Effects of bulky ligands and water in Pd-catalyzed oxidative carbonylation of phenol

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Abstract

A diaryloxy Pd complex with a bulky 6,6′-dimethyl-2,2′-bipyridyl (6,6′-Me$_2$bpy) ligand reacted with pressurized CO (5 MPa) at 25 °C to produce a diaryl carbonate, whereas a diaryloxy Pd complex with an unsubstituted 2,2′-bipyridyl (bpy) ligand hardly reacted. ^{1}H and ^{13}C NMR studies revealed that CO inserts into one of the Pd–O bonds in the latter complex to form a Pd aryloxycarbonyl complex, but that the subsequent reductive elimination of diaryl carbonate is slow. This is consistent with the much higher catalytic activity of the Pd-(6,6′-Me$_2$bpy) system for the oxidative carbonylation of phenol compared to the Pd–bpy system. To verify the steric effects of the ligands, the catalytic performance was also examined using 2,2′-bioxazolyl ligands with various substituents. Introducing bulky substituents at the 4,4′-position effectively promoted the catalytic reaction. The TONs of DPC increased in the following order: methyl < benzyl < *iso*-butyl < *tert*-butyl. The methylene-bridged bioxazolyl ligand with *tert*-butyl groups gave the highest TON (54 mol-DPC/mol-Pd in 3 h), which is higher than the TON for the 6,6′-Me$_2$bpy ligand. The addition of molecular sieve 3A to the reaction system further improved the TON and suppressed phenyl salicylate formation. The addition of the molecular sieve also prevented CO$_2$ formation, probably due to suppression of the reaction between CO and water, in addition to suppression of the hydrolysis of DPC.
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1. Introduction

Diphenyl carbonate (DPC) is an important precursor for producing polycarbonates by a melt-polymerization process [1,2]. DPC is currently synthesized by converting dimethyl carbonate through transesterification or using highly toxic and corrosive phosgene. Thus, a more direct, environmentally benign synthesis of DPC is desirable. Oxidative carbonylation of phenol is a possible DPC synthetic method (Eq. (1)). Numerous catalytic systems that include Pd have been reported [3–13]. However, the catalytic activities must be further improved for practical applications. In addition, there are few studies on the reaction mechanism [14] and the proposed mechanisms are speculative.

$$2PhOH + CO + \tfrac{1}{2}O_2 \rightarrow PhOCO_2Ph + H_2O \qquad (1)$$

We recently isolated L$_2$Pd(OPh)$_2$ (L = ligand) and L$_2$Pd(CO$_2$Ph)X (X = halogen) complexes, which are key intermediates for the DPC forming reaction, and investigated their reactivity [15,16]. We found that DPC is formed from both complexes via L$_2$Pd(OPh)(CO$_2$Ph), although the reductive elimination of DPC is slow. It is known that introducing bulky substituents onto bidentate N–N ligands in Pd complexes effectively promotes the reaction [17–19]. It is assumed that the reductive elimination of DPC from L$_2$Pd(OPh)(CO$_2$Ph) is accelerated. However, the reductive elimination rates of DPC using ligands with vastly different steric hindrances have not been compared.

This study initially focused on bipyridyl ligands, which exhibit marked substitution effects on the Pd-catalyzed oxidative carbonylation of phenol [19]. We synthesized diaryloxy
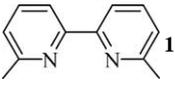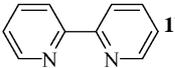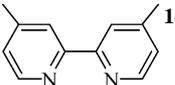
Pd complexes with a catalytically efficient 6,6′-dimethyl-2,2′-bipyridyl (6,6′-Me$_2$bpy) ligand **1a** and an inefficient 2,2′-bipyridyl (bpy) ligand **1b**. Then the relative rates of reductive elimination of DPC were compared through the reaction with pressurized CO at a complex level. The catalytic performance using bioxazolyl ligands with various substituents was also investigated to verify the steric effects of substituents. Bioxazolyl ligands are advantageous since they are easily synthesized, stable in an oxidative environment, and the steric effects are tunable. Furthermore, the effects of dehydrating agents and the CO$_2$ formation routes in the oxidative carbonylation of phenol were examined.

