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Synthesis and reactivity of phenoxycarbonyl palladium complex: relevant to the mechanism of oxidative carbonylation of phenol

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Abstract

Phenoxycarbonyl palladium complex was synthesized and its reactivity was investigated relevant to the mechanism of the palladium-catalyzed oxidative carbonylation of phenol to produce diphenyl carbonate (DPC). The phenoxycarbonyl palladium complex $PdCl(CO_2Ph)(PPh_3)_2$ (**1**) was synthesized by oxidative addition of phenyl chloroformate to $Pd(PPh_3)_4$. Complex **1** could be isolated as single crystals and characterized by X-ray crystallography. The thermolysis of **1** resulted in DPC formation, although degradation of the PPh_3 ligand to PhCl and $PhCO_2Ph$ simultaneously occurred. $PdCl_2(PPh_3)_2$ was a major newly formed palladium species. An efficient DPC formation was observed for the reaction of **1** with phenyl chloroformate. On the other hand, the reaction of **1** with sodium phenoxide (one equivalent) proceeded at -20 °C causing the instant formation of a new species assignable to $Pd(OPh)(CO_2Ph)(PPh_3)_2$ (**2**) as judged by NMR (^{1}H, $^{13}C\{^{1}H\}$, and $^{31}P\{^{1}H\}$) spectroscopy; the nucleophilic attack by phenoxide preferentially took place on the palladium center rather than on the carbonyl group. When the reaction mixture was heated, DPC was produced probably via the reductive elimination from **2**. These results as well as the previous finding that diaryl carbonate is formed from palladium diaryloxide by carbonylation and subsequent reductive elimination suggest that $Pd(OPh)(CO_2Ph)L_2$ is the final intermediate toward DPC: the reductive elimination requires a relatively high temperature.

Keywords: Phenoxycarbonyl palladium complex; Oxidative carbonylation of phenol; Diphenyl carbonate

1. Introduction

Diphenyl carbonate (DPC), a key material for manufacturing polycarbonates by transesterification, is industrially synthesized by reacting phenol with phosgene in the presence of bases. Oxidative carbonylation of phenol with carbon monoxide and oxygen is an attractive and promising method for synthesizing DPC without using highly toxic and corrosive phosgene [1]. Various catalytic systems, generally consisting of a palladium complex, a redox catalyst, and ammonium halide, have been proposed for the reaction [2]. However, the catalytic efficiency is still far from the commercially feasible level. In addition, little has been known about the DPC formation mechanism for the palladium-catalyzed oxidative carbonylation of phenol. We recently confirmed the quantitative diaryl carbonate formation via the reaction of palladium diaryloxide $Pd(OAr)_2L_2$ ($Ar = C_6H_4$-*p*-*t*-Bu; L_2 = TMEDA) with carbon monoxide. We also characterized the intermediate aryloxycarbonyl complex $Pd(OAr)(CO_2Ar)L_2$ [3]. Therefore, the formation of palladium diphenoxide followed by carbonylation and subsequent reductive elimination is considered to be one of the possible DPC formation routes (routes **a** and **b** in Scheme 1).

The alternative routes involve phenoxycarbonyl palladium complex $PdX(CO_2Ph)L_2$, which may be attacked by phenol to produce DPC (routes **c** and **b** or route **d** in Scheme 1). Indeed, it is reported that dimethyl carbonate is formed in an almost quantitative yield through $PdCl(CO_2Me)(PPh_3)_2$ by reacting $PdCl_2(PPh_3)_2$ with methanol in the presence of trialkylamine and carbon monoxide [4]. Thus, our interest in the mechanistic study on the DPC formation led us to synthesize phenoxycarbonyl palladium complex as another key intermediate and investigate its reactivity. Although the formation of late transition metal aryloxycarbonyl

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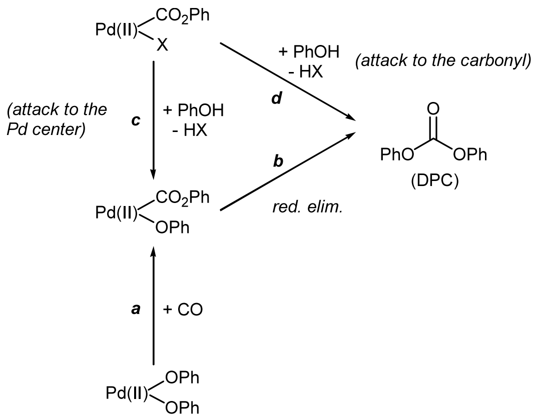


