1216 *Organometallics* **2002,** *21,* 1216−1220

Reactivity of Diaryloxy Palladium Complex with TMEDA (*N,N,N′,N′*-Tetramethylethylenediamine) Ligand toward Carbon Monoxide and Carbon Dioxide

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Received October 5, 2001

The reactivity of the diaryloxy palladium complex toward carbon monoxide was investigated relevant to the mechanism of the palladium-catalyzed oxidative carbonylation of phenol to produce diphenyl carbonate (DPC). (TMEDA)Pd(OC_6H_4-*p*-*t*-Bu)$_2$ (**1**) reacted at high CO pressures (10−80 atm) at 100 °C to give the di(*p*-*tert*-butyl)phenyl carbonate. The yield of the carbonate increased with the increase in the CO pressure and with the addition of triphenylphosphine. The $^{13}C\{^1H\}$ NMR and IR spectroscopic studies at room temperature under high CO pressure (50 atm) revealed that CO inserts into one of the Pd−O bonds in **1**. Thus, the formation of palladium phenoxide followed by carbonylation and subsequent reductive elimination is considered to be one of the possible DPC formation routes in the oxidative carbonylation of phenol; the reductive elimination is slower than the carbonylation. The reactivity of **1** with carbon dioxide was also examined relating to the DPC synthesis from carbon dioxide and phenol. The reaction of **1** with CO_2 led to the formation of a palladium carbonate complex, (TMEDA)Pd(η^2-CO_3) (**2**), whose molecular structure was determined by X-ray crystallography.

Introduction

Oxidative carbonylation of phenol to produce diphenyl carbonate (DPC), which is a raw material for the production of aromatic polycarbonates by the melt-polymerization process, has attracted considerable attention as one of the environmentally benign synthetic routes for DPC without using toxic and corrosive phosgene.[1] Various catalytic systems[2−8] have been proposed for the oxidative carbonylation of phenol, generally involving palladium-based redox catalysts. However, the catalytic performances are still unsatisfactory, and fundamental studies on the DPC formation mechanism are very limited (Figure 1).

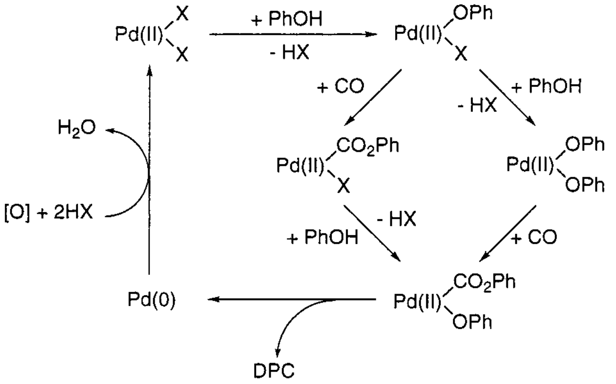

Figure 1. Possible catalytic cycle for the oxidative carbonylation of phenol.

One of the key steps in the catalytic cycle of the palladium-catalyzed oxidative carbonylation of phenol would be the carbonylation of the palladium phenoxide complex. However, no clear evidence has yet been obtained for carbon monoxide insertion into the Pd−O bond in palladium aryloxides.[9] For example, aryloxopalladium(II) hydrides [Pd(PCy_3)$_2$(H)(OAr)]·ArOH (Ar = Ph, C_6F_5) react with CO to give polynuclear palladium carbonyls via reductive elimination of ArOH.[10] For the

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(1) (a) Shaikh, A. G.; Sivaram, S. *Chem. Rev.* **1996**, *96*, 951. (b) Ono, Y. *Appl. Catal. A* **1997**, *155*, 133. (c) Komiya, K.; Fukuoka, S.; Aminaka, M.; Hasegawa, K.; Hachiya, H.; Okamoto, H.; Watanabe, T.; Yoneda, H.; Fukawa I.; Dozono, T. *ACS Symp. Ser.* **1996**, *626*, 20; (d) *Chem. Br.* **1994**, *30*, 970; (e) *Eur. Chem. News* **1998**, *21*, 29.

(2) (a) Hallgren, J. E.; Matthews, R. O. *J. Organomet. Chem.* **1979**, *175*, 135. (b) Hallgren, J. E.; Lucas, G. M. *J. Organomet. Chem.* **1981**, *212*, 135.

