-CH of eq-^{c}Hex), 1.58 (6H, m, 4-CH of eq-^{c}Hex, 3-CH of eq-^{c}Hex), 1.78 (4H, m, 3-CH of ax-^{c}Hex), 2.09 (2H, m, 2-CH of eq-^{c}Hex), 5.07 (2H, br, N–CH (^{c}Hex)), 6.23 (2H, s, N–CH_2–N), 7.49 (2H, br s, CH(imid)), 7.58 (2H, br s, CH(imid)); ^{13}C-NMR (d_6-DMSO): d 24.8 (3-CH_2 (^{c}Hex)), 25.4 (4-CH_2 (^{c}Hex)), 33.9 (2-CH_2 (^{c}Hex)), 59.4 (*n*-CH_2–N), 62.7 (1-CH_2 (^{c}Hex)), 118.9 (CH(imid)), 122.1 (CH(imid)), 158.5 (carbene); ESI-MS: calc. for $^{12}C_{19}{}^{1}H_{28}{}^{79}Br^{14}N_4{}^{108}Pd$ *m/z* 499.053, obs. 499.052; $C_{19}H_{28}Br_2N_4Pd$: calc.: C, 39.44; H, 4.88; N, 9.68; found: C, 38.96; H, 4.64; N, 9.42%.

2.9. Synthesis of {1,1′-diphenyl-3,3′-methylenediimidazolin-2,2′-diylidene}palladium(II) dibromide ($PdBr_2$(c1-Ph))

$PdBr_2$(c1-Ph) was prepared by the same method as described above by using 1,1′-diphenyl-3,3′-methylenediimidadolium dibromide (0.46 g, 1 mmol) and $Pd(OAc)_2$ (0.22 g, 1 mmol). Yield: 439 mg (77%); ESI-MS: calc. for $^{12}C_{21}{}^{1}H_{19}{}^{79}Br^{14}N_5{}^{108}Pd$ *m/z* 527.98, obs. 528.02; $C_{19}H_{16}Br_2N_4Pd$: calc.: C, 40.28; H, 2.85; N, 9.89; found: C, 40.31; H, 2.72; N, 9.44%

2.10. Synthesis of DPC

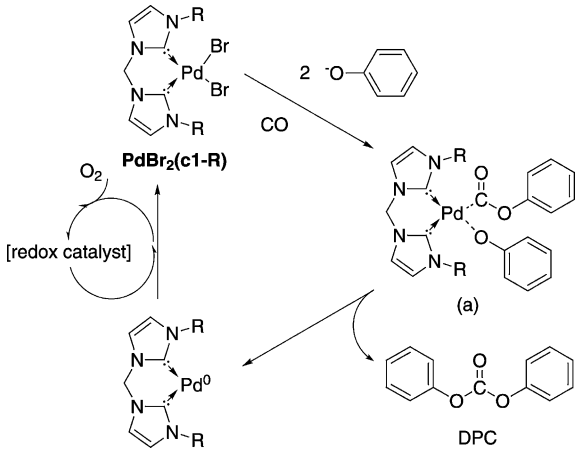
Pd–carbene complex (0.0125 mmol), inorganic redox cocatalyst (0.075 mmol), hydroquinone (HQ) (0.375 mmol), organic salt (0.375 mmol), and molecular sieve 3 Å 1 g were charged to a 50 ml stainless steel autoclave, then the mixture was dried at 70 °C for 2 h under vacuum. After dried phenol (8.33 mmol) and dichloromethane were added, 6.0 MPa CO and 0.3 MPa O_2 were charged. The autoclave was placed in an oil bath and kept at 100 °C for 3 h. After the specified time, the reaction was quenched immediately by cooling the autoclave in a water bath.

2.11. Characterization

Reaction products were identified and quantified by gas chromatography using a Hewlett-Packard HP6890 series GC system with a TC-1 column.

3. Results and discussion

The catalyst system consists of palladium complex, inorganic redox cocatalyst, organic cocatalyst, organic onium salt, and dehydrating agent. The general structure of the palladium complex $PdBr_2$(c1-R) is shown in Scheme 2. The ligands are heterocyclic carbenes bridged with a methylene unit (c1). The inorganic redox reagent and HQ cooperatively work as mediators for regeneration of Pd(II) from Pd(0). The molecular sieve 3 Å is a dehydrating agent to remove the water produced during the reaction and prevent hydrolysis of the produced DPC to phenol. The organic salt prevents the formation of Pd black [31,32].



Scheme 2. Plausible reaction mechanism of Pd–carbene complex catalyzed oxidative carbonylation of phenol.

The generally accepted mechanism of the reaction is shown in Scheme 2. In the first step, a Pd–carbene complex interacts with phenol and CO to produce an active complex. Reductive elimination from the active complex gives rise to DPC and a Pd(0) complex, and the Pd(0) complex is redoxidized with a redox cocatalyst to form a Pd(II) complex.

