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Note

Phenoxide-assisted P–C bond cleavage in $PdCl_2(PPh_3)_2$ under very mild conditions

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Abstract

$PdCl_2(PPh_3)_2$ reacted with NaOAr (Ar = Ph, *p*-tolyl) at 0 °C to afford $PdCl(Ph)(PPh_3)_2$, instead of $PdCl(OAr)(PPh_3)_2$, in 12–16% isolated yields based on Pd. The structure was confirmed by NMR and X-ray crystallography. GC–MS analysis of the reaction solution revealed that $OPPh_2(OAr)$, $OPPh(OAr)_2$, and $OP(OAr)_3$ are formed, while NMR studies indicated that $PdCl(Ph)(PPh_3)_2$ is produced when $PdCl(OAr)(PPh_3)_2$ decomposes. The reaction of $PdCl_2(PPh_3)_2$ with $Bu_3Sn(OC_6H_4\text{-}p\text{-}OMe)$ also gave $PdCl(Ph)(PPh_3)_2$ in 8% isolated yield. These results suggest that $PdCl(OAr)(PPh_3)_2$ is highly labile and the aryloxy ligand exchanges with the phenyl groups in triphenylphosphine even under very mild conditions.

Keywords: P–C bond cleavage; Triphenylphosphine; $PdCl_2(PPh_3)_2$; $PdCl(Ph)(PPh_3)_2$; Phenoxide; Aryloxy-aryl exchange

1. Introduction

Decomposition of tertiary phosphine ligands is an important phenomenon relevant to catalyst degradation or byproduct formation in homogeneous catalysis by phosphine-ligated transition metal complexes [1,2]. P–C bond cleavage in Pd triphenylphosphine complexes such as $PdCl_2(PPh_3)_2$ and $Pd(PPh_3)_4$ is especially important since these complexes are used in numerous reactions that require Pd(II) and Pd(0)-catalyzed processes. Examples include C–C bond forming reactions such as Stille coupling, Suzuki coupling, Heck arylation, Sonogashira coupling, etc. [3]. During our attempts to synthesize PPh_3-ligated Pd phenoxide complexes by reacting $PdCl_2(PPh_3)_2$ with NaOPh, we found that the P–C bond in $PdCl_2(PPh_3)_2$ is easily cleaved even at 0 °C. Herein, we report an aryloxide-assisted transfer of the phenyl group bound to P to Pd in $PdCl_2(PPh_3)_2$ under very mild conditions.

2. Results and discussion

Our interest in the mechanism of diphenyl carbonate formation in the Pd-catalyzed oxidative carbonylation of phenol led us to synthesize a Pd phenoxide complex, $PdX(OPh)L_2$ (X = halogen), and investigate its reactivity [4]. Thus, we attempted to prepare a Pd chloro(phenoxy) complex, $PdCl(OPh)(PPh_3)_2$, by reacting $PdCl_2(PPh_3)_2$ with NaOPh.

When $PdCl_2(PPh_3)_2$ reacted with 1 equiv. of NaOPh in THF at 0 °C, the solution color instantly changed from yellow to orange and then turned dark brown/black. After stirring for 2 h, the work-up using the procedure described in Section 3 provided a brown powder. This complex exhibited a singlet at δ 23.2 ppm in ^{31}P NMR. Based on ^1H NMR, the complex contained a phenyl group (δ 6.2–6.6 ppm) and two triphenylphosphines (δ 7.2–7.5 ppm). These results are consistent with the formation of $PdCl(OPh)(PPh_3)_2$. However, the X-ray structural analysis of the single crystals obtained from the complex revealed that it was not $PdCl(OPh)(PPh_3)_2$, but $PdCl(Ph)(PPh_3)_2$ [5]. The ^1H and ^{31}P NMR spectra were remeasured by dissolving the single crystals in THF-d_8 and were in agreement

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with the spectra from the reaction mixture of $PdCl_2(PPh_3)_2$ and NaOPh in THF-d_8 at room temperature (vide infra). The isolated yield of $PdCl(Ph)(PPh_3)_2$ based on Pd was 16% (Scheme 1).

