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Note

Stepwise selective oxidation of tris(2-(diphenylphosphino)ethyl)phosphine on thiolato palladium(II) complexes

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Abstract

One of the equatorially coordinated terminal phosphorus atoms of tris(2-(diphenylphosphino)ethyl)phosphine (pp_3) ligand on the five-coordinate trigonal-bipyramidal palladium(II) complex, $[Pd(4\text{-}Cltp)(pp_3)](BF_4)$ (4-Cltp = 4-chlorothiophenolate), was selectively oxidized by photolysis to form the four-coordinate square-planar complex. Further selective oxidation of another coordinated terminal phosphorus atom proceeded quantitatively by the substitution reaction with 4-chlorothiophenolate. The solid state structures of these stepwise-oxidized square-planar complexes were determined by X-ray crystal structure analyses, and the structures of the starting trigonal-bipyramidal and the oxidized complexes in solution have been characterized by ^{31}P NMR spectroscopy.

Keywords: Stepwise oxidation; Tetradentate phosphine ligands; Photolysis; Thiolato ligands; Trigonal-bipyramidal palladium(II) complexes

1. Introduction

Selective chemical modification of compounds is one of the important aims of the synthetic studies. Because donor atoms, which are usually reactive sites, can be protected by coordination to metal ions, the partial dissociation of multidentate ligands in the intermediate or under the equilibrium between two different coordination numbers can be quite useful for the selective modification. Recently, it was found that the palladium(II) complexes with the tetradentate phosphine ligand, tris(2-(diphenylphosphino)ethyl)phosphine (pp_3), form the stable five-coordinate trigonal-bipyramidal geometry, $[PdX(pp_3)]^{2+\text{ or }+}$ (X = halide ions [1], thiolates [2], acetonitrile [3]), comparable to the four-coordinate square-planar geometry with the terdentate phosphine ligand, $[PdX(p_3)]^{2+\text{ or }+}$, ($p_3$ = bis(2-(diphenylphosphino)ethyl)phenylphosphine), with the same monodentate ligands X [4,5]. Taking account of the comparable stability of the two different coordination numbers, we have investigated the selective oxidation reaction of one phosphino group of the pp_3 ligand on the five-coordinate palladium(II) complex expecting that the oxidation is terminated by forming the four-coordinate one. Furthermore, we have examined the further oxidation of the coordinated phosphino group on the square-planar complex by the attack of the entering ligand. In this work, we used 4-chlorothiophenolate (4-Cltp) as the entering and bound X ligands because thiolates have relatively strong π donating ability to dissociate the neighboring coordinated phosphino group and the steric and electronic effects of the entering and bound ligands can be controlled by change in their substituent groups.

2. Experimental

2.1. Reagents

Chloroform (Wako, ∞ pure) was dried over activated 4A Molecular Sieves. Tris(2-(diphenylphosphino)

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ethyl)phosphine (pp_3, Aldrich), tetrakis(acetonitrile) palladium(II) tetrafluoroborate (Aldrich), and 4-chlorothiophenol (H4-Cltp, Wako) were used for preparation of palladium(II) complexes without further purification.

The sodium 4-chlorothiophenolate was prepared by neutralization of acetonitrile solution of 4-chlorothiophenol with 0.5 M aqueous NaOH under a nitrogen atmosphere. The reaction solution was concentrated to give the white salt. *Anal.* Calc. for $C_6H_4NaSCl \cdot 3H_2O$: C, 32.66; H, 4.57; N, 0.00%. Found: C, 32.75; H, 4.25; N, 0.00%. ^1H NMR (CD_3CN): δ 6.80 and 7.20 (AB system, $J = 8.4$ Hz, Ph), 3.17 (s, H_2O).