Scheme 1.

complexes is described in the literature [3,5–13], the number of the complexes that are isolated and well-characterized has been very limited. For example, it has been reported that $Ir(OPh)(CO)(PPh_3)_2$ reacts with CO to form $Ir(CO_2Ph)(CO)_2(PPh_3)_2$ which is characterized only by IR spectroscopy [5,6]. $Pd(pnp)(CO_2Ph)Cl$ (pnp = 2,6-bis(diphenylphosphinomethyl)pyridine) is isolated by the reaction of $Pd(pnp)Cl_2$ with sodium phenoxide and carbon monoxide [7]. $Pt(CO_2Ph)_2(dppf)$ (dppf = 1,1′-bis(diphenylphosphino)ferrocene) is also isolated in a similar reaction using $PtCl_2(dppf)$ [10]. However, the structural information of these complexes is limited to the elemental analysis and IR spectroscopy. On the other hand, Kubiak et al. have isolated the aryloxycarbonyl platinum complexes $[Pt(triphos)(CO_2Ar)][PF_6]$ (triphos = bis(2-diphenylphosphinoethyl)phenyl phosphine) by reacting $[Pt(triphos)(OAr)][PF_6]$ with CO and elucidated the first X-ray structure of an aryloxycarbonyl complex, $[Pt(triphos)(CO_2C_6H_4\text{-}p\text{-}Me)][PF_6]$ [12,13].

Otsuka et al. have previously attempted the synthesis of $PdCl(CO_2Ph)(PPh_3)_2$ by oxidative addition of phenyl chloroformate to $Pd(PPh_3)_4$ and concluded that the complex is unable to be isolated because decarbonylation readily takes place [14]. Toniolo et al. have reported although alkoxycarbonyl palladium complexes are synthesized by reacting $PdCl_2L_2$ (L = PPh_3, L_2 = 1,2-diphenylphosphinoethane) with alcohols under high CO pressures (10–50 atm) in the presence of triethylamine, aryloxycarbonyl complexes cannot be obtained by the similar reaction with phenols [15]. In this work, we succeeded in isolating the phenoxycarbonyl palladium complex $PdCl(CO_2Ph)(PPh_3)_2$ and confirmed the DPC formation via the reaction of the complex with phenoxide or even via simple thermolysis. Here, we report the synthesis, X-ray crystal structure, and reactivity of $PdCl(CO_2Ph)(PPh_3)_2$.

2. Results and discussion

2.1. Synthesis and structure

The reaction of $Pd(PPh_3)_4$ with one equivalent of phenyl chloroformate at room temperature in toluene afforded the phenoxycarbonyl palladium complex $PdCl(CO_2Ph)(PPh_3)_2$ (**1**) in 98% yield as a pale yellow solid (Eq. (1)). Otsuka et al. have previously attempted the same reaction at 80 °C to give $PdCl(PPh_3)_3$ [14]. In the present study, the lower reaction temperature enabled the phenoxycarbonyl complex to be isolated.

$$Pd(PPh_3)_4 + ClCO_2Ph \underset{\text{toluene}}{\overset{\text{r.t.}}{\rightarrow}} \underset{\mathbf{1}}{PdCl(CO_2Ph)(PPh_3)_2} \quad (1)$$

