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Pd(NHC) Electrocatalysis for Phosgene-Free Synthesis of Diphenyl Carbonate

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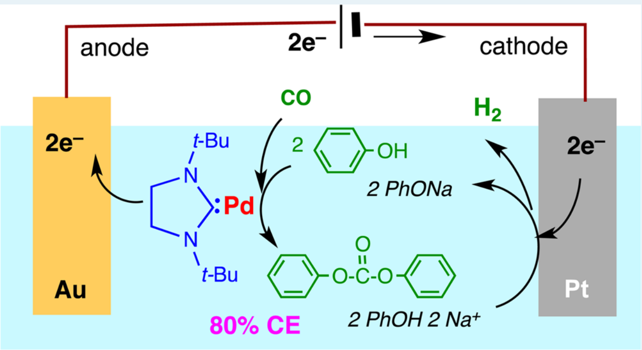
S Supporting Information

ABSTRACT: Electrocarbonylation of phenol with CO to diphenyl carbonate was studied using a homogeneous Pd electrocatalyst. Various ligands were screened, and N-heterocyclic carbene (NHC) groups, such as 1,3-dimesitylimidazol-2-ylidene, were found to be effective for the electrocarbonylation. An in situ-generated NHC derived from a 1,3-dialkylimidazolium chloride was also effective for the electrocarbonylation, and 1,3-di(*tert*-butyl)imidazoline chloride was the most effective NHC precursor, with a stronger electron-donating ability to $PdCl_2(MeCN)_2$ electrocatalyst.



KEYWORDS: *electrocatalysis, palladium, carbene ligands, carbonylation, phosgene-free*

INTRODUCTION

Diphenyl carbonate (DPC) is expected to serve as an alternative phosgene reagent; therefore, DPC is an essential material for phosgene-free processes for the manufacture of polycarbonate. The polycarbonate process involves the transesterification of bisphenol A with DPC. DPC is manufactured by two indirect synthesis methods: (1) production from phosgene and PhOH and (2) production from dimethyl carbonate and PhOH by an ester-exchange reaction.[1] The oxidative carbonylation of PhOH to DPC with O_2 is an alternative. However, large amounts of CO_2 and tar are produced under current reaction conditions because water as a coproduct of DPC enhances CO_2 and tar formations.[2−10]

Electrochemical oxidation is a potential useful oxidant method for organic synthesis.[11−21] The electrocarbonylation of PhOH to DPC has recently been achieved using $PdCl_2$/activated carbon and Pd^0/Ketjen Black (KB) anodes at a $P(CO) = 1$ atm and 25 °C.[22−24] One of the conclusions from our previous studies is that Pd^0 nanoparticles smaller than 2 nm are active for DPC formation.[24] Therefore, this model suggests that the smallest Pd^0 particle, atomic Pd^0, should be even more active for electrocarbonylation. As a result, various ligands for a $PdCl_2(CH_3CN)_2$ electrocatalyst were screened, and the N-heterocyclic carbene (NHC) group was found to be effective for the electrocarbonylation in this work. NHC compounds have been widely used in various catalytic reactions.[25−27] This study aims to identify and study effective homogeneous Pd(NHC) electrocatalysts for the electrocarbonylation of PhOH to DPC.

RESULT AND DISCUSSION

The time course of DPC formation by the electrocarbonylation of PhOH was investigated using $PdCl_2(CH_3CN)_2$ at a Au wire anode (Figure 1a and b). A one-compartment electrolysis glass cell was used for the carbonylation (Supporting Information Figure S1); the details are mentioned in the experimental section of the Supporting Information (SI). At the beginning of the reaction, the rapid formation of DPC was observed within 10 min. After 10 min, the quantity of DPC increased linearly with the electrolysis time. The initial formation of DPC was due to the stoichiometric carbonylation of PhOH with Pd^{2+}, as indicated by the dotted line (- - -) in Figure 1a. The latter formation of DPC was due to the electrochemical formation of DPC.[23] Thus, the electrochemical formation rate and CE of DPC were calculated from the slope of the time course after 10 min. The formation rate corresponds to a CE under galvanostatic electrolysis conditions. The CE was only 13.8% for DPC formation using the $PdCl_2(CH_3CN)_2$ electrocatalyst.