2. Results and discussion

2.1. Reaction catalyzed by Pd complexes with bipyridyl ligands

To ascertain the effectiveness of substituted 2,2′-bipyridyl ligands for the Pd-catalyzed oxidative carbonylation of phenol, the catalytic activity of DPC formation using **1a**–**1c** was measured. The reaction was conducted in the presence of Mn(TMHD)$_3$ (TMHD = 2,2,6,6-tetramethyl-3,5-heptanedionate) and (Ph$_3$P=)$_2$NBr (bis(triphenylphosphoranylidene)ammonium bromide) using (MeCN)$_2$PdCl$_2$ as a Pd source. Table 1 lists the turnover number (TON) of DPC, TON of phenyl salicylate, and the selectivity for DPC. The Pd complex with **1a** efficiently catalyzed the reaction to produce DPC. On the other hand, **1b** or **1c** resulted in a low activity and selectivity of DPC. These results are consistent with the previous report [19]. Thus, a pronounced substitution effect of the 2,2′-bipyridyl ligand at the 6,6′-position is confirmed.

Table 2
Reaction of diaryloxy Pd complexes with CO[a]

Entry	Complex	Time (h)	Yield (%)[b]
1	**2a**	0.5	57
2	**2a**	3	61
3	**2b**	0.5	0.3
4	**2b**	3	8

[a] Reaction conditions: Pd complex, 30 mg; THF, 5 ml; CO, 5 MPa; 25 °C.
[b] Yield of di(*p-tert*-butyl)phenyl carbonate based on the Pd complex.

2.2. Reactivity of diaryloxy Pd complexes with bipyridyl ligands toward CO

New diaryloxy Pd complexes **2a** and **2b**, which are possible model intermediates in this reaction, were prepared by reacting Pd(OAc)$_2$ with two equivalents of sodium *p-tert*-butylphenoxide in the presence of **1a** and **1b**, respectively [20]. Complexes **2a** and **2b** were characterized by ^{1}H and ^{13}C NMR spectroscopies as well as elemental analysis. **2b** was characterized by X-ray crystallography, but the residual values were unsatisfactory.

Ar = C$_6$H$_4$-*p-t*-Bu

We examined the reactivity of **2a** and **2b** with pressurized CO. Di(*p-tert*-butyl)phenyl carbonate was instantly formed when **2a** was reacted with CO (5 MPa) in THF at 25 °C. The yield of carbonate formation based on the palladium complex after 0.5 h was 57% (Table 2). In contrast, the reaction of **2b** with CO was very slow and the yields of the carbonate after 0.5 and 3 h were 0.3 and 8%, respectively.

To understand this difference, the reactions of **2a** and **2b** with CO were monitored by high-pressure NMR spectroscopy. A signal assigned to the carbon of Pd*C*OO [15]

Table 1
Pd-catalyzed oxidative carbonylation of phenol using 2,2′-bipyridyl ligands[a]

Entry	Ligand	TON (DPC)[b]	TON (PS)[c]	Selectivity of DPC (%)[d]
1	**1a**	48	8	77
2	**1b**	4	5	34
3	**1c**	2	5	28

[a] Reaction conditions: phenol, 32 mmol; (MeCN)$_2$PdCl$_2$, 0.012 mmol; ligand, 0.012 mmol; Mn(TMHD)$_3$, 0.024 mmol; (Ph$_3$P=)$_2$NBr, 0.24 mmol; CO, 3 MPa; air, 1.5 MPa; 100 °C; 3 h.
[b] Turnover number of DPC (mol-DPC/mol-Pd).
[c] Turnover number of phenyl salicylate (mol-PS/mol-Pd).
[d] DPC percentage in the products evaluated from the peak areas on GC and the products identified by GC–MS.