The structure of **1** was elucidated by the ^{1}H-NMR signals of the phenoxy group at δ 5.4–6.8 ppm and those of the phenyl groups in PPh_3 at δ 7.3–7.8 ppm, the $^{13}C\{^1H\}$-NMR signal of the carbonyl group at δ 182.2 ppm, the IR absorption of ν(CO) at 1686 cm^{-1}, and its elemental analysis. The $^{31}P\{^1H\}$-NMR spectrum showed a singlet at δ 18.33 ppm, suggesting a *trans* configuration in **1**. It is probable that *trans*-$PdCl(CO_2Ph)(PPh_3)_2$ was yielded via isomerization of *cis*-$PdCl(CO_2Ph)(PPh_3)_2$ formed by the oxidative addition of phenyl chloroformate to $Pd(PPh_3)_4$. In the ^{1}H-NMR, the *ortho* protons in the phenoxy group are significantly shifted up-field compared with phenyl chloroformate. No such up-field resonance position is observed for the *ortho* protons of the phenyl group in *trans*-$PdCl(Ph)(PPh_3)_2$ [16]. This characteristic up-field shift may be due to the influence of the ring current in the carbonyl group.

A single crystal of **1** was obtained from a THF–hexane solution at 4 °C. The molecular structure of **1**, as determined by X-ray crystallography, is shown in Fig. 1; selected bond distances and angles are provided in

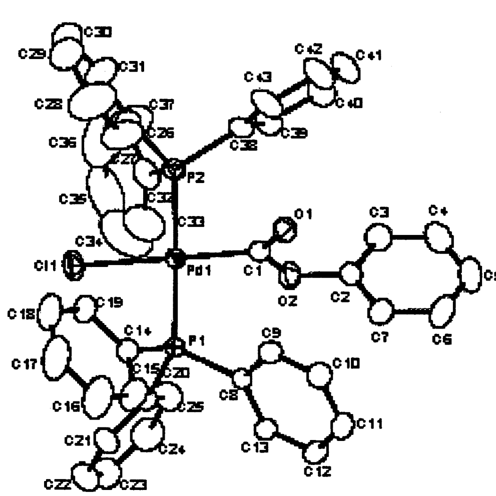


Fig. 1. ORTEP drawing of $PdCl(CO_2Ph)(PPh_3)_2$ (**1**). Ellipsoids represent 30% probability.

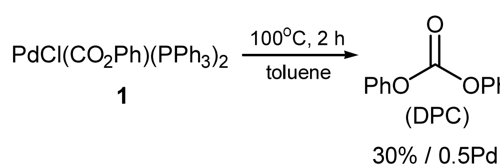
Table 1
Selected bond distances (Å) and angles (°) for **1**

Bond distances			
Pd(1)–C(1)	1.961(3)	Pd(1)–Cl(1)	2.3883(9)
Pd(1)–P(1)	2.3263(8)	Pd(1)–P(2)	2.3241(8)
C(1)–O(1)	1.191(4)	C(1)–O(2)	1.388(4)
O(2)–C(2)	1.409(4)		
Bond angles			
Cl(1)–Pd(1)–P(1)	90.76(3)	Cl(1)–Pd(1)–P(2)	87.89(3)
Cl(1)–Pd(1)–C(1)	177.18(10)	P(1)–Pd(1)–P(2)	178.65(3)
P(1)–Pd(1)–C(1)	91.01(9)	P(2)–Pd(1)–C(1)	90.34(9)
Pd(1)–C(1)–O(1)	129.6(3)	Pd(1)–C(1)–O(2)	109.6(2)
O(1)–C(1)–O(2)	120.8(3)	C(1)–O(2)–C(2)	118.7(3)