The activity of DPC synthesis was measured for initial 3 h while excess phenol remained. The DPC yield is affected by inorganic redox cocatalysts. Various inorganic redox cocatalysts were therefore investigated in the $PdBr_2$(c1-Me) reaction. The results are shown in Table 1. The reaction without an inorganic mediator resulted in a low DPC yield (entry 1). The reaction rate and yield were greatly affected by central metals and ligands of redox catalysts. For example, Ce showed better catalytic efficiency than Cu, Mn, and Co. Among Ce-based redox catalysts, the yield of DPC decreased in the following order: $Ce(TMHD)_4$ (TMHD: 2,2,6,6-tetramethyl-3,5-heptanedionate) > $Ce(acac)_3{\cdot}3H_2O$ (acac: acetylacetonate) > $Ce(Trop)_4$ (Trop: troporonate) > $Ce(OAc)_3{\cdot}xH_2O$. These results indicate that the ligand with high electron donation enhances the electron density of the reduced central metal and facilitates reoxidation of Ce(III) to Ce(IV). The best result was obtained for $Ce(TMHD)_4$, turnover frequency (TOF) reaching 26.6 mol-DPC/mol-Pd h.

Steric hindrance of substituents on Pd-2,2′-bipyridyl complexes greatly influences the activity [20]. The effect of substituents R at the 1,1′-position of

Table 1
Oxidative carbonylation of phenol catalyzed by $PdBr_2$(c1-Me) with redox catalyst[a,b]

Entry	Inorganic redox cocatalyst	DPC		PS (yield (%))[c]
		TOF (DPC/Pd) (mol/(mol h))	Yield (%)	
1	–	2.9	2.8	0.0
2	$Cu(OAc)_2$	13.4	12.0	0.1
3	$Ce(TMHD)_4$[d]	26.6	24.7	0.2
4	$Ce(Trop)_4$[e]	5.4	4.9	0.0
5	$Ce(OAc)_3{\cdot}xH_2O$	4.4	3.9	0.0
6	$Ce(acac)_3{\cdot}3H_2O$	15.4	14.3	0.2
7	$Mn(TMHD)_3$	10.7	9.8	0.0
8	$Mn(OAc)_2$	12.2	10.7	0.1
9	$Mn(acac)_3$	5.1	4.7	0.0
10	$Co(acac)_3$	5.8	5.3	0.0

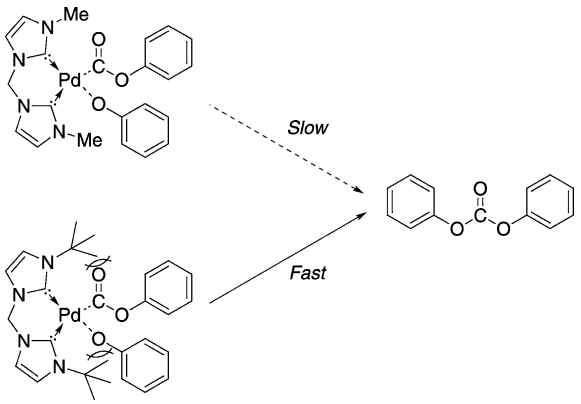
[a] Reaction conditions: phenol 8.33 mmol, $PdBr_2$(c1-Me) 0.0125 mmol, inorganic redox cocatalyst 0.075 mmol, $^nBu_4NBr$ 0.375 mmol, HQ 0.375 mmol, CH_2Cl_2 5 ml, molecular sieve 3 Å 1 g, CO 6.0 MPa, O_2 0.3 MPa, 100 °C, 3 h.
[b] Analyzed by GC. The yield was based on the amount of charged phenol.
[c] PS: phenyl salicylate.
[d] TMHD: 2,2,6,6-tetramethyl-3,5-heptanedionate.
[e] Trop: troponorate.

$PdBr_2$(c1-R) was studied, and the results are summarized in Table 2. TOF increased with increasing bulkiness of the substituents, probably because the bulky substituents of ligands could accelerate the reductive elimination rate by increasing steric repulsion on the crowded palladium center of intermediates (Scheme 3). $PdBr_2$(c1-Ph) has bulky phenyl groups that are similar in size to cyclohexyl groups, but its TOF was lower than those of $PdBr_2$(c1-Me) and $PdBr_2$(c1-^{c}Hex), suggesting that electron donating substituents are preferable to electron withdrawing ones such as a phenyl group. This was supported by the fact that the Mesityl group having three methyl groups in the 2, 4, and 6-positions gave a higher TOF. The high Lewis basicity of bis(heterocyclic carbene) ligands may lower the redox potential of central metals [33]. However, $PdBr_2$(c1-^{n}Bu) with electron-donating substituents showed the lowest efficiency in Table 2. This may be explained by interference in the attack of the phenol on the palladium atoms by long-chain alkyl substituents (Scheme 4).