(3) Moiseev, I. I.; Vargaftik, M. N.; Chernysheva, T. V.; Stromnova, T. A.; Gekhman, A. E.; Tsirkov, G. A.; Makhlina, A. M. *J. Mol. Catal. A* **1996**, *108*, 77.

(4) Takagi, M.; Miyagi, H.; Yoneyama, T.; Ohgomori, Y. *J. Mol. Catal. A* **1998**, *129*, L1.

(5) (a) Goyal, M.; Nagahata, R.; Sugiyama, J.; Asai, M.; Ueda, M.; Takeuchi, K. *Catal. Lett.* **1998**, *54*, 29. (b) Ishii, H.; Goyal, M.; Ueda, M.; Takeuchi, K.; Asai, M. *J. Mol. Catal. A* **1999**, *148*, 289.

(6) (a) Vavasori, A.; Toniolo, L. *J. Mol. Catal. A* **1999**, *139*, 109. (b) Vavasori, A.; Toniolo, L. *J. Mol. Catal. A* **2000**, *151*, 37.

(7) Yin, G.; Jia, C.; Kitamura, T.; Yamaji, T.; Fujiwara, Y. *Catal. Lett.* **2000**, *69*, 89.

(8) Song, H. Y.; Park, E. D.; Lee, J. S. *J. Mol. Catal. A* **2000**, *154*, 243.

(9) It is known that carbon monoxide inserts into the metal−oxygen bond in iridium and platinum aryloxides, see: (a) Rees, W. M.; Churchill, M. R.; Fettinger, J. C.; Atwood, J. D. *Organometallics* **1985**, *4*, 2179. (b) Ni, J.; Kubiak, C. P. In *Homogeneous Transition Metal Catalyzed Reactions*; Moser, W. R., Slocum, D. W., Eds.; Advances in Chemistry Series; American Chemical Society: Washington, DC, 1992; Vol. 230, p 515. (c) Dockter, D. W.; Fanwick, P. E.; Kubiak, C. P. *J. Am. Chem. Soc.* **1996**, *118*, 4846.

10.1021/om010877m CCC: $22.00

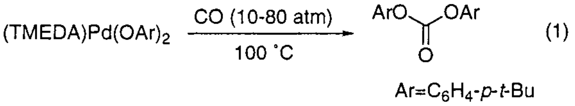
dinuclear palladium aryloxides, $Pd_2L_2(OAr)_2$ (L = dmpm, dppm; Ar = Ph, OC_6H_3-2,6-Me), CO insertion predominantly occurs at the Pd−Pd bond, although the possibility of CO insertion into the Pd−O bond is also suggested.[11] Methylpalladium(II) phenoxides, $L_2Pd(Me)(OPh)$ ($L_2 = (PMe_3)_2$, dppe, tmeda, bpy), react with CO to produce phenyl acetate, $MeCO_2Ph$.[12] In this reaction, however, $L_2Pd(COMe)(OPh)$ rather than $L_2Pd(Me)(CO_2Ph)$ is assumed to be the intermediate. Indeed, the acylpalladium(II) aryloxide, $(PEt_3)_2Pd(COMe)(OC_6H_4$-*p*-CN), is isolated by reacting $(PEt_3)_2Pd(Me)(OC_6H_4$-*p*-CN) with CO.[13]

In this study, we investigated the reactivity of the diaryloxy palladium complex toward carbon monoxide relevant to the mechanism of the palladium-catalyzed oxidative carbonylation of phenol to produce DPC. We present here evidence for the insertion of CO into the Pd−O bond in the palladium aryloxide to yield the aryloxycarbonyl palladium complex, followed by the formation of the diaryl carbonate via reductive elimination. We also examined the reactivity of the palladium diaryloxide with carbon dioxide relating to a possible DPC synthesis from carbon dioxide and phenol. We reported the analogous dimethyl carbonate synthesis from carbon dioxide and methanol (or methanol derivatives) catalyzed by tin dimethoxides.[14]

Results and Discussion

The diaryloxy palladium complex with the TMEDA (*N*,*N*,*N*′,*N*′-tetramethylethylenediamine) ligand $(TMEDA)Pd(OC_6H_4$-*p*-*t*-Bu$)_2$ (**1**) was prepared by reacting palladium acetate with 2 equiv of sodium *p*-*tert*-butylphenoxide at room temperature in the presence of TMEDA according to the method reported by van Koten et al.[15] Recrystallization from a CH_2Cl_2-ether solution gave an orange crystalline solid of **1** in 82% yield. Elemental analysis and NMR (^1H and $^{13}C\{^1H\}$) spectroscopy confirmed the formation of the complex **1**.