Table 1. This is the first X-ray structure of a neutral aryloxycarbonyl complex. The complex has a *trans* configuration as expected from the $^{31}P\{^1H\}$-NMR, and an approximate square-planar coordination geometry around the palladium center: The two *trans* angles are Cl(1)–Pd(1)–C(1) of 177.18(10)° and P(1)–Pd(1)–P(2) of 178.65(3)°; the *cis* angles range from P(1)–Pd(1)–C(1) of 91.01(9)° to Cl(1)–Pd(1)–P(2) of 87.89(3)°. Another feature of the molecular geometry is that the carbonyl plane in the phenoxycarbonyl ligand is nearly perpendicular to the palladium coordination plane, whereas the phenyl ring is rather parallel to the coordination plane. The Pd(1)–C(1) and Pd(1)–Cl(1) bond distances in **1** are 1.961(3) and 2.3883(9) Å respectively, almost identical to the values of 1.99(2) and 2.407(4) Å for the methoxycarbonyl analogue *trans*-$PdCl(CO_2Me)(PPh_3)_2$ [17] and those of 1.970(5) and 2.4035(15) Å for *trans*-$PdCl(CO_2Me)(Ph_2Ppy)_2$ (Ph_2Ppy = 2-pyridyldiphenylphosphine) [18]. The average distance of 2.3252(8) Å for the Pd(1)–P(1) and Pd(1)–P(2) bonds in **1** is also comparable with the average Pd–P distance of 2.335(4) Å for *trans*-$PdCl(CO_2Me)(PPh_3)_2$ and that of 2.332(1) Å for *trans*-$PdCl(CO_2Me)(Ph_2Ppy)_2$. The C(1)–O(1) bond distance of 1.191(4) Å is typical for carbon–oxygen double bonds, but fairly longer than the carbonyl distance of 1.08(1) Å seen for the only structurally characterized aryloxycarbonyl complex [Pt(triphos)($CO_2C_6H_4$-*p*-Me)][PF_6] [12], in which the artificial shortening of the bond length is noted. On the other hand, the C(1)–O(2) bond distance is 1.388(4) Å, approximately 0.04 and 0.11 Å longer than the average distance of 1.35 Å for the corresponding C–O bonds in methoxycarbonyl palladium complexes [17–23] and the corresponding C–O distance of 1.28(1) Å in [Pt(triphos)($CO_2C_6H_4$-*p*-Me)][PF_6], respectively. The Pd(1)–C(1)–O(2) angle of 109.6(2)° is smaller than the Pd(1)–C(1)–O(1) and O(1)–C(1)–O(2) angles of 129.6(3)° and 120.8(5)°, respectively. Similar tendency is observed for the Pt–C–OAr angle of 110.2(6)° in [Pt(triphos)($CO_2C_6H_4$-*p*-Me)][PF_6] and the Pd–C–OMe angles of 111(1)° and 109.3(3)° in *trans*-$PdCl(CO_2Me)(PPh_3)_2$ and *trans*-$PdCl(CO_2Me)(Ph_2Ppy)_2$, respectively.

2.2. Thermolysis

The reactivity of **1** was investigated relevant to the mechanism of the palladium-catalyzed oxidative carbonylation of phenol. We first examined the thermal decomposition behavior. When **1** was heated to 100 °C in toluene, DPC was produced in 30% yield based on PhO present (Eq. (2)). The $^{31}P\{^1H\}$-NMR spectrum of the resulting mixture showed that **1** was completely consumed whereas several phosphine-containing species including 32% based on palladium of $PdCl_2(PPh_3)_2$ were formed. Although precise mechanistic discussion is premature, three possible routes for the DPC formation are (a) disproportionation of **1** followed by decarbonylation and reductive elimination, (b) decarbonylation of **1** followed by transfer of phenoxide to another **1**, and (c) bimetallic reductive elimination of DPC between palladium phenoxide species and **1**.



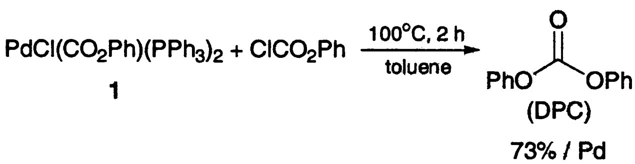
(2)

In the course of the thermolysis, chlorobenzene (7%/Pd), phenyl benzoate (18%/Pd), biphenyl (2%/Pd), and phenol (17%/Pd) were produced along with DPC. On the other hand, the thermolysis of $PdCl(CO_2Ph)(P(p\text{-tolyl})_3)_2$ (**3**) gave *p*-chlorotoluene, phenyl 4-methylbenzoate, 4,4′-dimethylbiphenyl, and phenol, in addition to DPC. Hence, the formation of chlorobenzene, phenyl benzoate, and biphenyl in Eq. (2) is assignable to the cleavage of the P–C bond in the PPh_3 ligand in **1** [24]. When the thermolysis was performed in the presence of PPh_3 (four equivalents), the DPC yield increased to 44% although the formation of chlorobenzene, phenyl benzoate, and biphenyl was observed again. PPh_3 possibly stabilizes the resulting unsaturated palladium(0) complexes. On the contrary, the thermolysis of **1** in the presence of CO (1 atm) produced DPC in 31% yield based on PhO present. Thus, the influence of CO on the DPC formation was small.