2.2. Preparation of complexes

2.2.1. [Pd(4-Cltp)(pp$_3$)](BF$_4$) (**1**)

To a saturated solution of $[Pd(pp_3)](BF_4)_2$ [3] (0.69 g, 0.73 mmol) in acetonitrile was added 4-chlorothiophenol (0.11 g, 0.76 mmol) and the solution was neutralized by adding 0.5 M aqueous NaOH. To the resultant deep red solution was added ethanol and water to give red crystals. The crystals were collected by filtration and air-dried. Yield: 0.64 g (87%). *Anal.* Calc. for $C_{48}H_{46}BF_4P_4SClPd$: C, 57.22; H, 4.60; N, 0.00%. Found: C, 57.20; H, 4.56; N, 0.00%. $^{31}P\{^1H\}$NMR ($CHCl_3$): δ 31.1 (d, 3P, terminal), 133.9 (q, 1P, center); $J_{P–P} = 8.3$ Hz. UV–Vis (in $CHCl_3$): λ_{max}/nm(log(ε/mol^{-1} kg cm^{-1})) 541 (3.51), 430 (3.90sh).

2.2.2. [Pd(4-Cltp)(pp$_3$O)](BF$_4$) (**2**)

A red solution of **1** (0.11 g, 0.11 mmol) in acetonitrile (1 dm^3) was stirred under a luminescent lamp for five days. The resultant yellow solution was concentrated to ≈5 cm^3. Yellow crystals were obtained by adding ethanol and water. Yield: 0.064 g (54%). *Anal.* Calc. for $C_{48}H_{46}BOF_4P_4SClPd \cdot C_2H_5OH \cdot H_2O$: C, 55.14; H, 4.99; N, 0.00%. Found: C, 54.88; H, 4.56; N, 0.00%. $^{31}P\{^1H\}$NMR ($CHCl_3$): δ 32.3 (d, 2P, oxide), 47.6 (d, 2P, terminal), 107.0 (dt, 1P, center); $J_{P(center)–P(oxide)} =$ 33.1 Hz, $J_{P(center)–P(terminal)} = 16.5$ Hz. UV–Vis (in $CHCl_3$): λ_{max}/nm (log(ε/mol^{-1} kg cm^{-1})) 431 (3.77), 360 (4.21sh).

The single crystals were obtained by recrystallization from chloroform by adding ethanol and water.

2.2.3. [Pd(4-Cltp)$_2$(pp$_3$O$_2$)] (**3**)

To a solution of **1** (0.094 g, 0.093 mmol) in acetonitrile (15 cm^3) was added 4-chlorothiophenol (0.026 g, 0.18 mmol) and 0.5 M aqueous NaOH (0.35 cm^3). The deep red solution was stirred under a luminescent lamp for several days to give the yellow solution that was then concentrated to dryness. The obtained yellow solid was dissolved in a minimum amount of chloroform and allowed to stand under vapor of diethylether to give tiny crystals. Yield: 0.070 g (69%). *Anal.* Calc. for $C_{54}H_{50}O_2P_4S_2Cl_2Pd$: C, 59.15; H, 4.60; N, 0.00%. Found: C, 58.98; H, 4.54; N, 0.00%. $^{31}P\{^1H\}$NMR ($CHCl_3$): δ 32.1 (d, 2P, oxide), 58.0 (d, 1P, terminal), 67.5 (td, 1P, center); $J_{P(center)–P(oxide)} = 47.9$ Hz, $J_{P(center)–P(terminal)} = 12.7$ Hz. It was confirmed by the ^1H NMR measurements that the diethylether in the crystals is volatile. UV–Vis (in $CHCl_3$): λ_{max}/nm (log(ε/mol^{-1} kg cm^{-1})) 450 (3.66sh), 406 (3.71).

The single crystals of **3** were obtained by growing the tiny crystals in the mother liquor under vapor of diethylether.