With respect to CO_2 formation, the stoichiometric formation was slow and continued for 60 min, as indicated the dotted line (- - -) in Figure 1b. It was confirmed that apparent slow formation of CO_2 was due to the residence of CO_2 in the gas phase of the cell; therefore, the CE for CO_2 formation was estimated from the amount of CO_2 formation after 60 min and was found to be 8.4%. The CEs and amounts of DPC and CO_2 formation are summarized in entry 1 of Table 1.

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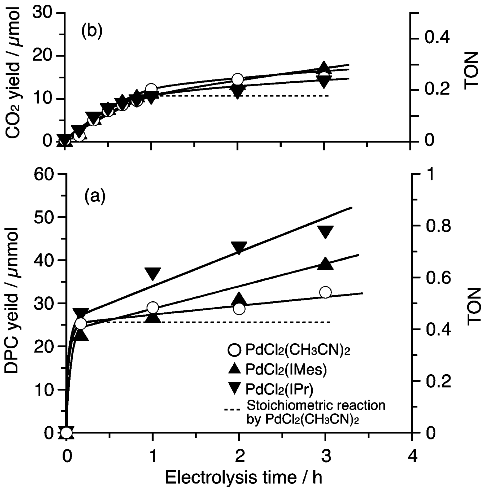

Figure 1. Time courses of electrocarbonylation of phenol to DPC by Pd (60 μmol) electrocatalysts and 1 mA galvanostatic electrolysis at 298 K. Anode, Au wire; cathode, Pt wire; electrolyte, 0.75 mol dm^{-3} PhOH/12.5 mmol dm^{-3} PhONa/CH_3CN (40 cm^{-3}); P(CO), 101 kPa.

Table 1. Effects of NHC Ligands and Ligand Precursors of 1,3-Dialkylimidazolium Chloride Ligands on DPC Formation by $PdCl_2(CH_3CN)_2$ Electrocatalyst[a]

	stoichiometric formation yield (μmol)		electrochemical formation CE (%)	
ligand[b]	DPC	CO_2	DPC	CO_2
(1) none	25.3	12.3	13.8	8.4
(2) IMes	22.8	11.6	31.2	15.3
(3) IPr	27.4	10.2	36.1	10.0
(4) IMesHCl	23.7	28.2	19.6	13.9
(5) IPrHCl	23.8	23.2	28.3	12.2
(6) I*t*BuHCl	29.9	13.5	32.8	11.3
(7) SI*t*BuHCl	30.5	12.8	42.5	7.7

[a] Electroysis: 1 mA, 3 h. Anode, Au wire; cathode, Pt wire. Electrolyte: 0.75 mol dm^{-3} PhOH/12.5 mmol dm^{-3} PhONa/CH_3CN (40 cm^{-3}). P(CO): 101 kPa. [b] Ligand and ligand precursor for $PdCl_2(CH_3CN)_2$: IMes, 1,3-dimesitylimidazol-2-ylidene; IPr, 1,3-diisopropylimidazol-2-ylidene; IMesHCl, 1,3-dimesitylimidazolium chloride; IPrHCl, 1,3-diisopropylimidazolium chloride; I*t*BuHCl, 1,3-di(*tert*-butyl)-imidazolium chloride; SI*t*BuHCl, 1,3-di(*tert*-butyl)imidazoline chloride.

Next, various ligands for Pd^{2+} ($PdCl_2(CH_3CN)_2$) were screened to enhance the electrocarbonylation of PhOH to DPC. Bipyridine, diene, and phosphine groups were not efficient for the stoichiometric carbonylation or electrocarbonylation, whereas the NHC groups of 1,3-dimestitylimidazol-2-ylidene (IMes) and 1,3-diisopropylimidazol-2-ylidene (IPr) promoted the electrocarbonylation, as shown in Figure 1.

