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Journal of Organometallic Chemistry 692 (2007) 813–818
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Rapid geometrical equilibrium of palladium(II) complexes with tris[2-(diphenylphosphino)ethyl]phosphine disulfide and diselenide and their catalytic activity for Suzuki coupling reaction

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Received 31 August 2006; received in revised form 9 October 2006; accepted 10 October 2006
Available online 18 October 2006

Abstract

Palladium(II) complexes with a tetradentate pseudo-tripodal ligand having two phosphino groups and two phosphine sulfide or selenide groups, pp_3X_2 (pp_3 = tris[2-(diphenylphosphino)ethyl]phosphine, X = S (**1**) or Se (**2**)), were prepared from $[PdCl(pp_3)]Cl$. Both of these phosphine chalcogenide complexes **1** and **2** showed rapid equilibrium between the five-coordinate $[PdCl(pp_3X_2)]Cl$ with two bound phosphine chalcogenide groups and four-coordinate $[PdCl_2(pp_3X_2)]$ with two dissociated pendant ones in chloroform. The thermodynamic parameters for the reaction, $[PdCl(pp_3X_2)]^+ + Cl^- \rightleftarrows [PdCl_2(pp_3X_2)]$, were obtained by low-temperature ^{31}P NMR as follows: $K^{298} = 3.7 \times 10^3$ and $5.4 \times 10^2\ mol^{-1}$, $\Delta H^\circ = 11.3 \pm 0.3$ and $13.4 \pm 0.4\ kJ\ mol^{-1}$, and $\Delta S^\circ = 106 \pm 2$ and $97 \pm 2\ J\ mol^{-1}\ K^{-1}$ for **1** and **2**, respectively. The rate for the geometrical change at 246.7 K for **1** was appreciably faster than that for **2**. These thermodynamic and kinetic results indicate that the phosphine selenide Se atoms can stabilize the five-coordinate structure by effective π-back donation from Pd(II) compared with the phosphine sulfide S atoms. Difference in retention of the catalytic activity for Suzuki coupling, **2** > **1** > $[PdCl(pp_3$ or $p_3)]Cl$, was explained by difference in the π-accepting ability that stabilizes the catalytically active Pd(0) species. Considering the rapid dissociation-coordination equilibrium of the phosphine chalcogenide groups on Pd(II), it is probable that the oxidative addition and the subsequent transmetallation of the Pd(II) species are hardly blocked by the phosphine chalcogenide groups.

Keywords: Phosphine sulfide; Phosphine selenide; Geometrical equilibrium; Suzuki coupling; π-accepting ability

1. Introduction

Palladium catalysts are now indispensable in organic syntheses since they can be used in various useful C–C coupling reactions [1]. For participation of Pd(II) complexes in the catalytic reactions, reduction of the Pd(II) complexes to the catalytically active Pd(0) species is essential for their entry into the catalytic cycle followed by their oxidative addition with substrates and subsequent reactions of the Pd(II) substrate adducts. Therefore, the fully ligated complexes, in which strongly coordinated ligands occupy all the coordination sites to form the stable Pd(II) complexes, can not be usually good C–C coupling catalysts because of difficulty in prereduction into the Pd(0) species and blocking the formation and subsequent reactions of the Pd(II) substrate adducts. On the other hand, the weakly ligated systems are liable to consume the catalysts because the Pd(0) species formed after the reductive elimination and prior to the next oxidative addition in the catalytic cycle are easily decomposed into inactive "palladium black". In the conservative phosphine-assisted method, oxidation of phosphine may contribute to the prereduction of Pd(II) and the phosphine remaining intact has been considered as the efficient ligand to stabilize the oxidation state of Pd(0). However, the resultant phosphine oxide can participate in coordination no longer, and furthermore, the

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doi:10.1016/j.jorganchem.2006.10.020

remaining phosphine is susceptible to oxidation and addition of excess phosphine inhibits the catalytic activity because of the strong σ donation blocking the reactions of the Pd(II) substrate adducts. Consequently, we need a new ligand system that can electronically stabilize the Pd(0) species and do not block the successive reactions of the Pd(II) substrate adducts as well.