Table 2
Substituent effect of the ligand on Pd complex[a,b]

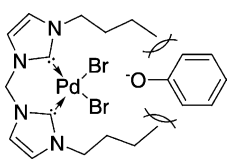
Entry	Pd complex	DPC		PS (yield (%))[c]
		TOF (DPC/Pd) (mol/(mol h))	Yield (%)	
1	$PdBr_2$	28.0	25.1	0.3
2	$PdBr_2$(c1-Me)	26.6	24.7	0.2
3	$PdBr_2$(c1-Et)	33.6	28.8	0.3
4	$PdBr_2$(c1-^{n}Bu)	9.7	9.3	0.1
5	$PdBr_2$(c1-^{t}Bu)	50.7	45.1	0.3
6	$PdBr_2$(c1-^{c}Hex)	27.7	24.8	0.0
7	$PdBr_2$(c1-Ph)	15.4	13.9	0.0
8	$PdBr_2$(c1-Mes)	25.5	22.5	0.2

[a] Reaction conditions: phenol 8.33 mmol, Pd complex 0.0125 mmol, inorganic redox cocatalyst (entry 1: $Cu(OAc)_2$, entries 2–8: $Ce(TMHD)_4$) 0.075 mmol, $^nBu_4NBr$ 0.375 mmol, HQ 0.375 mmol, CH_2Cl_2 5 ml, molecular sieve 3 Å 1 g, CO 6.0 MPa, O_2 0.3 MPa, 100 °C, 3 h.
[b] Analyzed by GC. The yield was based on the amount of charged phenol.
[c] PS: phenyl salicylate.



Scheme 3. Effect of substituents at the 1,1′-position of Pd–carbene complex on reactivity with phenol.

Reductive elimination reaction is accelerated by electron-withdrawing substituents but re-oxidation reaction is accelerated by electron-donating substituents. Inductive effect of the substituents will work reversely in each redox reaction. On the other hand,



Scheme 4. Long-chain substituent effect of the ligand on Pd complex.

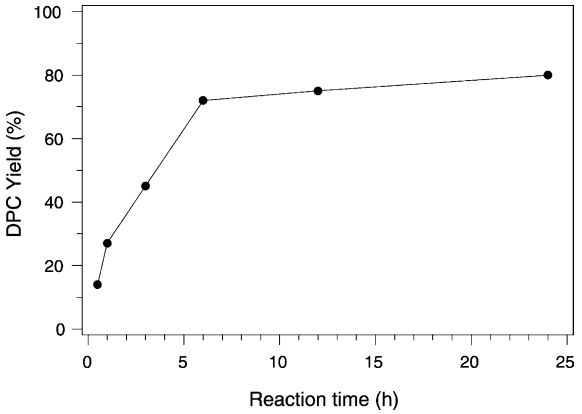


Fig. 1. Time course of oxidative carbonylation. Reaction conditions: phenol 8.33 mmol, $PdBr_2$(c1-^{t}Bu) 0.0125 mmol, Ce(TMHD)$_4$ 0.075 mmol, ^{n}Bu$_4$NBr 0.375 mmol, HQ 0.375 mmol, molecular sieve 3 Å 1 g, CH_2Cl_2, 100 °C.

steric repulsion seems to affect only reductive elimination reaction. While the rate-determining step in the catalytic cycle has not been clarified, steric positive factor could cancel the inductive negative factor at reductive elimination step.

The best results were obtained for $PdBr_2$(c1-^{t}Bu), with the TOF of DPC reaching 50.7 (mol-DPC/mol-Pd h). This TOF is double that of a conventional $PdBr_2$ catalytic system without ligands (entry 1), and the selectivity for DPC based on phenol was up to 95%. The other minor products were small amounts of phenyl salicylate, carbon dioxide (CO_2), and trace amounts of about 10 by-products including phenoxyphenols and biphenols, which were detected by GC. The by-product such as a carbonate of HQ was not founded; thus HQ only worked as a redox agent.

The time-yield correlation curve on the $PdBr_2$(c1-^{t}Bu) system was shown in Fig. 1. An induction period was not found, indicating thus the catalytic system works smoothly since the initial stage. The DPC yield increased with increasing reaction time, achieving 75% after 24 h.

4. Conclusions

Pd–carbene complexes with bis(heterocyclic carbene) ligands $PdBr_2$(c1-R) were found to be efficient catalysts for oxidative carbonylation of phenol to diphenyl carbonate, where catalysts were composed of Pd complex/Ce(TMHD)$_4$/HQ/^{n}Bu$_4$NBr/molecular sieve 3 Å. In particular, $PdBr_2$ (c1-^{t}Bu) exhibited the highest TOF of 50.7 (mol-DPC/mol-Pd h), giving a 45% DPC yield. Pd–carbene complexes with the following characteristics showed good performance: (1) ligands with bulky structures (R: ^{t}Bu), and (2) ligands with electro-donating substituents (R: Me, Et, and ^{t}Bu). To improve the efficiency of oxidative carbonylation, a more detailed optimization study and an investigation on the direct synthesis of polycarbonate are in progress.

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