The reactivity of **1** toward electrophiles was also studied. When **1** was heated in the presence of methyl iodide (one equivalent), phenyl acetate and anisole were produced along with DPC in 58 and 4% yields, respectively (Eq. (3)). The formation of anisole suggests that the palladium phenoxide species is generated during the thermolysis [25]. On the other hand, an efficient DPC formation was observed upon heating of **1** with one equivalent of phenyl chloroformate (Eq. (4)). During the reaction, $PdCl_2(PPh_3)_2$ was the only observable palladium species as judged by $^{31}P\{^1H\}$-NMR.

The yield of $PdCl_2(PPh_3)_2$ was nearly quantitative based on palladium.

$$\underset{\mathbf{1}}{PdCl(CO_2Ph)(PPh_3)_2} + MeI \xrightarrow[\text{toluene}]{100^{\circ}C,\ 2\ h} MeCO_2Ph,\ MeOPh \quad \begin{array}{l} MeCO_2Ph\text{: 58\% / Pd} \\ MeOPh\text{: 4\% / Pd} \end{array} \qquad (3)$$



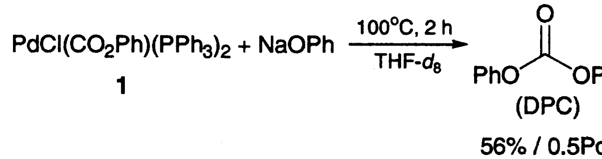
(4)

2.3. Reaction with phenoxide

The reactivity of **1** toward phenol (four equivalents) was examined in the presence of triethylamine (four equivalents) in toluene. However, no reaction proceeded at room temperature judged by $^{31}P\{^{1}H\}$- and ^{1}H-NMR spectroscopy. When the temperature was raised to 100 °C, DPC was formed in 28%, a similar yield obtained under simple thermolysis of **1**. In other words, the addition of phenol and amine did not promote the DPC formation.

The reaction of **1** with sodium phenoxide (one equivalent) was performed in THF-d_8 at −20 °C. The ^{1}H-, $^{13}C\{^{1}H\}$-, and $^{31}P\{^{1}H\}$-NMR data were consistent with the formation of **2** (Eq. (5)). It is noteworthy that DPC was not formed at this stage as judged by $^{13}C\{^{1}H\}$-NMR. Thus, the nucleophilic attack by phenoxide preferentially takes place on the palladium center rather than on the carbonyl group in **1**, resulting in the formation of **2**. Moreover, the reductive elimination of DPC from **2** is, if any, very slow at −20 °C. We attempted the isolation of **2**, but did not succeed due to its instability. When the reaction mixture was heated to 100 °C, DPC was produced in 56% yield (Eq. (6)). The DPC yield was higher than the yield for the simple thermolysis of **1**, but still not very high due to simultaneous occurrence of the decomposition of the PPh_3 ligand as mentioned earlier.

$$\underset{\mathbf{1}}{PdCl(CO_2Ph)(PPh_3)_2} + NaOPh \xrightarrow[\text{THF-}d_8]{-20^{\circ}C} \underset{\mathbf{2}}{Pd(OPh)(CO_2Ph)(PPh_3)_2} \qquad (5)$$



(6)

On the other hand, when the reaction using three equivalents of sodium phenoxide was conducted under otherwise identical conditions DPC was afforded only in 40% yield, which was rather lower than the yield with one equivalent of sodium phenoxide. Therefore, the influence of a nucleophilic attack by phenoxide to the carbonyl group of the phenoxycarbonyl ligand in **2** on the DPC formation seems small. These results suggest that in the oxidative carbonylation of phenol DPC is formed by the reductive elimination from $Pd(OPh)(CO_2Ph)L_2$ rather than the nucleophilic attack of phenoxide to Pd-CO_2Ph moiety. This is consistent with the previous finding that DPC is formed from palladium diphenoxide followed by carbonylation and reductive elimination [3].