Recently, some phosphine chalcogenides such as phosphine sulfides and selenides have been employed as monodentate and bidentate ligands for some metal ions [2]. However, very few applications of these ligands to the palladium-catalyzed C–C coupling reactions have been reported so far [3]. Considering relatively long P=S and P=Se double bonds in phosphine chalcogenides [2], the π bonding orbitals between the P and S or Se atoms are not so stabilized and the π antibonding orbitals are not so activated either. The moderately low π^* orbitals on the phosphine chalcogenide S or Se atoms are expected to be good accepting orbitals for the electron-rich Pd(0) center in the catalytically active species. Furthermore, because the S and Se atoms in phosphine chalcogenides are weak σ donors for Pd(II) compared with phosphine P atoms, the phosphine chalcogenide groups are not likely to block the formation and subsequent reactions of the Pd(II) substrate adducts compared with the phosphino groups.

Previously, we reported stepwise oxidation of five-coordinate trigonal-bipyramidal $[Pd(4\text{-Cltp})(pp_3)]^+$ (4-Cltp$^-$ = 4-chlorothiophenolate, pp_3 = tris[2-(diphenylphosphino)-ethyl]phosphine) to give square–planar $[Pd(4\text{-Cltp})(pp_3O)]^+$ and $[Pd(4\text{-Cltp})_2(pp_3O_2)]$ [4], where pp_3O and pp_3O_2 act entirely as terdentate and bidentate ligands, respectively, because the phosphine oxide groups do not participate in the complexation at all (Scheme 1). In the present work, we have designed the new pp_3S_2 and pp_3Se_2 ligand systems considering the catalytic application.

2. Experimental

2.1. Reagents

Deuterated chloroform ($CDCl_3$, Aldrich) was dried over activated 4A Molecular Sieves and used as a solvent for equilibrium and kinetic measurements. Sulfur (Wako), selenium (Wako), tetra-*n*-butylammonium chloride (Bu_4NCl, Wako), iodobenzene (Kanto Chemical), phenylboronic acid (Sigma–Aldrich), and bis(2-butoxyethyl) ether (Wako) were used without further purification.

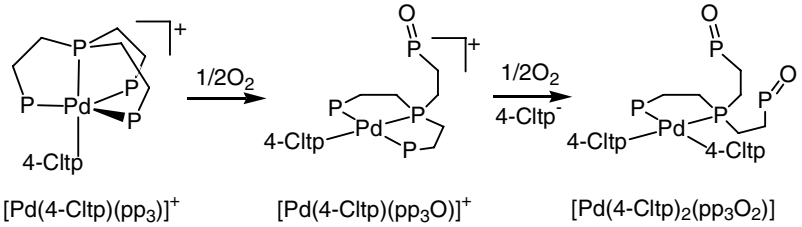
2.2. Preparation of complexes

2.2.1. $[PdCl_2(pp_3S_2]\cdot 2CHCl_3$ (**1**)