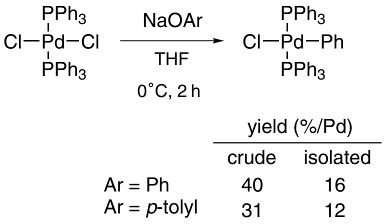
An analogous reaction using NaO(*p*-tolyl) also resulted in the formation of $PdCl(Ph)(PPh_3)_2$ in 12% isolated yield based on Pd, confirming that the phenyl group bound to Pd in $PdCl(Ph)(PPh_3)_2$ originated from the triphenylphosphine ligand and not from phenoxide (Scheme 1) [6]. The GC–MS of the reaction solution of $PdCl_2(PPh_3)_2$ and NaO(*p*-tolyl) contained $OPPh_2$(O-*p*-tolyl), OPPh(O-*p*-tolyl)$_2$, and OP(O-*p*-tolyl)$_3$, in addition to PPh_3 and $OPPh_3$. This suggests that the aryloxy ligand, which would have to coordinate to Pd, exchanges with the phenyl groups in the triphenylphosphine ligand under very mild conditions (Scheme 2). The formations of OPPh(O-*p*-tolyl)$_2$ and OP (O-*p*-tolyl)$_3$ indicate multiple aryloxy–phenyl exchanges. The reason that the aryloxyphosphines were detected on the GC–MS as their oxides may be because the aryloxyphosphines were oxidized by air in the injector port (200 °C). In fact, when PPh_2(O-*p*-tolyl) was synthesized and analyzed by GC–MS, PPh_2(O-*p*-tolyl) was partly detected as $OPPh_2$(O-*p*-tolyl). Another plausible reason is the pyrolysis of the phosphonium salts in the GC–MS injector port [7]. The intermediacy of a phosphonium salt in the aryloxy–phenyl exchange will be discussed later.

To confirm that the Pd aryloxy complex formed in the initial stage of the aryloxy–phenyl exchange, the reaction of $PdCl_2(PPh_3)_2$ and NaO(*p*-tolyl) in THF-d_8 was monitored by low temperature NMR spectroscopy. A single peak immediately appeared at δ 19.0 ppm in the ^{31}P NMR spectrum when the reaction was allowed to start at −40 °C by thawing the mixture. Note that this peak is not attributed to $PdCl_2(PPh_3)_2$. Since the solubility of $PdCl_2(PPh_3)_2$ in THF-d_8 at −40 °C is extremely poor, the ^{31}P NMR peak due to $PdCl_2(PPh_3)_2$ is, if any, very small. In addition to triphenylphosphine (δ 7.3–7.7 ppm) and NaO(*p*-tolyl) (δ 6.4–6.7 ppm), the ^{1}H NMR spectrum had a new *p*-tolyl group at δ 6.2–6.3 ppm. Judging from the integrated intensity ratio of the new *p*-tolyl group to the triphenylphosphine, the species at δ 19.0 ppm in ^{31}P NMR is probably PdCl(O(*p*-tolyl))$(PPh_3)_2$ formed by the reaction of slightly dissolved $PdCl_2(PPh_3)_2$ and NaO(*p*-tolyl). Upon stepwise increasing the temperature every 2 h to 0 °C and 20 °C, the ^{31}P NMR peak assigned to PdCl(O(*p*-tolyl))$(PPh_3)_2$ (δ 18.0 ppm at 20 °C) gradually diminished with the concomitant appearance and growth of the peak due to $PdCl(Ph)(PPh_3)_2$ (δ 23.2 ppm at 20 °C). During the reaction several peaks due to P-containing species other than $PdCl_2(PPh_3)_2$ (δ 22.7 ppm at 20 °C) were also observed. When the temperature was further increased to 40 °C, the peak assigned to PdCl(O(*p*-tolyl))$(PPh_3)_2$ completely disappeared and the peak due to $PdCl(Ph)(PPh_3)_2$ became the major one. Other weak peaks due to several P-containing species were also present. These results suggest that $PdCl(Ph)(PPh_3)_2$ is produced during the decomposition of PdCl(O(*p*-tolyl))$(PPh_3)_2$, the initial product in the reaction of $PdCl_2(PPh_3)_2$ and NaO(*p*-tolyl) (Scheme 2).

The reaction of $PdCl_2(PPh_3)_2$ with 1 equiv. of Bu_3Sn-(OC_6H_4-*p*-OMe) instead of NaOAr was also attempted in toluene at 80 °C in order to obtain PdCl(OC_6H_4-*p*-OMe)$(PPh_3)_2$. However, $PdCl(Ph)(PPh_3)_2$ was the only isolated Pd complex in 8% yield (Scheme 3). The result also indicates that PdCl(OC_6H_4-*p*-OMe)$(PPh_3)_2$ is labile and the aryloxy–phenyl exchange readily occurs, even if PdCl(OC_6H_4-*p*-OMe)$(PPh_3)_2$ is generated during the reaction.