The initial stoichiometric formation of DPC using IMes was similar to that without IMes, whereas the electrochemical formation of DPC was accelerated in the presence of the IMes ligand. When the electrolysis time was extended to 12 h, a gradual exponential increase in DPC formation, rather than a linear increase, was confirmed. In the case of IPr, the initial stoichiometric formation of DPC increased slightly, and then the steady electrochemical formation of DPC was as good as that observed for IMes. With respect to CO_2 formation, neither the stoichiometric nor the electrochemical formations were strongly affected by the use of IMes or IPr, as shown in Figure 1b. Detailed data for the carbonylation using IMes and IPr are summarized in runs 2 and 3 in Table 1, respectively. The CEs for DPC formation increased from 13.8% to 31.2 and 36.1% when using IMes and IPr, respectively. On the other hand, the influence of IMes and IPr on the CEs for CO_2 was not clear. For the 12 h electrolysis, the CE of DPC was 42% larger than 31% at 3 h, and the CE of CO_2 was 10% smaller than 15.3% at 3 h. Therefore, a longer electrolysis time is favorable for DPC formation.

Various NHC compounds were synthesized, but their isolation was not successful. Thus, electrocarbonylation was examined using in situ-generated NHC compounds. It was proposed that the carbene would be generated in the electrolyte from 1,3-dialkylimidazolium chloride (IMesHCl, IPrHCl, I*t*BuHCl, SI*t*BuHCl)[28] and a base reagent of PhONa, which is used as a promoter for the electrocarbonylation. The results are indicated for runs 4−7 in Table 1, respectively.

The initial stoichiometric DPC formation was SI*t*BuHCl ≈ I*t*BuHCl > IPrHCl ≈ IMesHCl ≈ no additives. Therefore, the stoichiometric formation of DPC was enhanced using SI*t*BuHCl and I*t*BuHCl. In the electrocarbonylation, the CEs of DPC corresponding to the formation rates were SI*t*BuHCl (42.5%) > I*t*BuHCl (32.8%) > IPrHCl (28.3%) > IMesHCl (19.6%) (> no NHC (13.8%)). Clearly, electrochemical formation rates of DPC were remarkably enhanced by the addition of NHC precursor 1,3-dialkylimidazolium chlorides. In addition, the CEs for CO_2 formation after 60 min were IMesHCl (13.9%)> IPrHCl (12.2%) > I*t*BuHCl (11.3%) > SI*t*BuHCl (7.7%), which is the reverse order of the DPC formation. DPC formation and CO_2 formation are competitive reactions. The enhancement of the selective formation of DPC by SI*t*BuHCl was particularly significant.

The effect of the quantity of SI*t*BuHCl addition versus Pd on electrochemical and stoichiometric formation of DPC and CO_2 is shown in Figure 2a and b, respectively. The electrochemical formation of DPC increased remarkably with the SI*t*BuHCl additions and reached to a maximum by addition of 3.0 equiv. The CE increased from 13.8% for no addition to 79% by the

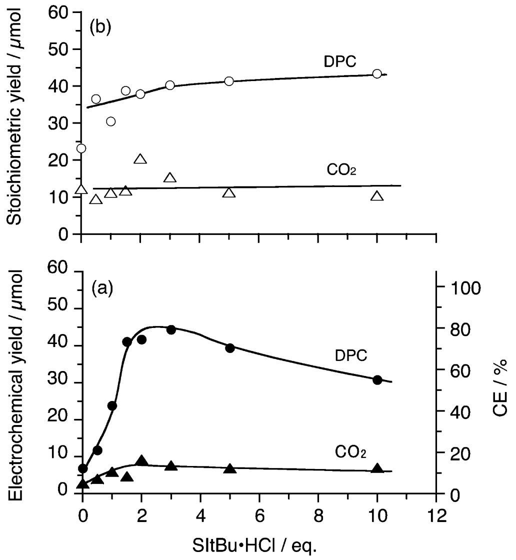

Figure 2. Effect of equivalent of SI*t*BuHCl addition against Pd on electrocarbonylation of PhOH (a) and stoichiometric carbonylation (b). Conditions were the same as Figure 1, except for the amounts of SI*t*BuHCl.

addition of 3.0 equiv. Notably, the excess addition of SI*t*BuHCl was not favorable for DPC formation. On the other hand, electrochemical formation of CO_2 increased slightly, and the CE for CO_2 increased from 8 to 12% by the SI*t*BuHCl addition of >3.0 equiv. Furthermore, the stoichiometric formation of DPC was also increased by the SI*t*BuHCl addition, as described in Table 1; however, this increase was not strongly affected by the amounts of SI*t*BuHCl addition (Figure 2b). Fortunately, the stoichiometric formation of CO_2 was not affected at all by the SI*t*BuHCl addition.