2.3. X-ray structure analysis

The crystal of complex **2** was sealed in a Lindemann glass-capillary tube with the mother liquor and the crystal of **3** was mounted on the glass fiber with epoxy. The X-ray diffraction measurements were performed on a Mac Science MXC3 diffractometer with Mo Kα radiation. The unit-cell parameters and orientation matrix were determined by a least-squares refinement of independent 18 reflections collected in the ranges of $21.4° < 2\theta < 24.4°$ for **2** and $19.0° < 2\theta < 32.2°$ for **3**, respectively. Data collection was performed with the θ–2θ scan mode with three standard reflections measured after every 100 scans, which showed no significant decay. An empirical absorption (Ψ scan) correction was applied. The solution and refinement were carried out using CRYSTAN-GM (version 6.3.3) [6]. The structures were solved by direct methods using the programs of sir 92 [7]. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were included in the calculated positions (C–H = 0.96 Å). The atomic scattering factors were taken from [8]. The crystallographic data are summarized in Table 1.

2.4. Measurements

The ^{31}P and ^1H NMR spectra were recorded on a JEOL JNM-A400 FT-NMR spectrometer. In order to determine the chemical shifts of the ^{31}P NMR, a 3 mm o.d. NMR tube containing the sample solution was coaxially mounted in a 5 mm o.d. NMR tube containing deuterated water and phosphoric acid as a lock solvent and a reference, respectively. The electronic absorption spectra were recorded on a Perkin–Elmer Lambda 19 spectrophotometer. The reactions from **1** to **2** and from **2** to **3** were followed by the absorption and ^{31}P NMR spectral changes, and the wavelength of light for irradiation experiments was controlled by the spectrophotometer or sharp-cut filters, Shiguma-Koki SCF-50S-52Y and UTF-50S-34U and 30U (transmission $\lambda > 520$, 340, and 300 nm, respectively).

Table 1
Crystallographic data for $\mathbf{2}\cdot C_2H_5OH\cdot H_2O$ and $\mathbf{3}\cdot (C_2H_5)_2O$

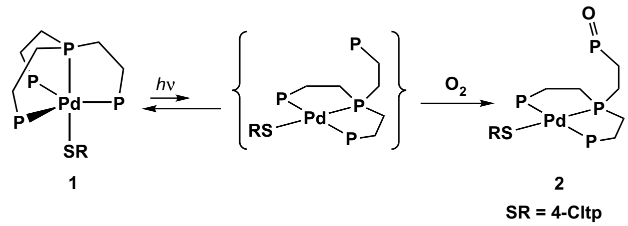
Compound	$\mathbf{2}\cdot C_2H_5OH\cdot H_2O$	$\mathbf{3}\cdot (C_2H_5)_2O$
Empirical formula	$C_{50}H_{54}BO_3F_4P_4SClPd$	$C_{58}H_{60}O_3P_4S_2Cl_2Pd$
Formula weight	1087.62	1170.47
Temperature (K)	298	298
Crystal size (mm)	0.80 × 0.40 × 0.30	0.60 × 0.15 × 0.15
Crystal system	monoclinic	triclinic
Space group	$P2_1/a$	$P\bar{1}$
a (Å)	31.25(2)	14.104(7)
b (Å)	15.349(8)	16.861(5)
c (Å)	10.64(2)	12.277(8)
α (°)	93.25(8)	95.63(4)
V (Å^3)	5092(10)	2775(2)
Z	4	2
D_{calc} (g cm^{-3})	1.42	1.40
μ (cm^{-1})	0.718	0.648
R^a,$R_w{}^b$	0.99, 0.116	0.086, 0.097

[a] $R = \sum ||F_o| - |F_c|| / \sum |F_o|$.

[b] $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$. $w = (\sigma^2(F_o) + 0.001F_o^2)^{-1}$.