In conclusion, we have synthesized the phenoxycarbonyl palladium complex **1** and elucidated the X-ray crystal structure. DPC was formed by the simple thermolysis of **1**, although the yield was not high due to the simultaneous occurrence of degradation of the PPh_3 ligand to chlorobenzene and phenyl benzoate. The reaction of **1** with sodium phenoxide at a low temperature resulted in the formation of a species assignable to **2**. Thus, the nucleophilic attack by phenoxide preferentially takes place on the palladium center rather than on the carbonyl group. On the other hand, a higher DPC yield than the simple thermolysis was given for the reaction of **1** with sodium phenoxide. DPC is considered to be produced via the reductive elimination from **2**. Because the yield of DPC was not improved by the presence of excess sodium phenoxide, the nucleophilic attack by phenoxide to the carbonyl group would not be involved.

3. Experimental

All manipulations were carried out under a purified Ar atmosphere using standard Schlenk and glovebox techniques. Solvents were purified by conventional means and were distilled immediately prior to use. Phenyl chloroformate, methyl iodide, triphenylphosphine, and tri-*p*-tolylphosphine were purchased from Tokyo Kasei Co. Sodium phenoxide was prepared by reacting phenol with sodium hydride. $Pd(PPh_3)_4$ and $Pd(P(p\text{-tolyl})_3)_4$ were prepared according to the literature [26]. The ^{1}H-, $^{13}C\{^{1}H\}$-, and $^{31}P\{^{1}H\}$-NMR spectra were recorded on a JEOL-LA400WB superconducting high-resolution spectrometer (400 MHz for ^1H). $^{31}P\{^1H\}$-NMR spectra were referenced to external 85% phosphoric acid. IR spectra were recorded on a Shimadzu FTIR-8500 spectrometer. The elemental analyses were carried out using a CE-EA 1110 automatic elemental analyzer. The reaction products were analyzed by GC using a capillary column: J&W Scientific DB-1 (60 m) on a Shimadzu GC-14A gas chromatograph equipped with a flame ionization detector (FID) using *o*-terphenyl as the internal standard. The GCMS analysis was performed using a Shimadzu GC-17A gas chromatograph connected to a QP-5000 mass spectrometer (EI 70 eV). The GC and GCMS analyses of the product solutions containing **1** were conducted after the solutions were mixed with excess 30% H_2O_2 and stirred for 2–3 h at room temperature (r.t.): The injection of a solution containing **1** alone in a GC or GCMS instrument brought about the production of DPC resulting from the decomposition of **1** in the injector port (200 °C). When excess 30% H_2O_2 was added to the solution of **1** followed by stirring for 2 h at room temperature, **1** was decomposed and no DPC formation was observed upon injection in the instrument.

3.1. Synthesis of $PdCl(CO_2Ph)(PPh_3)_2$ (1)

To a solution of $Pd(PPh_3)_4$ (1.07 g, 0.93 mmol) in toluene (60 ml) was added phenyl chloroformate (0.12 ml, 0.93 mmol). After stirring the reaction mixture for 1 h at room temperature, the solvent was evaporated. The resulting product was repeatedly washed with ether and dried under vacuum to give a pale yellow solid (0.72 g, 98% yield). Recrystallization from a THF–hexane solution at 4 °C gave yellow single crystals of **1**. ^1H-NMR (400 MHz, THF-d_8, 25 °C, ppm): δ 5.47 (m, 2H, *ortho-H*, CO_2Ph), 6.76 (m, 3H, *meta- and para-H*, CO_2Ph), 7.32–7.80 (m, 30H, PPh_3). $^{13}C\{^1H\}$-NMR (100.4 MHz, THF-d_8, 25 °C, ppm): δ 121.96, 124.27, 128.17, 154.04 (CO_2*Ph*), 128.96, 131.05, 132.74, 135.87 (P*Ph*$_3$), 182.18 (*C*O). $^{31}P\{^1H\}$-NMR (161.7 MHz, THF-d_8, 25 °C, ppm): δ 18.33 (s). IR (KBr, cm^{-1}): 1686 (ν_{CO}). Anal. Calc.: C, 65.58; H, 4.48; Cl, 4.50. Found: C, 64.94; H, 4.67; Cl, 4.92%.