Fig. 1. ^{13}C NMR spectra of **2b** in CD_2Cl_2: (a) without CO and (b) with CO (5 MPa) at 25 °C.
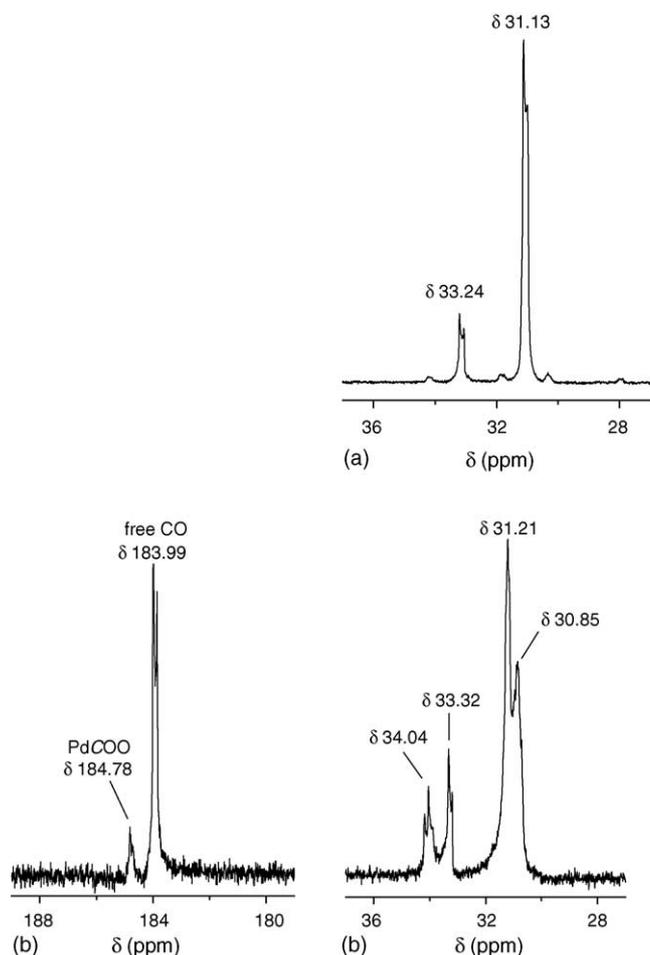
appeared at 184.78 ppm in the ^{13}C NMR spectrum for the reaction of **2b** with CO (5 MPa) at 25 °C in CD_2Cl_2 (Fig. 1(b)). In addition, a signal due to $C(CH_3)$ in the *tert*-butyl groups (33.24 ppm) splits into two peaks with almost a 1:1 ratio (34.04 and 33.32 ppm) and the C(CH_3) signal (31.13 ppm) also splits into two close to 1 to 1 (31.21 and 30.85 ppm) (Fig. 1(a) and (b)). In ^{1}H NMR, the splitting of the singlet due to the *tert*-butyl groups (1.23 ppm) was observed. On the other hand, signals due to di(*p-tert*-butyl)phenyl carbonate were not detected in ^{1}H and ^{13}C NMR spectra. These results presumably demonstrate that at 25 °C CO readily inserts into one of the two Pd–O bonds in **2b** to form (bpy)Pd(CO_2Ar)(OAr), while subsequent reductive elimination of diaryl carbonate is slow. This is consistent with our previous findings on (tmeda)Pd(OAr)$_2$ (tmeda = *N,N,N′,N′*-tetramethylethylenediamine) [15]. It is noteworthy that tmeda is an inefficient ligand for the Pd-catalyzed oxidative carbonylation of phenol [18].

In contrast, the ^{1}H and ^{13}C NMR spectra for the reaction of **2a** with CO at 25 °C revealed the formation of di(*p-tert*-butyl)phenyl carbonate. In this case, a signal due to PdCOO was unobservable in ^{13}C NMR. This clearly demonstrates
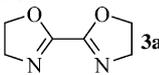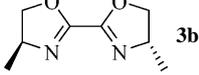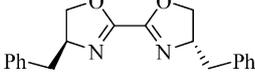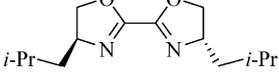
that the methyl groups in the 6,6′-position of **1b** accelerate the reductive elimination of diaryl carbonate. Presumably, the methyl groups sterically destabilize the aryloxycarbonyl intermediate. These results suggest that using bidentate ligands with sterically bulkier substituents give a better catalyst for the Pd-catalyzed oxidative carbonylation of phenol.