3. Results and discussion

The ^{31}P NMR spectrum of **1** in chloroform (see Section 2 and Scheme 1) exhibits two signals at 31.1 and 133.9 ppm with weak coupling to each other assigned to the three equivalent terminal phosphorus atoms in the equatorial position for the former and the central phosphorus atom in the axial position for the latter indicating the trigonal-bipyramidal geometry with C_3 symmetry. The electronic absorption spectrum of **1** in chloroform (see Section 2) is also consistent with the five-coordinate trigonal-bipyramidal geometry showing two d–d absorption bands in the visible region assigned to the transitions from $^1A_1{}'$ to $^1E'$ and $^1E''$ [1,9]. These NMR and absorption spectral behaviors are quite similar to those of [Pd(pt)(pp$_3$)](BF$_4$) (pt = 1-propanethiolate) [2]. The perspective views of the complex cation of **2** and complex molecule of **3** are displayed in Figs. 1 and 2, respectively. The complex **2** has the square-planar structure where the dissociated terminal phosphorus atom is oxidized. For the complex **3**, the coordination of another thiolate is accompanied by the oxidation of another terminal phosphorus atom. The ^{31}P NMR spectra of **2** and **3** in chloroform (see Section 2 and Scheme 2) are also consistent with the square-planar structure in the crystal exhibiting three signals corresponding to the oxidized free phosphorus atoms with coupling to the central phosphorus atom (33.1 ppm for **2** and 32.1 ppm for **3**) and the coordinated terminal and central phosphorus atoms with coupling to each other (47.6 and 107.0 ppm for **2** and 58.0 and 67.5 ppm for **3**, respectively).



Scheme 1. Oxidation reaction of **1** to **2**.

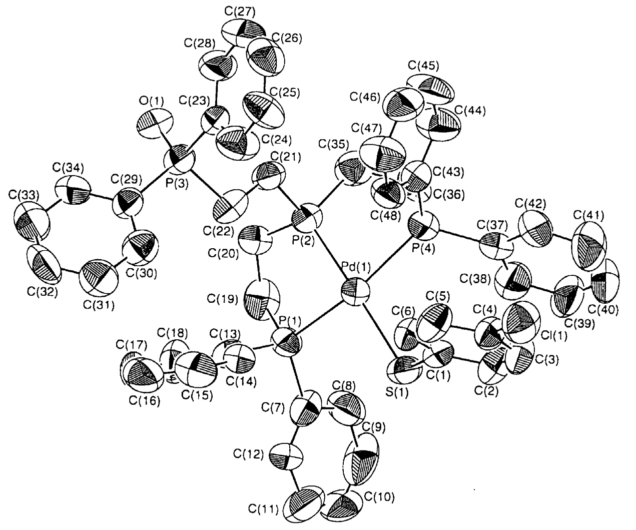


Fig. 1. ORTEP diagram of complex cation of **2**.

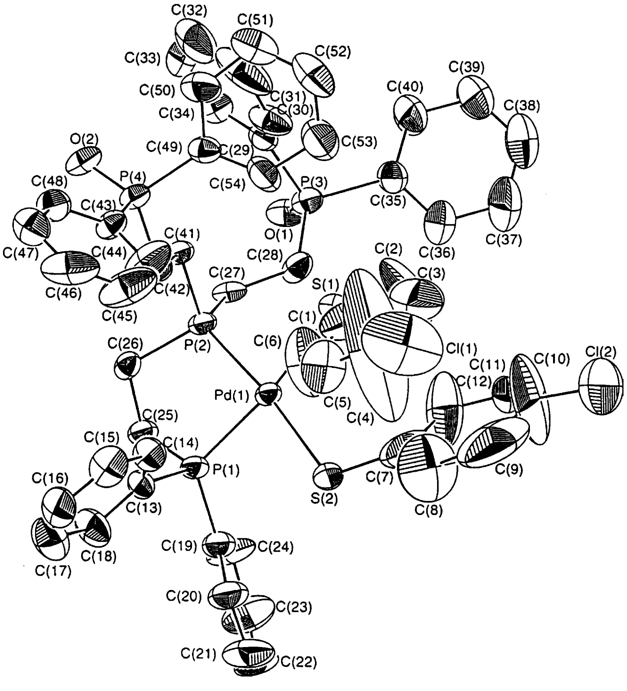
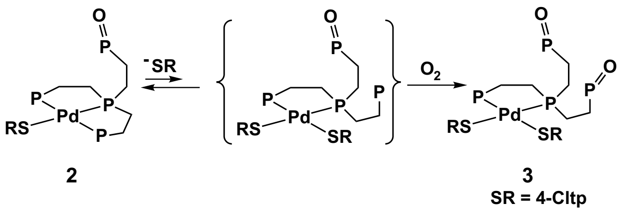


Fig. 2. ORTEP diagram of **3**.