Reactivity with Carbon Monoxide. The reactivity of **1** toward CO was investigated at 100 °C in the presence of *p*-*tert*-butylphenol (4 equiv). The reaction of **1** with atmospheric CO hardly proceeded, whereas **1** reacted with highly pressurized CO (10−80 atm) to produce di(*p*-*tert*-butyl)phenyl carbonate (eq 1).



(1)

The yield of di(*p*-*tert*-butyl)phenyl carbonate based on the palladium complex after 24 h is summarized in Table 1. The reaction with CO (10 atm) gave 25.3% of the carbonate (entry 2). When triphenylphosphine (2 equiv) was added to the reaction system, the yield increased to 42.0% (entry 3). The increase in the CO pressure from 10 to 80 atm also resulted in an increase in the yields to 61.8% in the absence of PPh_3 and to 94.5% (95.5% after 48 h) in the presence of PPh_3. The absence of *p*-*tert*-butylphenol produced a similar yield (entry 7), indicating almost no influence by the addition of *p*-*tert*-butylphenol on the carbonate formation. Briefly, di(*p*-*tert*-butyl)phenyl carbonate was quantitatively formed from **1** by reacting with CO at a pressure of 80 atm at 100 °C in the presence of PPh_3. The reason the addition of PPh_3 promotes the carbonate formation is not clear, but PPh_3 presumably contributes to the stabilization of the palladium(0) complex formed by reductive elimination of the diaryl carbonate. Another possible explanation is that the PPh_3-ligated palladium diaryloxide such as $(PPh_3)_2Pd(OAr)_2$ and/or (TMEDA)$(PPh_3)Pd(OAr)_2$ is produced during the reaction,[16] and CO insertion and/or subsequent reductive elimination are accelerated because the three-coordinate palladium diaryloxide species, which is assumed to be the intermediate in both reactions,[17] would form more easily from the palladium diaryloxides with monodentate ligands than from palladium diaryloxides with a bidentate ligand like TMEDA.

Table 1. Reaction of 1 with Carbon Monoxide[a]

entry no.	pressure of CO (atm)	additive	yield of carbonate[b] (%)
1	1	none	tr.
2	10	none	25.3
3	10	PPh_3	42.0
4	80	none	61.8
5	80	PPh_3	94.5
6[c]	80	PPh_3	95.5
7[d]	80	PPh_3	99.9

[a] Reaction conditions: **1** (0.58 mmol), *p*-*tert*-butylphenol (2.30 mmol), additive (1.15 mmol), 24 h at 100 °C. [b] Yield of di(*p*-*tert*-butylphenyl) carbonate based on **1**. [c] After 48 h. [d] *p*-*tert*-Butylphenol was not added.

The efficient formation of diaryl carbonate stated above allows us to assume that the palladium aryloxycarbonyl complex acts as an intermediate. Thus, the insertion of CO into **1** was investigated by high-pressure NMR spectroscopy. For the reaction of **1** with CO (10−50 atm) at −30 °C in CD_2Cl_2, the $^{13}C\{^1H\}$ NMR spectra of the reaction mixture were the same as the spectra of **1** except for the appearance of the signal arising from free CO at 184.67 ppm. The $^{13}C\{^1H\}$ NMR spectrum at 50 atm is shown in Figure 2a. When the temperature was increased to 20 °C, a signal due to the carbon of Pd*C*OO appeared at 185.69 ppm in $^{13}C\{^1H\}$ NMR (Figure 2b). In addition, the apparent splittings of signals due to aromatic carbons (110−170 ppm), N*C*H_2 and N*C*H_3 in TMEDA (40−70 ppm), as well as *C*$(CH_3)_3$ and C(*C*$H_3)_3$ in *tert*-butyl groups (30−40 ppm) were

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(10) Bugno, C. D.; Pasquali, M.; Leoni, P.; Sabatino, P.; Braga, D. *Inorg. Chem.* **1989**, *28*, 1390.

(11) (a) Kullberg, M. L.; Kubiak, C. P. *Organometallics* **1984**, *3*, 632. (b) Krafft, T. E.; Hejna, C. I.; Smith, J. S. *Inorg. Chem.* **1990**, *29*, 2682.