2.3. Reaction catalyzed by Pd complexes with bioxazolyl ligands

Since we confirmed that the reductive elimination of DPC from Pd(OPh)(CO_2Ph)L$_2$ is accelerated by increasing steric hindrance around Pd, we chose bioxazolyl ligands and investigated the influence of the substituents at the 4,4′-position of the 2,2′-bioxazolyl ligands (**3**) 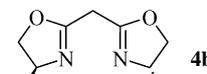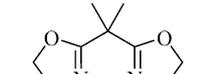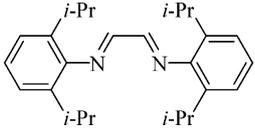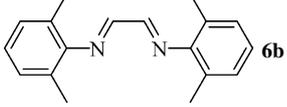on the catalytic activity and selectivity for the oxidative carbonylation. Table 3 summarizes the TON and the selectivity of DPC formation at 100 °C for 3 h. Although DPC was produced without additional ligands, the TON was low and a large amount of phenyl salicylate was formed (Table 3, entry 1). The addition of 2,2′-bioxazolyl ligands greatly improved the catalytic activity and selectivity, which strongly depended on the structure of the ligands: Introducing methyl groups at the 4,4′-position of **3a** was ineffective for producing DPC. On the other hand, the TON of DPC formation significantly increased with increasing bulkiness of the substituents (methyl (**3b**) < benzyl (**3c**) < *iso*-butyl (**3d**) < *tert*-butyl (**3e**)), and reached 48 mol-DPC/mol-Pd for the *tert*-butyl substitution (Table 3, entries 3–6). As expected, introducing bulky substituents is also effective for promoting the reaction in the 2,2′-bioxazolyl ligands.

Interestingly, further substituting H-atoms at the 4,4′-position of **3b** with methyl groups (**3f**) also enhanced the TON and the selectivity (Table 3, entry 7), possibly due to larger steric effects compared to mono-substitution. We also examined the carbon-spaced bioxazolyl ligands, in which the oxazoline rings are bridged with a methylene unit (**4**) or an isopropylene unit (**5**). The methylene-bridged bioxazolyl ligand with *tert*-butyl groups at the 4,4′-position (**4a**) gave the highest TON of DPC (54 mol-DPC/mol-Pd) (Table 3, entry 8). In contrast, the bioxazolyl ligand with phenyl groups (**4b**) was inefficient. This suggests that introducing bulky, but electron-withdrawing substituents are ineffective. A similar tendency was obtained for the isopropylene-bridged bioxazolyl ligands (**5a** versus **5b**). The bioxazolyl ligands (**3e**, **3f**, and **4a**) gave similar TONs and slightly higher selectivities, compared to the previously reported bulky diimine ligand **6a** [18] and the bulky bipyridyl ligand **1a** (Table 1, entry 1). It has been assumed that the diimine ligands are effective for oxidative carbonylation of phenol because conjugation with aromatic substituents decreases the electron density of the Pd center, which facilitates the coupling between CO and phenol on the Pd [18]. However, the present results show that even nonresonant bioxazolyl ligands are highly efficient.

Table 3
Pd-catalyzed oxidative carbonylation of phenol using 2,2′-bioxazolyl ligands[a]

Entry	Ligand	TON (DPC)[b]	TON (PS)[c]	Selectivity of DPC (%)[d]
1	None	8	13	53
2	3a	20	9	68
3	3b	18	6	75
4	3c	26	5	76
5	3d	33	6	79
6	3e	48	6	85
7	3f	44	5	87
8	4a	54	8	84
9	4b	8	8	66
10	5a	42	6	83
11	5b	5	4	54
12	6a	60	9	81
13	6b	52	10	77
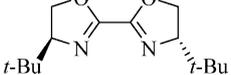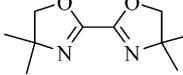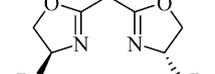
[a] Reaction conditions: phenol, 32 mmol; $(MeCN)_2PdCl_2$, 0.012 mmol; ligand, 0.012 mmol; $Mn(TMHD)_3$, 0.024 mmol; $(Ph_3P=)_2NBr$, 0.24 mmol; CO, 3 MPa; air, 1.5 MPa; 100 °C; 3 h.