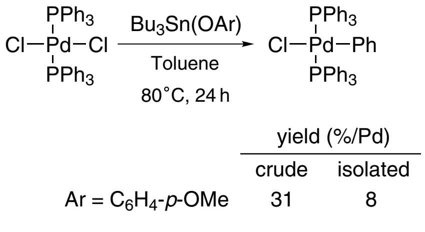
Although it is often reported that in Pd complexes the aryl [8], alkyl [9], or acetoxy [10] ligand exchanges with the aryl of the triarylphosphine ligand, to our best knowledge, this is the first report on the aryloxy–aryl exchange mediated by Pd [11,12]. It is noteworthy that the Pd-mediated aryloxy–aryl exchange reported here proceeds under even milder conditions than the usual aryl–aryl or alkyl–aryl exchange.

The three possible mechanisms for the aryloxy–aryl exchange are roughly classified: oxidative addition of arylphosphines involving *ortho*-metalation, nucleophilic attack of aryloxy groups on coordinated phosphines, and aryl transfer from the phosphine ligands via phosphonium species (Scheme 4) [1a]. The reaction between $PdCl_2$-$(P(p\text{-tolyl})_3)_2$ and NaOPh formed *para*-tolyl Pd complex,



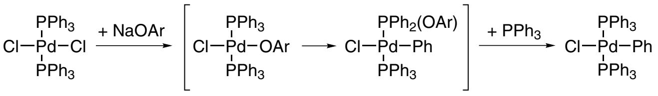
	yield (%/Pd)	
	crude	isolated
Ar = Ph	40	16
Ar = *p*-tolyl	31	12

Scheme 1.

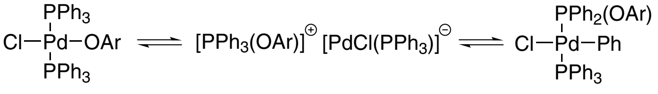


	yield (%/Pd)	
	crude	isolated
Ar = C_6H_4-*p*-OMe	31	8

Scheme 3.



Scheme 2.



Scheme 4.

which is inconsistent with the *ortho*-metalation mechanism. On the other hand, it is possible that the aryloxy–aryl exchange proceeds via a phosphonium salt such as $[PPh_3(OAr)][PdCl(PPh_3)]$, since these phosphonium salts are fairly stable [13].

Numerous Pd aryloxides with phosphine ligands, such as monodentate PMe_3, PCy_3, $PMePh_2$, and bidentate DPPM (bis(diphenylphosphino)methane), have been synthesized and characterized [14]. For instance, $[Pd(H)(OPh)(PCy_3)_2]\cdot PhOH$ is synthesized by reacting $Pd(PCy_3)_2$ with phenol at room temperature [14e], and $Pd(OAr)_2(PMe_3)_2$ ($Ar = C_6H_4$-*p*-NO_2) is obtained from Pd(styrene)$(PMe_3)_2$ and CF_3CO_2Ar at room temperature [14b]. There are also a few reports on the synthesis of PPh_3-ligated Pd aryloxides [15,16], but the structural evidence is quite weak [17]. Strengthening the coordination by electron-donating alkylphosphines or bidentate phosphines, and stabilizing the complexes by introducing electron-withdrawing substituents onto the aryloxy groups may enable these aryloxide complexes to be isolated. The reason $PdCl(OPh)(PPh_3)_2$ is highly labile remains unknown. A large P–O bond energy may be related to the facile aryloxy–aryl exchange.

In summary, we have demonstrated that reacting $PdCl_2(PPh_3)_2$ with NaOAr under very mild conditions yields $PdCl(Ph)(PPh_3)_2$. It is likely that the reaction proceeds via an intermediate, $PdCl(OAr)(PPh_3)_2$, and subsequent aryloxy–phenyl exchange that involves P–C bond cleavage.

3. Experimental

All manipulations were conducted in a purified Ar atmosphere using standard Schlenk and glovebox techniques. Solvents were dried in a typical manner and distilled prior to use. All other reagents were used without further purification. NaOAr (Ar = Ph, *p*-tolyl) was prepared by reacting the corresponding phenol with sodium hydride. $PdCl_2(PPh_3)_2$ and $PdCl_2(P(p\text{-tolyl})_3)_2$ were prepared by reacting $PdCl_2(PhCN)_2$ with PPh_3 and $P(p\text{-tolyl})_3$, respectively. PPh_2(O-*p*-tolyl) was prepared by reacting PPh_2Cl with Na(O-*p*-tolyl). $Bu_3Sn(OC_6H_4$-*p*-OMe) was prepared according to the literature [18]. The ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on a JEOL LA400 WB spectrometer (400 MHz for ^1H). $^{31}P\{^1H\}$ NMR spectra were referenced to external 85% phosphoric acid. The reaction products were analyzed by a Shimadzu GC-17A gas chromatograph connected to a QP-5000 mass spectrometer (70 eV EI) (GC–MS) using a capillary column (J&W Scientific, DB-1, 30 m).