Sulfur (0.0389 g, 1.21 mmol) and $[PdCl(pp_3)]Cl$ [5] (0.505 g, 0.596 mmol) were dissolved in chloroform (12 cm^3) and reacted at 40 °C for 4 days and then filtered. The filtrate was concentrated to ca. 4 cm^3 and ethanol was added dropwise. The mixture was kept in a freezer and the resultant colorless crystals were filtered and air-dried. Yield 0.462 g (67%). Anal. Calc. for $C_{42}H_{42}Cl_2P_4PdS_2\cdot 2CHCl_3$: C, 45.80; H, 3.84; N, 0.00. Found: C, 45.34; H, 3.84; N, 0.00%. $^{31}P\{^1H\}$ NMR (CH_3CN/H_2O 10:1 v/v): δ 45.2 (dd, 2P, sulfide), 70.0 (m, 1P, terminal), 75.8 (td, 1P, center); $^3J_{P(sulfide)\text{-}P(center)}$ = 35.4 Hz, $^3J_{P(sulfide)\text{-}P(terminal)}$ = 4.2 Hz, $^3J_{P(center)\text{-}P(terminal)}$ = 11.2 Hz. ^{13}C NMR (CD_3CN/D_2O 10:1 v/v): δ 20.5 (d, P*C*H$_2$CH$_2$P(S)Ph$_2$, $^1J_{C\text{-}P}$ = 27.3 Hz), 24.2 (dd, P*C*H$_2$CH$_2$PPh$_2$, $^1J_{C\text{-}P}$ = 33.5 Hz, $^2J_{C\text{-}P}$ = 12.8 Hz), 27.0 (d, PCH$_2$*C*H$_2$P(S)Ph$_2$, $^1J_{C\text{-}P}$ = 53.6 Hz), 29.8 (dd, PCH$_2$*C*H$_2$PPh$_2$, $^1J_{C\text{-}P}$ = 35.5 Hz, $^2J_{C\text{-}P}$ = 11.5 Hz). ^1H NMR (CD_3CN/D_2O 10:1 v/v): δ 2.0–3.4 (m, CH$_2$), δ 7.4–8.1 (m, Ph).

2.2.2. $[PdCl_2(pp_3Se_2)]$ (**2**)

Selenium (0.163 g, 2.06 mmol) was suspended in a solution containing $[PdCl(pp_3)]Cl$ [5] (0.501 g, 0.591 mmol) in chloroform (12 cm^3) at 40 °C for 10 days. The remaining selenium powder was filtered off and the filtrate was concentrated to ca. 3 cm^3. To this was added ethanol dropwise, and the mixture was kept in freezer. The resultant colorless crystals were filtered and air-dried. Yield 0.48 g (81%). Anal. Calc. for $C_{42}H_{42}Cl_2P_4PdSe_2$: C, 50.15; H, 4.21; N, 0.00. Found: C, 49.56; H, 4.26; N, 0.00%. $^{31}P\{^1H\}$ NMR (acetonitrile/H_2O 10:1 v/v): σ 35.2 (dd, 2P, selenide), 69.0 (m, 1P, terminal), 73.8 (td, 1P, center); $^3J_{P(selenide)\text{-}P(center)}$ = 35.4 Hz, $^3J_{P(selenide)\text{-}P(terminal)}$ = 5.2 Hz, $^3J_{P(center)\text{-}P(terminal)}$ = 12.5 Hz. ^{13}C NMR (CD_3CN/D_2O 10:1 v/v): δ 21.7 (d, P*C*H$_2$CH$_2$P(Se)Ph$_2$, $^1J_{C\text{-}P}$ = 28.9 Hz), 25.2 (dd, P*C*H$_2$CH$_2$PPh$_2$, $^1J_{C\text{-}P}$ = 33.4 Hz, $^2J_{C\text{-}P}$ = 13.7 Hz), 27.2 (d, PCH$_2$*C*H$_2$P(Se)Ph$_2$, $^1J_{C\text{-}P}$ = 48.7 Hz), 29.2 (dd, PCH$_2$*C*H$_2$PPh$_2$, $^1J_{C\text{-}P}$ = 34.6 Hz, $^2J_{C\text{-}P}$ = 10.7 Hz). ^1H NMR (CD_3CN/D_2O 10:1 v/v): δ 2.0–3.5 (m, CH$_2$), δ 7.4–8.1 (m, Ph).



Scheme 1.