$PdCl(CO_2Ph)(P(p\text{-tolyl})_3)_2$ (**3**) was synthesized in 82% yield as yellow crystalline solids as described for the synthesis of **1**, but using $Pd(P(p\text{-tolyl})_3)_4$ as a starting material. Complex **3** had a better solubility in ether than **1**. ^1H-NMR (400 MHz, THF-d_8, 25 °C, ppm): δ 2.33 (s, 18H, Me), 5.41 (m, 2H, *ortho-H*, CO_2Ph), 6.75 (m, 3H, *meta- and para-H*, CO_2Ph), 7.14 (d, 12H, *meta-H*, *p*-tolyl), 7.63 (m, 12H, *ortho-H*, *p*-tolyl). $^{31}P\{^1H\}$-NMR (161.7 MHz, THF-d_8, 25 °C, ppm): δ 14.68 (s).

3.2. Thermolysis

A solution of **1** (50 mg, 0.063 mmol) in toluene (5 ml) was heated to 100 °C and stirred at the same temperature for 2 h. The solution color quickly changed from yellow to dark brown. After cooling, *o*-terphenyl (50 mg) was added to the reaction mixture as the internal standard for GC analysis. Then excess 30% H_2O_2 was added to the product solution as mentioned above. The yield of DPC was 30% on 0.5 Pd by GC. The products were further identified using GCMS by the comparison of the retention time and fragmentation pattern with authentic samples. The thermolysis was also followed by $^{31}P\{^1H\}$-NMR. To an NMR tube (5 mm in diameter) containing **1** (20 mg, 0.025 mmol) was added toluene-d_8 (0.5 ml). The NMR tube was sealed under vacuum, and then heated at 100 °C for 24 h. After cooling, the $^{31}P\{^1H\}$-NMR spectrum was recorded at r.t. The $^{31}P\{^1H\}$-NMR showed that **1** was completely converted whereas $PdCl_2(PPh_3)_2$ was a major palladium species among several phosphine-containing species. The yield of $PdCl_2(PPh_3)_2$ was determined as follows. Because the solubility of $(PPh_3)_2PdCl_2$ in toluene is poor, the toluene was removed under vacuum after the thermolysis and the products were dissolved in $CDCl_3$. Then, the yield was measured by ^{31}P-NMR using $PMe(CH_2CH_2CF_3)_2$ sealed in a glass tube as the external standard. The yield of $PdCl_2(PPh_3)_2$ thus estimated was 32% based on Pd. The thermolysis of **1** in the presence of four equivalents of PPh_3 was carried out analogously. The yield of DPC was 44% on 0.5 Pd. The thermolysis of **1** in the presence of CO (1 atm) was also carried out analogously. The yield of DPC was 31% on 0.5 Pd.

3.3. Reaction with methyl iodide

To a toluene (5 ml) solution of **1** (50 mg, 0.063 mmol) was added one equivalent of methyl iodide (4.3 µl, 0.069 mmol) at room temperature. The reaction mixture was then heated to 100 °C and stirred for 2 h. The yields of phenyl acetate, anisole, and DPC determined by GC were 58% (on Pd), 4% (on Pd), and 9% (on 0.5 Pd), respectively.

3.4. Reaction with phenyl chloroformate

To a toluene (5 ml) solution of **1** (50 mg, 0.063 mmol) was added one equivalent of phenyl chloroformate (7.9 µl, 0.063 mmol). The reaction mixture was heated at 100 °C for 2 h. The yield of DPC on Pd was 73% based on GC. The reaction with phenyl chloroformate was also followed by $^{31}P\{^1H\}$-NMR. To an NMR tube (5 mm in diameter) containing **1** (20 mg, 0.025 mmol) were added toluene-d_8 (0.5 ml) and phenyl chloroformate (3.1 µl, 0.025 mmol). The mixture was heated at 100 °C for 2 h. The $^{31}P\{^1H\}$-NMR at room temperature revealed that $PdCl_2(PPh_3)_2$ was the only formed palladium species. The yield of $PdCl_2(PPh_3)_2$ estimated in a similar manner as the thermolysis of **1** was nearly quantitative based on Pd.