3.1. Reaction of $PdCl_2(PPh_3)_2$ with NaOAr

3.1.1. Schlenk tube reaction

To a THF (5 mL) solution of $PdCl_2(PPh_3)_2$ (0.20 g, 0.28 mmol) was added NaOPh (0.035 g, 0.30 mmol) at 0 °C. After stirring the reaction mixture for 2 h at 0 °C, the solvent was evaporated. The residue was extracted with toluene (5 mL) at 0 °C, filtered, and fully evaporated to dryness. The resulting product was washed with ether (2 × 5 mL) and dried under a vacuum to give the crude product, $PdCl(Ph)(PPh_3)_2$, as a brown powder (0.085 g, 40% yield based on Pd). Recrystallization from a THF–hexane solution at room temperature gave a brown crystalline solid of $PdCl(Ph)(PPh_3)_2$ (0.034 g, 16% yield on Pd). ^1H NMR (400 MHz, THF-d_8, 25 °C, ppm): δ 6.18 (m, 2H, *meta-H*, Pd–Ph), 6.30 (m, 1H, *para-H*, Pd–Ph), 6.64 (d, 2H, *ortho-H*, Pd–Ph), 7.20–7.54 (m, 30H, PPh_3). $^{31}P\{^1H\}$ NMR (161.7 MHz, THF-d_8, 25 °C, ppm): δ 23.2 (s). The NMR data is consistent with the literature [5].

The reaction of $PdCl_2(PPh_3)_2$ (0.20 g, 0.28 mmol) and NaO(*p*-tolyl) (0.037 g, 0.28 mmol) was analogously conducted to give the crude product, $PdCl(Ph)(PPh_3)_2$ (0.065 g, 31% yield on Pd). Recrystallization gave $PdCl(Ph)(PPh_3)_2$ (0.025 g, 12% yield on Pd).

3.1.2. NMR tube reaction

In an NMR tube (5 mm in diameter), THF-d_8 (0.5 mL) was vacuum-transferred into a mixture of $PdCl_2(PPh_3)_2$ (20 mg, 0.028 mmol) and 1 equiv. of NaO(*p*-tolyl) (3.7 mg, 0.028 mmol). The NMR tube was sealed under a vacuum while the mixture was frozen. When the mixture was thawed at −40 °C, the solution was orange. The $^{31}P\{^1H\}$ and ^1H NMR spectra were monitored for 1 h at −40 °C, where the peaks assigned to PdCl(O(*p*-tolyl))-$(PPh_3)_2$ appeared. ^1H NMR (400 MHz, THF-d_8, −40 °C, ppm): δ 2.12 (s, 3H, Me), 6.21 (d, 2H, *meta-H*, *p*-tolyl), 6.33 (d, 2H, *ortho-H*, *p*-tolyl), 7.32–7.68 (m, 30H, PPh_3). $^{31}P\{^1H\}$ NMR (161.7 MHz, THF-d_8, −40 °C, ppm): δ 19.0 (s). Then the temperature was increased, stepwise, every 2 h to 0 and 20 °C. The temperature was finally increased to 40 °C. The $^{31}P\{^1H\}$ and ^1H NMR spectra were periodically recorded throughout the reaction.

3.2. Reaction of $PdCl_2(PPh_3)_2$ with $Bu_3Sn(OC_6H_4$-*p*-OMe)

Toluene (5 mL) and $Bu_3Sn(OC_6H_4$-*p*-OMe) (0.12 g, 0.29 mmol) were added to a Schlenk tube containing $PdCl_2(PPh_3)_2$ (0.20 g, 0.28 mmol). After stirring for 24 h at 80 °C, the reaction mixture was fully evaporated to dryness. The resulting product was washed with ether (2 × 5 mL) and dried under a vacuum to give the crude product, $PdCl(Ph)(PPh_3)_2$ (0.065 g, 31% yield on Pd). Recrystallization from a THF–hexane solution at room temperature gave $PdCl(Ph)(PPh_3)_2$ (0.017 g, 8% yield on Pd).

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