2.3. Measurements

^{31}P, ^{13}C, and ^{1}H NMR spectra were recorded on a JEOL JNM-A400 FT-NMR spectrometer operating at 160.70, 100.4, and 399.65 MHz, respectively. In order to determine the chemical shifts of ^{31}P NMR signals, 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 NMR samples for equilibrium and kinetic experiments for **1** and **2** were prepared by vacuum distillation of dried $CDCl_3$ into NMR tubes containing the completely dried sample that were then flame-sealed after degassing. The equilibrium constants were evaluated from the initial concentrations of **1** (1.4×10^{-3} mol kg^{-1}) and **2** (1.8×10^{-3} mol kg^{-1}) and the relative intensities of the non-decoupled ^{31}P NMR signals for the equilibrated species obtained by taking a sufficiently long acquisition time in the temperature ranges from 237.0 to 305.8 K for **1** and from 246.7 to 272.5 K for **2**. The chemical exchange rate constants were given by increase in the transverse relaxation rates obtained from the ^{31}P NMR spectral simulation [6] of the line-broadening data for **1** (1.4×10^{-3} mol kg^{-1}) and **2** (1.8×10^{-3} mol kg^{-1}) at 246.7 K, changing concentration of tetra-*n*-butylammonium chloride (0–5.0×10^{-2} mol kg^{-1} for **1** and 0–6.9×10^{-2} mol kg^{-1} for **2**). The temperatures of the sample solutions in the NMR probe were determined by direct measurements of the solvent temperature in an NMR tube set in the probe using a Technol Seven D617 digital thermister and were controlled within ±0.1 K.

2.4. General procedure for the C–C coupling reaction

Reactions of iodobenzene (21 mmol) with phenylboronic acid (27 mmol) in DMF (2.5 cm^3) degassed with nitrogen were carried out at 125 °C in the presence of K_2CO_3 (25 mmol) as a base and **1**, **2**, [PdCl(pp$_3$)]Cl, or [PdCl(p$_3$)]Cl (3.6×10^{-3} mmol) as catalysts. The yields were calculated by the ^{1}H NMR intensity of the ortho protons of biphenyl formed on the basis of the intensity of the ethylene protons of bis(2-butoxyethyl) ether contained as an internal reference and followed as a function of time.

3. Results and discussion

3.1. Structure of complexes in solution

The reaction solution of [PdCl(pp$_3$)]Cl [5] with 1 equiv of sulfur in chloroform showed the ^{31}P NMR spectrum assignable to that of the square–planar complex with a pendant phosphine sulfide group, [PdCl(pp$_3$S)]$^+$ (Fig. 1), where the doublet at 45.1 ppm with $^3J_{P\text{-}P} = 37.5$ Hz, the doubly intense doublet at 45.7 ppm with $^3J_{P\text{-}P} = 7.3$ Hz, and the doublet of broad triplet at 113.3 ppm with the two kinds of coupling, are reasonably assigned to the pendant phosphine sulfide, two terminal, and central P atoms, respectively, by comparison with the ^{31}P NMR spectrum of square–planar [Pd(4-Clpt)(pp$_3$O)]$^+$ ($^{31}P\{^1H\}$ NMR ($CHCl_3$): δ 32.3 (d, 1P, oxide), 47.6 (d, 2P, terminal), 107.0 (dt, 1P center); $^3J_{P(oxide)\text{-}P(center)} = 33.1$ Hz, $^3J_{P(terminal)\text{-}P(center)} = 16.5$ Hz) [4]. While the reaction solution for the preparation of **1** using excess sulfur initially showed the ^{31}P NMR signals for the square–planar monosulfide complex, [PdCl(pp$_3$S)]$^+$, the final product **1** exhibited the signals for the two phosphine sulfide P atoms (45.2 ppm) coupled with the central and terminal P atoms ($^3J_{P\text{-}P} = 35.4$ and 4.2 Hz, respectively) and the central and terminal P atoms (75.8 and 70.0 ppm, respectively) coupled with each other ($^3J_{P\text{-}P} = 11.2$ Hz) in acetonitrile/H_2O (10:1 v/v) (Fig. 2). The weak coupling between the terminal and sulfide P atoms indicates that both phosphine sulfide groups also participate in the complexation. The pseudo-tripodal pp$_3$S$_2$ ligand can hardly take the usual four-coordinate square–planar geometry and the soft donor atoms in the tetradentate tripodal ligands such as pp$_3$ [7], tris[2-(diphenylphosphino)ethyl]amine [7c,7d,7e,7h,7i,8] and the arsenic analogues [8a,9], and the sulfur- or selenium-containing analogues [10] tend to form the five-coordinate trigonal-bipyramidal d^8 metal complexes with an axial monodentate ligand. Therefore, it is obvious that **1** takes the five-coordinate pseudo-trigonal-bipyramidal structure as in Fig. 2. From the ^{31}P NMR spectrum, **2** in wet acetonitrile can be also assigned to the five-coordinate structure similar to **1** with two coordinated phosphine selenide groups instead of sulfide ones (see Section 2).