[b] Turnover number of DPC (mol-DPC/mol-Pd).

[c] Turnover number of phenyl salicylate (mol-PS/mol-Pd).

[d] DPC percentage in the products evaluated from the peak areas on GC and the products identified by GC–MS.
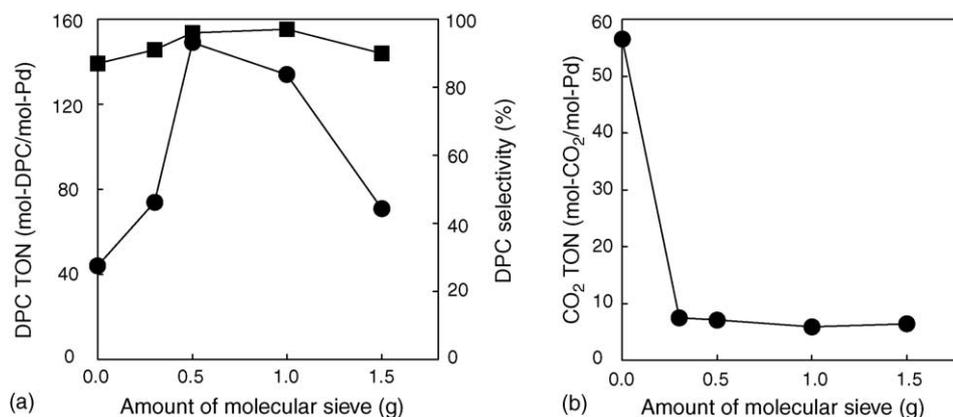
Fig. 2. Effects of the amount of molecular sieve 3A: (a) on TON (●) and selectivity of DPC (■); and (b) on TON of CO_2. Reaction conditions: phenol, 32 mmol; $(MeCN)_2PdCl_2$, 0.012 mmol; **3f**, 0.012 mmol; $Mn(TMHD)_3$, 0.024 mmol; $(Ph_3P=)_2NBr$, 0.24 mmol; CO, 3 MPa; air, 1.5 MPa; 100 °C; 3 h.

2.4. Effects of water

The addition of dehydrating agents is effective for the oxidative carbonylation of phenol [3,6,10]. We examined the effects of adding molecular sieve 3A (MS-3A) to the system using **3f**. Fig. 2(a) shows the dependences of TON and selectivity of DPC on the amount of MS-3A added. Upon the addition of 0.5 g of MS-3A, the TON reached 150 mol-DPC/mol-Pd (44 mol-DPC/mol-Pd without MS-3A). The selectivity of DPC also improved from 87 to 96%. The reason the activity is enhanced by adding MS-3A is unclear, but may be that the hydrolysis of DPC is prevented (Eq. (2)). It has been mentioned that water reacts with DPC to produce CO_2 and phenol [10]. Another possible reason the activity is enhanced is that Pd does not have to catalyze the water–gas-shift reaction between CO and formed water (Eq. (3)), as discussed below. Further additions of MS-3A decreased the amounts of DPC formation. Yin et al. hypothesized that excessive MS-3A increases the viscosity of molten phenol and decreases the probability of reoxidation of Pd(0) by cocatalysts [10].