The effects of the quantity of IMes added to the reaction is demonstrated in SI Figure S2a and b. The electrochemical formation of DPC increased with the quantity of IMes and reached a maximum at 1.5 equiv of IMes addition with 48% CE (SI Figure S2a); however, electrochemical formation of CO_2 was also slightly accelerated by the IMes addition (SI Figure S2b). On the other hand, the stoichiometric formation of DPC was slightly increased by the IMes addition, but the stoichiometric formation of CO_2 did not change.

To obtain effect of Cl^- on the electrocarbonylation, NBu_4Cl and LiCl were used instead of SI*t*BuHCl, and the CEs of DPC were decreased from 13.8% to 11 and 9%, respectively. The addition of Cl^- decreased the carbonylation activity of the Pd electrocatalyst. The experimental observations indicate that IMes and SI*t*Bu generated in situ from SI*t*BuHCl and PhONa, should coordinate to Pd and enhance the carbonylation activity of Pd^{2+} or accelerate the reoxidation of Pd^0 to Pd^{2+}. The stronger electron-donating ability of a group substituted at the 9 and 10 positions of the NHC and the saturated C−C bond of SI*t*BuHCl would stabilize a generated carbene; therefore, the addition of SI*t*BuHCl was most effective for the carbonylation. The stronger electron-donating property of the SI*t*Bu ligand to the Pd electrocatalyst should also accelerate the stoichiometric and electrochemical formation of DPC and decelerated the CO_2 formation. Therefore, $PdCl_2(CH_3CN)_2$ and 3(SI*t*BuHCl) were suitable electrocatalyst precursors for the electrocarbonylation of PhOH. When electrolysis time of the carbonylation was extended from 3 to 12 h, the amount of DPC formation increased linearly while the amount of CO_2 formation reached a plateau. The turnover number (TON) for DPC formation was ∼4, and the CEs for DPC and CO_2 formation were 80% and 7%, respectively. A long electrolysis time is favorable for the selective formation of DPC because impurity water was consumed.

To obtain information regarding the function of NHC in the carbonylation, UV−vis and cyclic voltammetry (CV) studies were conducted. They were first carried out using in situ generated SI*t*Bu (SI*t*BuHCl and PhONa), but significant data has not yet been obtained. Thus, they were conducted using IMes. Figure 3 presents the difference UV−vis spectra for various mixtures of $PdCl_2(CH_3CN)$ and IMes against IMes. The adsorption peak at 240 nm was assigned to Pd^{2+}. This absorption peak decreased smoothly with increasing IMes/Pd ratios until the ratio became 2. Broad absorptions around 260 nm were observed when additional IMes was added (IMes/Pd ratios of 5 and 10). This broad absorption was also observed for free IMes (SI Figure S2). Thus, the UV absorption data suggest that 2 equiv of IMes can coordinate to $PdCl_2(CH_3CN)_2$ in CH_3CN.

CV studies using $PdCl_2(CH_3CN)_2$ in a PhOH/PhONa/CH_3CN solution without and with the addition of IMes at a Au-wire electrode (0.5 cm^{-2}) were conducted. Large broad oxidation and reduction currents for Pd^{2+} and Pd^0 formation were observed in He. The onset potentials for the oxidation and reduction were >+0.5 V (Ag^+/Ag^0) and <−0.5 V, respectively (SI Figure S4). The redox reactions were slow and electrochemically irreversible. Figure 4 shows the CV of $PdCl_2(CH_3CN)_2$ with the addition of IMes (SI Figure S2). In this case, the oxidation and reduction currents of CV(a) decreased to 1/10 of those without IMes. The onset potential of the oxidation current also shifted to a negative potential at +0.3 V, and the onset potential of the reduction current shifted to positive potential at −0.1 V. The decrease in current caused by the addition of IMes may be due to coordination of the bulky IMes ligand of Pd and the fact that the diffusion rate of $PdCl_2(IMes)$ is much slower than that of $PdCl_2(CH_3CN)_2$.