3.5. Reaction with phenol and triethylamine

In an NMR tube (5 mm in diameter), four equivalents of phenol (9.4 mg, 0.1 mmol) and four equivalents of triethylamine (14 µl, 0.10 mmol) were added to a toluene-d_8 (0.5 ml) solution of **1** (20 mg, 0.025 mmol). The $^{31}P\{^1H\}$- and ^1H-NMR spectra showed that no reaction proceeded at room temperature. The mixture was then heated at 100 °C for 2 h. The yield of DPC on 0.5 Pd was 28% based on GC using *o*-terphenyl (20 mg) as the internal standard. The same yield was obtained for the reaction in a Schlenk tube.

3.6. Reaction with sodium phenoxide

In an NMR tube (5 mm in diameter), THF-d_8 (0.5 ml) was vacuum-transferred into a mixture of **1** (20 mg, 0.025 mmol) and one equivalent of sodium phenoxide (2.9 mg, 0.025 mmol). The NMR tube was sealed under vacuum with the mixture frozen. When the mixture was thawed at −20 °C, the color of the solution instantly changed from yellow to orange. The $^{31}P\{^1H\}$-NMR spectrum measured at −20 °C showed the instant disappearance of **1** with concurrent growth of a new singlet at δ 9.50 ppm together with a very weak and broad signal around δ 16–20 ppm. The ^1H- and $^{13}C\{^1H\}$-NMR spectra revealed the formation of **2**. In the ^1H-NMR spectrum, another phenyl group, which may arise from the phosphine ligands with δ 16–20 ppm in $^{31}P\{^1H\}$-NMR, was observed at δ 7.0–7.2 ppm. **2**: ^1H-NMR (400 MHz, THF-d_8, −20 °C, ppm): δ 5.27 (m, 2H, *ortho-H*, CO_2Ph), 5.74 (t, 1H, *para-H*, OPh), 5.93 (d, 2H, *ortho-H*, OPh), 6.16 (t, 2H, *meta-H*, OPh), 6.76 (m, 3H, *meta- and para-H*, CO_2Ph), 7.29–7.73 (m, 30H, PPh_3). $^{13}C\{^1H\}$-NMR (100.4 MHz, THF-d_8, −20 °C, ppm): δ 153.67 (*ipso-C* CO_2Ph), 167.88 (*ipso-C* OPh) 181.74 (*C*O). The other $^{13}C\{^1H\}$-NMR peaks due to **2** were not assignable because of contamination of unidentified species. $^{31}P\{^1H\}$-NMR (161.7 MHz, THF-d_8, −20 °C, ppm): δ 9.50 (s). The reaction mixture was then heated at 100 °C for 2 h. The yield of DPC determined by GC using *o*-terphenyl (20 mg) was 56% on 0.5 Pd. The reaction of **1** (20 mg, 0.025 mmol) with three equivalents of sodium phenoxide (9.2 mg, 0.079 mmol) was carried out analogously. The yield of DPC was 40% on 0.5 Pd.

3.7. X-ray crystallography

Data collection and refinement parameters for **1** are summarized in Table 2. The data were collected on a Rigaku AFC 7R diffractometer at 183 K using graphite-monochromated Mo–K_α 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.

Table 2
Crystallographic data for **1**

Formula	$C_{43}H_{35}P_2O_2ClPd$
Formula weight	787.55
Crystal system	Monoclinic
Space group	$P2_1/n$ (No. 14)
a (Å)	9.449(6)
b (Å)	32.637(7)
c (Å)	12.426(5)
β (°)	100.01(4)
V (Å^3)	3773(2)
Z	4
μ (Mo–K_α) (cm^{-1})	6.83
Number of measured reflections	9355
Number of unique reflections	9065
R_{int}	0.016
Number of observations ($I > 2\sigma(I)$)	7170
Number of variables	442
R [a]	0.044
R_w [b]	0.062

[a] $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$.
[b] $R_w = \{\Sigma w(|F_o|-|F_c|)^2/\Sigma wF_o^2\}^{1/2}$.

4. Supplementary material

Crystallographic data for the structural analysis of complex **1** have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 200708. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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