(12) (a) Kim, Y.-J.; Osakada, K.; Takenaka, A.; Yamamoto, A. *J. Am. Chem. Soc.* **1990**, *112*, 1096. (b) Kapteijn, G. M.; Dervisi, A.; Verhoef, M. J.; van den Broek, M. A. F. H.; Grove, D. M.; van Koten, G. *J. Organomet. Chem.* **1996**, *517*, 123.

(13) Komiya, S.; Akai, Y.; Tanaka, K.; Yamamoto, T.; Yamamoto, A. *Organometallics* **1985**, *4*, 1130.

(14) (a) Choi, J.-C.; He, L.-N.; Yasuda, H.; Sakakura, T. Manuscript in preparation. (b) Choi, J.-C.; Sakakura, T.; Sako, T. *J. Am. Chem. Soc.* **1999**, *121*, 3793.

(15) (a) Kapteijn, G. M.; Grove, D. M.; Kooijman, H.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *Inorg. Chem.* **1996**, *35*, 526. (b) Alsters, P. L.; Baesjou, P. J.; Janssen, M. D.; Kooijman, H.; Sicherer-Roetman, A.; Spek, A. L.; van Koten, G. *Organometallics* **1992**, *11*, 4124.

(16) The reaction of **1** with 2 equiv of PPh_3 was done at room temperature in an NMR tube. The resulting $^{31}P\{^1H\}$, ^1H, and $^{13}C\{^1H\}$ NMR spectra showed the formation of several phosphine-containing species accompanied by the partial liberation of TMEDA, suggesting the substitution of the rather weakly coordinating TMEDA by PPh_3.

(17) (a) Gillie, A.; Stille, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 4933. (b) Ozawa, F.; Ito, T.; Nakamura, Y.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1868. (c) Ozawa, F.; Yamamoto, A. *Chem. Lett.* **1981**, 289.

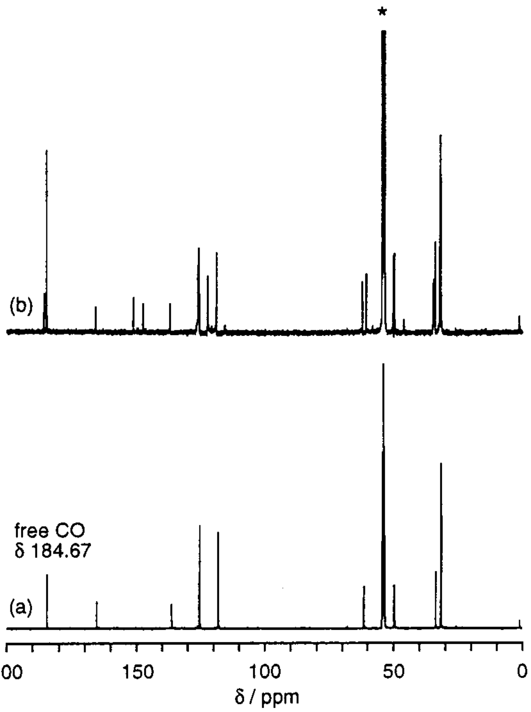


Figure 2. $^{13}C\{^1H\}$ NMR spectra of (TMEDA)Pd(OC_6H_4-*p*-*t*-Bu)$_2$ (**1**) in CD_2Cl_2 in the presence of CO (50 atm) (a) at −30 °C and (b) at 20 °C.

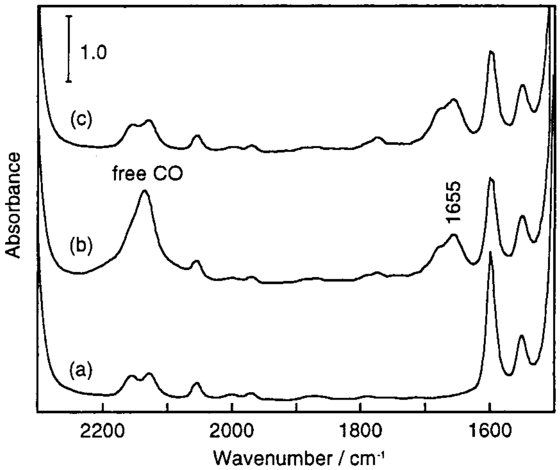
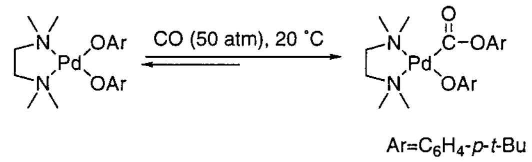