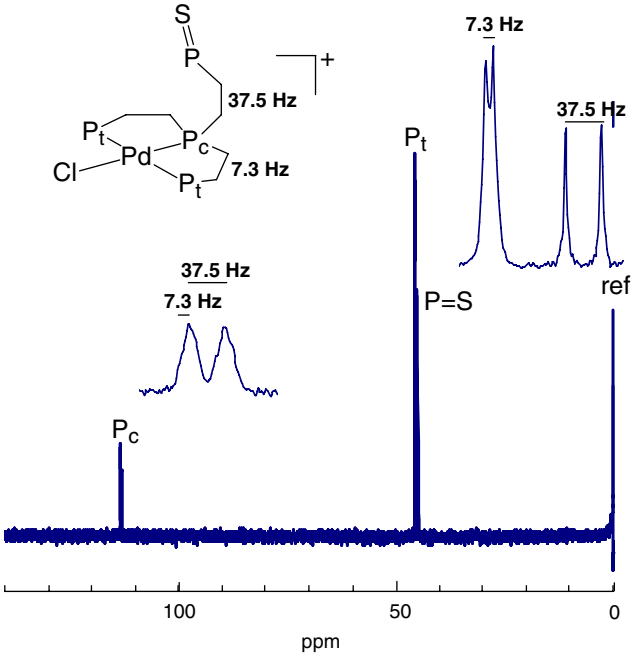


Fig. 1. ^{31}P NMR spectrum of [PdCl(pp$_3$S)]$^+$ in chloroform. Reference denotes the signal for D_3PO_4 in outer D_2O.

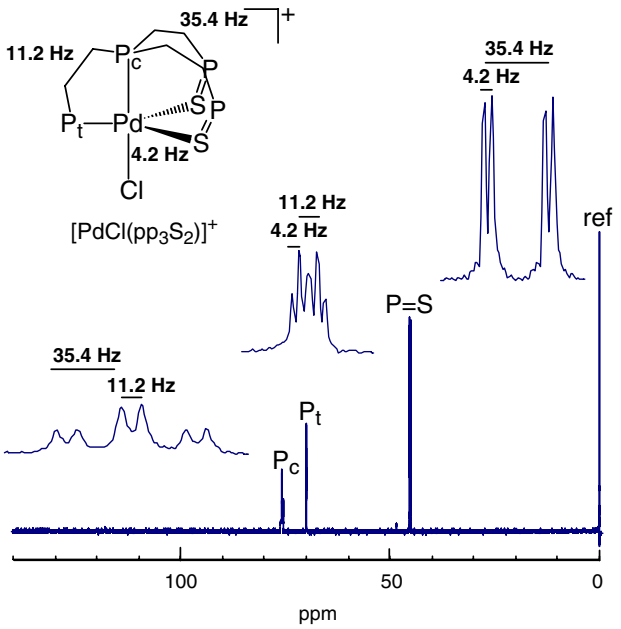


Fig. 2. ^{31}P NMR spectrum of **1** in acetonitrile/H_2O (10:1 v/v). Reference denotes the signal for D_3PO_4 in outer D_2O.