It was confirmed by the ^{31}P NMR and absorption spectral measurements that the complex **1** was oxidized to form the complex **2** quantitatively in acetonitrile on exposure to visible light by using a luminescent lamp



Scheme 2. Oxidation reaction of **2** to **3**.

Table 2
Selected bond distances (Å) and angles (°) for **2** and **3**

Pd1–S1	2.349(8)	Pd1–S1	2.364(6)
Pd1–P1	2.302(8)	Pd1–S2	2.361(6)
Pd1–P2	2.266(7)	Pd1–P1	2.271(6)
Pd1–P4	2.322(7)	Pd1–P2	2.277(5)
S1–Pd1–P1	91.5(3)	S1–Pd1–S2	98.3(3)
S1–Pd1–P4	100.3(3)	S1–Pd1–P2	88.9(2)
P1–Pd1–P2	84.9(3)	S2–Pd1–P1	87.8(2)
P2–Pd1–P4	82.3(3)	P1–Pd1–P2	85.0(2)

with a sharp-cut filter SCF-50S-52Y ($\lambda > 520$ nm) and the spectrophotometer (irradiation $\lambda = 535$–540 nm) but no reaction proceeded in the dark or in the deoxygenated solution. Considering the complex **2** was similarly formed in chloroform, which is non-coordinating solvent, the selective oxidation of one terminal phosphorus atom of pp_3 proceeds via the photolysis of the coordinated equatorial phosphorus atom of **1** followed by the irreversible oxidation (Scheme 1). Further oxidation of **2** to **3** in acetonitrile did not proceed by photolysis, but quantitatively by addition of excess sodium 4-chlorothiophenorate. It is possible that another terminal phosphorus atom of **2** was dissociated by the substitution reaction with 4-chlorothiophenorate followed by the irreversible oxidation to give **3** (Scheme 2). The bond distance for the terminal phosphorus atom of **3** (Pd–P1 = 2.271 Å) is obviously shorter than those of **2** (Pd–P1 = 2.302 Å and Pd–P3 = 2.322 Å) due to the absence of the *trans* influence of the phosphorus atoms and the chelate strain of the terdentate ligand (Table 2). These electronic and steric effects are probably the reasons why further oxidation of **3** does not proceed even in the presence of excess 4-chlorothiophenorate. From the fact that such oxidation reactions were hardly observed for the corresponding halo complexes $[PdX(pp_3)]X$ ($X = Cl^-, Br^-, I^-$), such reactivity can be attributed to the electronic characteristics of thiolates. [1]

In the case of the former reaction from **1** to **2**, the square-planar intermediate is readily formed on exposure to visible light with wavelength in the lower-energy d–d transition (from $^1A_1'$ to $^1E'$) region of **1**, and once the complex **2** is formed, neither further oxidation nor reverse reaction is occurred by photolysis. This quantitative reaction can be applied to the oxygen assay and sensing system because this reaction is accompanied by the distinct color change from red to yellow. Since we found that the intermediates in Schemes 1 and 2 were readily bridged to another metal ion to give the mixed-metal bridged complexes with intended sequence of the metal centers, the further investigation is in progress in order to apply the bridging reaction to the synthesis of the new mixed-metal catalysts with phosphine ligands.

4. Supplementary material

Detailed crystallographic data in CIF format for $\mathbf{2}\cdot C_2H_5OH\cdot H_2O$ and $\mathbf{3}\cdot(C_2H_5)_2O$ and ^{31}P NMR spectra for **1**, **2**, and **3** (Scheme 1) are available from the author upon request.

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[1] Similar oxidation reactions of pp_3 ligand were observed for $[Pd(SR)(pp_3)]^+$ (SR = thiophenolate and alkylthiolate derivatives).