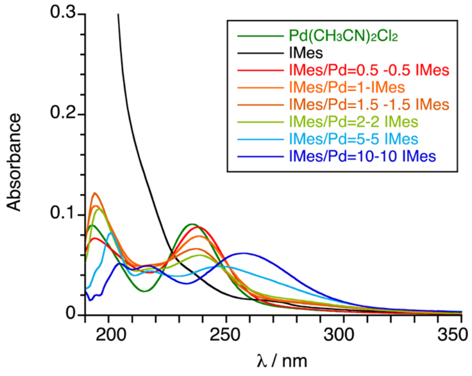

Figure 3. Difference UV−vis spectra as function of ratio of $PdCl_2(CH_3CN)_2$ and IMes. $PdCl_2(CH_3CN$, 3.0×10^{-6} mol dm^{-3}; IMes/Pd, 0.5−10.0.

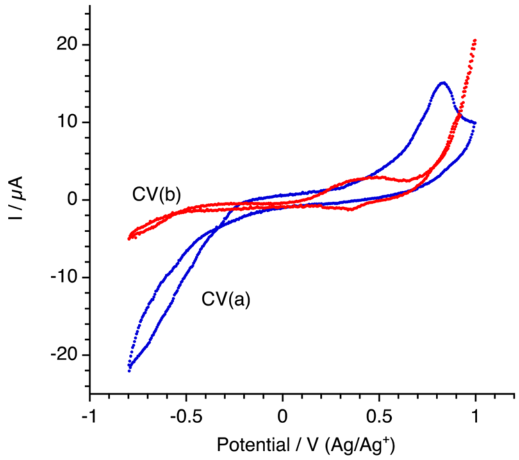

Figure 4. Cyclic voltammetry of $PdCl_2(IMes)$ in He (a) and CO (b) at a scan rate of 20 mV s^{-1} using a Au wire electrode (0.2ø × 5.0 mm) and a Ag/Ag^+ reference electrode.

When CO was introduced (CV(b)), the onset potential of oxidation shifted to a positive potential at +0.75 V, and the oxidation current increased rapidly above +0.75 V; in contrast, the reduction current below −0.1 V remarkably decreased. The CV spectra indicated that electrochemically produced Pd^{2+} was immediately consumed in the carbonylation, and Pd^0 was regenerated. Thus, a rapid increase in current was observed above +0.75 V. In addition, the remarkable decrease in the reduction current below −0.1 V was caused by the consumption of Pd^{2+} in the carbonylation. These CV and UV−vis data suggest that the electrocarbonylation on Pd was accelerated by the coordination of IMes to $PdCl_2(CH_3CN)_2$.

NHCs and in situ-generated NHCs were effective ligands for a $PdCl_2(CH_3CN)_2$ electrocatalyst in the galvanostatic electrocarbonylation of PhOH to DPC. The stronger electron-donating ability of the NHCs enhanced the stoichiometric and electrochemical formation of DPC. In situ-generated SI*t*Bu from SI*t*BuHCl and PhONa was the most effective ligand in the Pd electrocatalyst among the tested NHC and in situ-generated NHC groups. The steady and stable electrocarbonylation of PhOH to DPC was performed for 12 h with a CE of 80%, which was improved in comparison with 50%, which was previously obtained at the Pd^0/KB anode.[24] In addition, the electrochemical formation of DPC at the Pd^0/KB anode was drastically suppressed to 6% CE by addition of SI*t*BuHCl to the electrolyte. SI*t*BuHCl is not effective for the heterogeneous Pd electrocatalyst. When the galvanostatic electrolysis was conducted using new solutions without $PdCl_2(CH_3CN)_2$ and the Au wire anode used for the electrocarbonylation, the electrolysis could not be continued more than 1 h because of over range of the terminal voltage. DPC and CO_2 were not produced during the electrolysis. This result proves that the actual active species of Pd is not deposited on the Au surface and is in the electrolyte solutions. Homogeneous Pd(NHC) species function as electrocatalysts and can be applicable in various syntheses.[25−27]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, a diagram of the one-compartment electrolysis cell, effects of IMes addition, UV−vis absorptions of IMes, CVs of $PdCl_2(CH_3CN)_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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