$$DPC + H_2O \rightarrow CO_2 + 2PhOH \qquad (2)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (3)$$
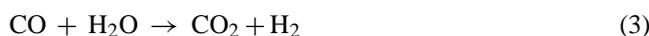
Notably, adding MS-3A remarkably prevented the formation of CO_2 (Fig. 2(b)). The TON of CO_2 was 56 mol-CO_2/mol-Pd without MS-3A, whereas the TONs decreased to around 7 mol-CO_2/mol-Pd with MS-3A. Therefore, it is considered that water is involved in CO_2 formation. Possible CO_2 formation routes in which water takes part are Eqs. (2) and (3). The oxidative carbonylation of phenol was conducted in the presence of $H_2{}^{18}O$. Indeed, we confirmed the formation of $CO^{18}O$; the gas phase analyzed by GC–MS had CO_2 peaks from two parent peaks with mass numbers of 44 and 46, and an intensity ratio of 2:1. This demonstrates that Eq. (2) or (3) is involved. Since the occurrence of Eq. (2) has already been suggested [10,13],

Table 4
Consideration of the CO_2 formation routes[a]

Entry	Catalyst	Air	Amount of CO_2 formation (mmol)
1	○	–	8.1×10^{-2}
2	–	–	2.9×10^{-3}
3	○	○	4.3×10^{-1}

[a] Reaction conditions: DMF, 3 ml; water, 0.1 ml; $(MeCN)_2PdCl_2$, 0.012 mmol; **3f**, 0.012 mmol; $Mn(TMHD)_3$, 0.024 mmol; $(Ph_3P=)_2NBr$, 0.24 mmol; CO, 3 MPa; air, 1.5 MPa; 100 °C; 3 h.

we investigated the possibility of CO_2 formation via Eq. (3).

When the reaction between CO and water was conducted under conditions similar to Table 3, the water–gas-shift reaction proceeded to form CO_2 (Table 4, entry 1), while CO_2 formation was negligible without metal catalysts (Table 4, entry 2). These observations suggest that CO_2 is formed via Eq. (3). The presence of air in the above reaction created a larger amount of CO_2 formation, indicating a simultaneous occurrence of CO oxidation (Table 4, entry 3). Therefore, we believe that adding MS-3A decreased the amount of CO_2 formed not only by suppressing Eq. (2) but also by suppressing Eq. (3).

3. Conclusion

We demonstrated that the reductive elimination rate of diaryl carbonate is much faster using **2a** than **2b** in the presence of highly pressurized CO. We also revealed that 2,2′-bioxazolyl with a bulky substituent at the 4,4′-position is an efficient ligand for Pd-catalyzed oxidative carbonylation of phenol. Increasing the steric hindrance around Pd effectively promoted the reaction. In the oxidative carbonylation of phenol, CO_2 is probably formed via the reaction between CO and the formed water (water–gas-shift reaction), in addition to the hydrolysis of DPC and CO oxidation.

4. Experimental

4.1. General

Phenol was purified by recrystallization from a petroleum ether solution. Solvents were dried in a typical manner and were distilled prior to use. Molecular sieve 3A (MS-3A) was purchased from Aldrich and activated prior to use by heating to 300 °C in a vacuum for 3 h. All other reagents were used without further purification. 2,2′-Bipyridyl ligands **1a**, **1b**, and **1c**, and 2,2′-bioxazolyl ligands **3c**, **4a**, **4b**, **5a**, and **5b** were used as received from Aldrich. Carbon monoxide (Takachiho Chemical Industrial Co., >99.95% purity) and air (Nippon Sanso Co., G1 grade) were also used without further purification. 2,2′-Bioxazolyl ligands **3a** [21], **3d** [22], **3e** [23], and **3f** [24], and diimine ligands **6a** [25] and **6b** [26] were prepared according to the literature. (MeCN)$_2$PdCl$_2$ was prepared by reacting PdCl$_2$ with acetonitrile. (Ph$_3$P=)$_2$NBr (bis(triphenylphosphoranylidene)ammonium bromide) was prepared by anion-exchange of (Ph$_3$P=)$_2$NCl [27]. Di(*p-tert*-butyl)phenyl carbonate was prepared by reacting *p-tert*-butylphenol with 1,1′-carbonyldiimidazole [28]. The ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a JEOL LA400WB spectrometer (400 MHz for ^{1}H). IR spectra were measured on a JASCO FT/IR-610 spectrometer. The elemental analyses were conducted using a CE Instruments EA1110 elemental analyzer. The reaction products were analyzed by a Shimadzu GC-14A gas chromatograph (GC) equipped with a flame ionization detector (FID) using a capillary column (J&W Scientific, DB-1, 30 m) and by a Shimadzu GC-14B GC with a thermal conductivity detector (TCD) using a packed column (GL Sciences Inc., Unibeads C, 3 m). The products were further identified using a Shimadzu GC-17A GC connected to a QP-5000 mass spectrometer (GC–MS) (70 eV EI).