Figure 3. IR spectra of (TMEDA)Pd(OC_6H_4-*p*-*t*-Bu)$_2$ (**1**) in CH_2Cl_2 at room temperature (a) in the absence of CO, (b) in the presence of CO (50 atm), and (c) in the presence of CO (1 atm) after CO was released from 50 to 1 atm.

observed. The result indicates the asymmetry of the formed aryloxycarbonyl complex. In other words, the insertion of CO occurs only at one of the Pd−O bonds in **1** (eq 2). This is the first clear evidence for the insertion of CO into the Pd−O bond in the palladium aryloxide. The insertion of CO was also confirmed by high-pressure IR spectroscopy. Figure 3a shows the IR spectrum of **1** in CH_2Cl_2 in the absence of CO. When the solution was pressurized with CO (50 atm) at room temperature, the absorption band assignable to the ν(CO) of the palladium aryloxycarbonyl species appeared at 1655 cm^{-1} with a shoulder around 1676 cm^{-1} (Figure 3b). In addition, the ν(CO) band almost remained when CO was released from 50 to 1 atm (Figure 3c). This result clearly demonstrates that the elimination of CO from the aryloxycarbonyl palladium species is, if any, very slow at room temperature (eq 2).



(2)

CO insertion into the Pd−OR bond in the palladium alkoxides has been reported by several groups.[12,18] For the nitrogen-ligated methylpalladium methoxide,[18d] CO (1 atm) first inserts into the Pd−OMe bond at −60 °C and then into the Pd−Me bond at −25 °C. On the other hand, the present study shows that CO insertion into the Pd−OAr bond in the TMEDA-ligated palladium diaryloxide requires a higher CO pressure and temperature. This is consistent with the previous findings that CO insertion preferentially takes place at the Pd−Me bond in the methylpalladium aryloxides.[12,13]

If these results are taken into account, the carbonylation of palladium diphenoxide at one of the phenoxy ligands followed by reductive elimination is considered to be a plausible DPC formation route in the palladium-catalyzed oxidative carbonylation of phenol. On the other hand, the influence of a nucleophilic attack by phenol on the carbonyl group of the phenoxycarbonyl ligand on the DPC formation seems to be small, seeing that the addition of phenol does not promote the diaryl carbonate formation (Table 1). It is noteworthy that the reductive elimination of DPC from $L_2Pd(CO_2Ph)(OPh)$ is slower than the carbonylation of $L_2Pd(OPh)_2$ since we could observe $L_2Pd(CO_2Ar)(OAr)$ at room temperature without any subsequent reductive elimination. Therefore, it is thought that the acceleration of reductive elimination together with reoxidation of the palladium(0) complex is important in the catalytic cycle of the oxidative carbonylation of phenol.

Reactivity with Carbon Dioxide. The direct reaction of carbon dioxide with phenol is a very ideal synthetic process for DPC. Alkyltin dimethoxides can catalyze the analogous reaction of dimethyl carbonate synthesis from carbon dioxide and methanol (or methanol derivatives).[14] Therefore, it is interesting to investigate the CO_2 insertion into the metal−oxygen bond in diaryloxide complexes. Darensbourg et al. have reported that $[Et_4N][W(CO)_5OAr]$ (Ar = Ph, C_6H_4-*m*-Me) inserts CO_2 into the tungsten−oxygen bond to produce tungsten pentacarbonyl aryl carbonate, $W(CO)_5OCO_2Ar^-$, which has been characterized by NMR (^1H and ^{13}C) and IR spectroscopies.[19] Thus, we further examined the reactivity of the diaryloxy palladium complex toward CO_2. The reaction of **1** with CO_2 was attempted at room temperature and monitored by NMR and IR spectroscopies. However, no evidence for the CO_2 insertion into the Pd−O bonds in **1** was obtained even at 200 atm. On the other hand, when

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[18] (a) Kim, Y.-J.; Osakada, K.; Sugita, K.; Yamamoto, T.; Yamamoto, A. *Organometallics* **1988**, *7*, 2182. (b) Tóth, I.; Elsevier, C. J. *J. Chem. Soc., Chem. Commun.* **1993**, 529. (c) Smith, G. D.; Hanson, B. E.; Merola, J. S.; Waller, F. J. *Organometallics* **1993**, *12*, 568. (d) Kapteijn, G. M.; Verhoef, M. J.; van den Broek, M. A. F. H.; Grove, D. M.; van Koten, G. *J. Organomet. Chem.* **1995**, *503*, C26.