4.2. Preparations of 2a and 2b

Diaryloxy Pd complex **2a** was prepared according to the literature [20]. CH$_2$Cl$_2$ (100 ml), **1a** (0.82 g, 4.45 mmol), and sodium *p-tert*-butylphenoxide (9.35 mmol, 0.94 M in THF solution) were added to a Schlenk tube containing Pd(OAc)$_2$ (1.00 g, 4.45 mmol). After stirring for 12 h at room temperature, the reaction mixture was fully evaporated to dryness. The crude product was extracted with CH$_2$Cl$_2$, filtered through Celite, and fully evaporated to dryness. The resulting product was repeatedly washed with pentane and dried under a vacuum. Recrystallization from a CH$_2$Cl$_2$–ether solution gave an ocher crystalline solid of **2a** (1.72 g, 66% yield). ^{1}H NMR (400 MHz, CD$_2$Cl$_2$, 25 °C, ppm): δ 7.89–7.81 (m, 4H, H_3, H_4), 7.25 (d, 2H, $J = 7.5$ Hz, H_5), 6.97–6.93 (m, 8H, H_m, H_o), 2.87 (s, 6H, CH_3), 1.22 (s, 18H, C$_4$$H_9$). ^{13}C{^{1}H} NMR (100.4 MHz, CD$_2$Cl$_2$, 25 °C, ppm): δ 164.55, 164.30, 156.24, 138.70, 127.16, 125.86, 124.70, 118.77, 118.54, 33.21 (*C*(CH$_3$)$_3$), 31.13 (C(*C*H$_3$)$_3$), 23.72 (*C*H$_3$). Analytically calculated for C$_{32}$H$_{38}$N$_2$O$_2$Pd: C, 65.24; H, 6.50; N, 4.76. Found: C, 64.94; H, 6.47; N, 4.66.

Diaryloxy Pd complex **2b** was analogously prepared by reacting Pd(OAc)$_2$ with sodium *p-tert*-butylphenoxide in the presence of **2a** to give a yellow powder in 58% yield. ^{1}H NMR (400 MHz, CD$_2$Cl$_2$, 25 °C, ppm): δ 8.76 (d, $J = 6.0$ Hz, 2H, H_6), 8.08–7.97 (m, 4H, H_3, H_4), 7.57 (t, $J = 6.8$ Hz, 2H, H_5), 7.14–7.00 (m, 8H, H_m, H_o), 1.23 (s, 18H, C$_4$$H_9$). ^{13}C{^{1}H} NMR (100.4 MHz, CD$_2$Cl$_2$, 25 °C, ppm): δ 164.89, 155.10, 149.29, 139.39, 136.92, 126.34, 124.97, 121.52, 118.44, 33.24 (*C*(CH$_3$)), 31.13 (C(*C*H$_3$)). Analytically calculated for C$_{30}$H$_{34}$N$_2$O$_2$Pd: C, 64.22; H, 6.11; N, 4.99. Found: C, 64.35; H, 6.22; N, 4.73.

4.3. Preparation of 3b

(*S,S*)-4,4′-Dimethyl-4,4′,5,5′-tetrahydro-2,2′-bioxazolyl ligand **3b** was prepared by modifying the procedure reported for **3a** [21]. IR (KBr, cm^{-1}): 1619 ($\nu_{C=N}$), 1145 (ν_{C-O}). ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C, ppm): δ 4.50 (t, $J = 8.5$ Hz, 2H, OC*H*HCH(CH$_3$)), 4.41–4.32 (m, 2H, OCH$_2$C*H*(CH$_3$)), 3.95 (t, $J = 8.5$ Hz, 2H, OCH*H*CH(CH$_3$)), 1.32 (d, $J = 6.8$ Hz, 6H, OCH$_2$CH(C*H*$_3$)). ^{13}C{^{1}H} NMR (100.4 MHz, CDCl$_3$, 25 °C, ppm): δ 154.59 (O*C*=N), 74.77 (O*C*H$_2$CHCH$_3$), 62.51 (OCH$_2$*C*HCH$_3$), 20.87 (OCH$_2$CH*C*H$_3$). Analytically calculated for C$_8$H$_{12}$N$_2$O$_2$: C, 57.12; H, 7.19; N, 16.66. Found: C, 56.48; H, 7.04; N, 16.22.

4.4. Oxidative carbonylation of phenol

The oxidative carbonylation of phenol was conducted with a high-pressure-resistant glass vessel (15 ml). Phenol (3.0 g, 32 mmol), (MeCN)$_2$PdCl$_2$ (3.1 mg, 0.012 mmol), a ligand (0.012 mmol), Mn(TMHD)$_3$ (14.5 mg, 0.024 mmol), (Ph$_3$P=)$_2$NBr 148.3 mg (0.24 mmol), and *o*-terphenyl (50 mg, internal standard for GC analysis) were charged to the vessel. The vessel was then heated to 100 °C using an oil bath and charged with CO (3 MPa) and air (1.5 MPa). After stirring the mixture at 100 °C for 3 h, the vessel was cooled to room temperature and the gaseous contents were vented. The resulting liquid products were diluted with acetone and analyzed using FID–GC and GC–MS. The same procedure was used for reactions with MS-3A except a stainless steel autoclave (30 ml) equipped with a mechanical stirrer was employed and phenol, (MeCN)$_2$PdCl$_2$, **3f**, Mn(TMHD)$_3$, (Ph$_3$P=)$_2$NBr, *o*-terphenyl, and the activated MS-3A were charged to the autoclave in a glove box under a nitrogen atmosphere.

4.5. Reactions of 2a and 2b with CO

In a glove box, **2a** (30 mg, 0.051 mmol) and THF (5 ml) were charged to a high-pressure-resistant glass vessel (15 ml) under a nitrogen atmosphere. After the vessel was sealed and removed from the glove box, the vessel was pressurized with CO (5 MPa). After stirring the mixture at 25 °C for 0.5 h, CO was released and *o*-terphenyl (50 mg) was added to the reaction mixture as an internal standard for GC analysis. The

resulting products were analyzed by FID–GC and GC–MS. In a separate experiment, the reaction time was prolonged to 3 h. The reaction of **2b** with CO was conducted in a similar manner.

High-pressure NMR spectra for the reaction of **2a** with CO were recorded using a sapphire NMR tube (10 mm in diameter). In the NMR tube, **2a** (100 mg, 0.17 mmol) and CD_2Cl_2 (2 ml) were charged under a nitrogen atmosphere. The NMR tube was then pressurized with CO (5 MPa) and the ^1H and ^{13}C NMR spectra were recorded at 25 °C. A similar measurement was also performed for the reaction of **2b** with CO.

4.6. Reaction between CO and water

A high-pressure-resistant glass vessel (15 ml) containing DMF (3 ml), water (0.1 ml), $(MeCN)_2PdCl_2$ (3.1 mg, 0.012 mmol), **3f** (0.012 mmol), $Mn(TMHD)_3$ (14.5 mg, 0.024 mmol), and $(Ph_3P=)_2NBr$ 148.3 mg (0.24 mmol) was heated to 100 °C and then pressurized with CO (3 MPa) and air (1.5 MPa). After stirring the mixture at 100 °C for 3 h. The vessel was cooled to room temperature and the gaseous contents were collected in a gas-sampling bag and analyzed by TCD–GC. Similar reactions were conducted without adding air and without adding $(MeCN)_2PdCl_2$, **3f**, $Mn(TMHD)_3$, $(Ph_3P=)_2NBr$, and air.

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