[19] (a) Darensbourg, D. J.; Sanchez, K. M.; Rheingold, A. L. *J. Am. Chem. Soc.* **1987**, *109*, 290. (b) Darensbourg, D. J.; Sanchez, K. M.; Reibenspies, J. H.; Rheingold, A. L. *J. Am. Chem. Soc.* **1989**, *111*, 7094.

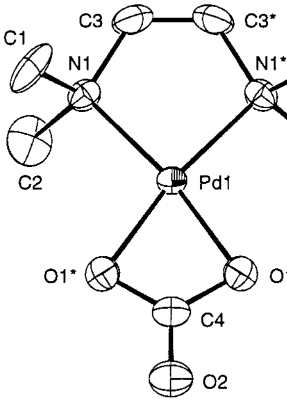

Figure 4. ORTEP drawing of (TMEDA)Pd(η^2-CO_3) (**2**). Ellipsoids represent 50% probability.

Table 2. Selected Bond Distances (Å) and Angles (deg) for 2

Distances			
Pd(1)−O(1)	2.001(4)	Pd(1)−N(1)	2.053(6)
O(1)−C(4)	1.318(8)	O(2)−C(4)	1.20(1)
Angles			
O(1)−Pd(1)−O(1*)	65.4(3)	O(1)−Pd(1)−N(1)	170.0(4)
O(1)−Pd(1)−N(1*)	104.8(2)	N(1)−Pd(1)−N(1*)	84.9(4)
Pd(1)−O(1)−C(4)	92.0(5)	O(1)−C(4)−O(1*)	110.2(10)
O(1)−C(4)−O(2)	124.5(5)		

the reaction mixture with CO_2 (4 equiv) in an NMR tube was left for a long time at room temperature, pale yellow single crystals of the TMEDA-ligated palladium carbonate complex (TMEDA)Pd(η^2-CO_3) (**2**) were formed along with the evolution of *p*-*tert*-butylphenol. The molecular structure of **2**, as determined by X-ray crystallography, is shown in Figure 4; selected bond distances and angles are provided in Table 2. The molecule lies on a 2-fold rotation axis in the crystal. The carbonate ligand is bound to palladium in a chelating manner, and the geometry around the palladium center is regarded as distorted square-planar. The Pd(1)−O(1) bond distance (2.001(4) Å) is comparable to the corresponding distances in the palladium carboxylates (1.99−2.12 Å).[20] The distance of O(2)−C(4) (1.20(1) Å) is shorter than that of O(1)−C(4) (1.318(8) Å), being characterized by a carbon−oxygen double bond. It has been reported that $W(CO)_5OCO_2Ar^-$ is readily converted into $W(CO)_4$(η^2-CO_3) in the presence of water.[19] It seems likely that the formation of **2** also proceeds through the reaction with water and CO_2.[21] The reaction of **1** with CO_2 (4 equiv) in the presence of water (2 equiv) immediately gave **2** in 97% yield, thus supporting this assumption.

In conclusion, we have shown that diaryl carbonate is quantitatively formed by reacting the diaryloxy palladium complex (TMEDA)Pd$(OAr)_2$ with carbon monoxide. We have also succeeded in characterizing the aryloxycarbonyl complex (TMEDA)Pd(CO_2Ar)(OAr) as an intermediate. In the reaction of the diaryl carbonate formation, reductive elimination from (TMEDA)Pd(CO_2-Ar)(OAr) is slower than the carbonylation of (TMEDA)-Pd$(OAr)_2$.

Experimental Section

General Comments. All manipulations were carried out under a purified argon atmosphere using standard Schlenk techniques. Solvents were purified by conventional means and were distilled immediately prior to use. *N*,*N*,*N*′,*N*′-Tetramethylethylenediamine (TMEDA), palladium acetate, *p*-*tert*-butylphenol, and triphenylphosphine were purchased from Tokyo Kasei Co. Sodium *p*-*tert*-butylphenoxide was prepared by reacting *p*-*tert*-butylphenol with sodium hydride. Carbon monoxide (Takachiho Co., Toyko, purity over 99.9%, water content less than 0.01%) and carbon dioxide (Showa Tansan Co., Kawasaki, purity over 99.99%) were used without further purification. The elemental analyses were carried out using a CE-EA 1110 automatic elemental analyzer. The ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a JEOL-LA400WB superconducting high-resolution spectrometer (400 MHz for ^1H). IR spectra under high CO and CO_2 pressures were measured on a JASCO FT/IR-5300 spectrometer using an IR cell with zinc sulfide windows. The inner volume of the cell was about 5 mL, and the thickness of the sample solution was 0.5 mm at the optical path. The reaction products were analyzed by GC using a capillary column: GL Science TC-1 (15 m) on a Shimadzu GC-14A gas chromatograph equipped with a flame ionization detector (FID) using *o*-terphenyl as the internal standard. The GC−MS analysis was performed using a Hewlett-Packard HP-5890 gas chromatograph connected to a HP-5971A mass spectrometer (EI 70 eV).

Synthesis of (TMEDA)Pd(OC_6H_4-*p*-*t*-Bu)$_2$ (1). (TMEDA)-Pd(OC_6H_4-*p*-*t*-Bu)$_2$ (**1**) was synthesized according to the literature method.[15] To a Schlenk tube containing $Pd(OAc)_2$ (1.17 g, 5.21 mmol) were added CH_2Cl_2 (100 mL), *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (0.624 g, 5.37 mmol), and sodium *p*-*tert*-butylphenoxide (10.6 mmol, 0.53 M in THF solution). After stirring for 1 h at room temperature, the reaction mixture was fully evaporated to dryness. The crude product was extracted with CH_2Cl_2, filtered through Celite, and fully evaporated to dryness. The resulting product was repeatedly washed with ether and hexane and dried under vacuum. Recrystallization from a CH_2Cl_2-ether solution gave an orange crystalline solid of **1** (2.23 g, 82% yield). ^1H NMR (400 MHz in $CDCl_3$ at 25 °C): δ 1.20 (s, 18H, $C(CH_3)_3$), 2.23 (s, 4H, N-CH_2), 2.31 (s, 12H, N-CH_3), 6.94 (d, $J = 8.6$ Hz, 4H, aromatic-H), 7.05 (d, $J = 8.6$ Hz, 4H, aromatic-H). $^{13}C\{^1H\}$ NMR (100 MHz in $CDCl_3$ at 25 °C): δ 31.78 ($C(\mathit{C}H_3)_3$), 33.58 ($\mathit{C}(CH_3)_3$), 49.70 (N-CH_3), 61.37 (N-CH_2), 118.65, 125.40, 136.38, 165.10 (aromatic-C). Anal. Calcd for $C_{26}H_{42}O_2N_2Pd$: C, 59.93; H, 8.12; N, 5.38. Found: C, 59.71; H, 8.06; N, 5.41.

Reaction of 1 with CO. (1) Autoclave Reaction. In a stainless steel autoclave (20 mL inner volume), CO was added to a mixture of **1** (0.58 mmol), *p*-*tert*-butylphenol (2.30 mmol), triphenylphosphine (1.15 mmol), and THF (5 mL) at room temperature. The autoclave was heated in an oil bath, and the initial pressure was adjusted to a desired value (10−80 atm) at 100 °C. After stirring for 24 h and then cooling, *o*-terphenyl (50 mg) was added to the reaction mixture as an internal standard in order to determine the product yields by GC. Products were further identified using GC−MS by the comparison of retention times and fragmentation patterns with authentic samples. A similar reaction of **1** with CO (1 atm) was also done in a Schlenk tube.

(2) NMR Tube Reaction. In a sapphire NMR tube (10 mm in diameter), CO (50 atm) was added to a CD_2Cl_2 (2.25 mL) solution of **1** (100 mg, 0.19 mmol), and the ^{13}C NMR spectrum was recorded at 20 °C. Similar measurements were also carried out at −30 °C and lower CO pressures (10−50 atm). $^{13}C\{^1H\}$ NMR (100 MHz in CD_2Cl_2 at 25 °C and 50 atm of CO): δ 31.64, 31.95 ($C(\mathit{C}H_3)_3$), 33.92, 34.64 ($\mathit{C}(CH_3)_3$), 49.50, 49.97 (N-CH_3), 60.53, 61.98 (N-CH_2), 118.84, 122.33, 125.65, 126.18, 136.82, 147.48, 151.30, 165.66 (aromatic-C), 184.67 (free CO), 185.69 (CO).

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[20] Mehrotra, R. C.; Bohra, R. *Metal Carboxylates*; Academic Press: London, 1983; p 284.

[21] Ganguly, S.; Mague, J. T.; Roundhill, D. M. *Inorg. Chem.* **1992**, *31*, 3831.

(3) IR Cell Reaction. In an IR cell, a CH_2Cl_2 (4.0 mL) solution of **1** (94 mg, 0.18 mmol) was placed under an argon atmosphere followed by the introduction of CO (50 atm). After stirring for 6 h at room temperature, the IR spectrum was measured. Afterward CO was released from 50 to 1 atm, and the IR spectrum was then measured again.

Reaction of 1 with CO_2. (1) NMR Tube Reaction. In an NMR tube (5 mm in diameter), CO_2 (0.17 mmol) was vacuum-transferred into a $CDCl_3$ (0.5 mL) solution of **1** (22 mg, 0.042 mmol). The resulting ^1H and $^{13}C\{^1H\}$ NMR spectra recorded at room temperature were the same as the spectra of **1**, indicating that no insertion of CO_2 occurs. After the reaction mixture was left for a long time at room temperature, pale yellow single crystals of (TMEDA)Pd(η^2-CO_3) (**2**) were deposited.

(2) IR Cell Reaction. In an IR cell, a CH_2Cl_2 (4.0 mL) solution of **1** (203 mg, 0.39 mmol) was placed under an argon atmosphere and pressurized with CO_2 (10−200 atm) at room temperature. The IR spectra were recorded with increasing CO_2 pressure from 10 to 100 and 200 atm and after stirring for 4−5 h at each pressure. However, no evidence for the CO_2 insertion into the Pd−O bonds in **1** was obtained even at 200 atm; we did not observe the absorption band due to ν(CO) in the range 1600−1800 cm^{-1}.

Synthesis of (TMEDA)Pd(η^2-CO_3) (2). (TMEDA)Pd(η^2-CO_3) (**2**) could also be synthesized in the presence of water. To a Schlenk tube containing **1** (78 mg, 0.15 mmol) were added THF (8 mL), water (5.4 μL, 0.30 mmol), and CO_2 (0.60 mmol). After stirring for 1 h at room temperature, hexane (15 mL) was added. The resulting pale yellow precipitate of **2** was collected by filtration and dried under vacuum (41 mg, 97% yield). ^1H NMR (400 MHz in CD_2Cl_2 at 25 °C): δ 2.67 (s, 4H, N-CH_2), 2.80 (s, 12H, N-CH_3). $^{13}C\{^1H\}$ NMR (100 MHz in CD_2Cl_2 at 25 °C): δ 51.19 (N-CH_3), 61.62 (N-CH_2), 167.80 (CO_3). Anal. Calcd for $C_7H_{16}O_3N_2Pd$: C, 29.75; H, 5.71; N, 9.91. Found: C, 29.77; H, 5.63; N, 9.80.

Table 3. Crystallographic Data for 2

formula	$C_7H_{16}O_3N_2Pd$
fw	282.64
cryst size (mm)	0.20 × 0.20 × 0.30
cryst syst	orthorhombic
space group	$Cmc2_1$ (No. 36)
a (Å)	8.438(2)
b (Å)	15.230(3)
c (Å)	8.603(2)
V (Å^3)	1105.6(4)
Z	8
T (K)	223
λ (Å)	0.71069
d_{calcd} (g cm^{-3})	1.866
μ(cm^{-1})	16.77
F(000)	624.00
R	0.029
R_w[a]	0.035
no. of variables	64
no. of observations ($I > 3\sigma(I)$)	598

[a] $w = [\sigma(F_o)]^{-2}$.

X-ray Crystallographic Study. The data collection and refinement parameters for **2** are summarized in Table 3. The data were collected using a Rigaku AFC 7R diffractometer at 223 K with graphite-monochromated Mo Kα radiation (=0.710 69 Å) and the ω scan mode ($2\theta \leq 55°$). Correction for the Lorentz and polarization effects and an empirical absorption correction (Ψ scan) were applied. The full matrix least-squares refinement was carried out by applying anisotropic thermal factors to all the non-hydrogen atoms. The hydrogen atoms were located by assuming an ideal geometry.

Supporting Information Available: Crystallographic data of **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM010877M