3.2. Geometrical equilibrium

The ^{31}P NMR of **1** in dried chloroform at room temperature exhibited the broadened signal for the terminal P atoms and the almost flattened signal for the central P atom. As the temperature was lowered, signals for two kinds of complexes were clearly observed (Fig. 3): one was the five-coordinate complex with the two coordinated phosphine sulfide groups, $[PdCl(pp_3S_2)]^+$, as observed in wet acetonitrile and the other was the square–planar complex with the two pendant phosphine sulfide groups, $[PdCl_2(pp_3S_2)]$, in which the pp_3 ligand acts as bidentate. The latter structure was reasonably assigned from the ^{31}P NMR spectrum of the pp_3 pentanuclear complexes having the same square–planar dichloropalladium(II) moieties with the bidentate pp_3 ligand (68.4–68.1 and 88.8–89.3 ppm for terminal and central P atoms, respectively) [11], in which the other two terminal phosphino groups bridge to Pt(II) and Rh(III) instead of forming sulfide. The ^{31}P NMR spectra for the above two complexes were completely coalesced at ca 50 °C (Fig. 3). The above reversible NMR spectral change with temperature revealed rapid equilibrium between the five-coordinate and four-coordinate geometries in chloroform. In wet acetonitrile solution, the solvation energy for the complex cation and chloride anion is enough to release the chloride ion into the solvent, and consequently, all the potentially binding groups of the pp_3S_2 ligand can be coordinated to the Pd(II) center to form the five-coordinate structure. On the other hand, the rapid equilibrium indicates that weakly polar solvents such as chloroform give rise to the competitive coordination between the chloride ion and the phosphine sulfide groups because the solvation of non-charged species is preferred. The selenide analogue **2** showed almost the same geometrical equilibrium in dried chloroform though the equilibrium lay far to the five-coordinate complex compared with that for **1**. The colorless crystals of **1** and **2** obtained from the chloroform solution (see Section 2) may contain the square–planar $[PdCl_2(pp_3X_2)]$ (X = S, Se) because the crystals give light yellow chloroform solutions at room temperature and yellow acetonitrile solutions attributable to formation of the five-coordinate complexes, $[PdCl(pp_3X_2)]^+$ (X = S, Se), with longer-wavelength shift of the d–d absorption bands [10].

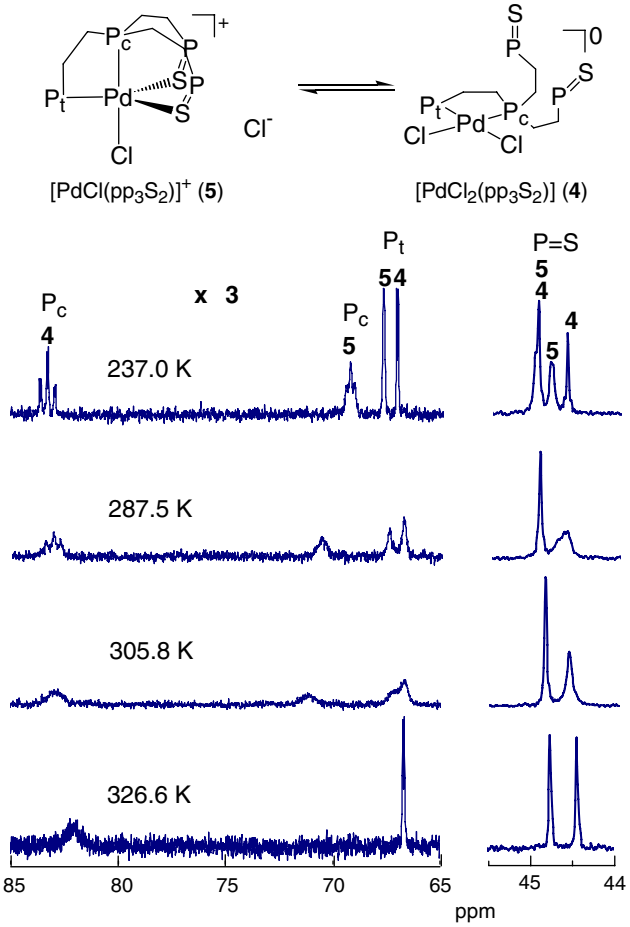


Fig. 3. ^{31}P NMR spectra of **1** in chloroform at various temperatures. **4** and **5** denote five-coordinate $[PdCl(pp_3S_2)]^+$ and four coordinate $[PdCl_2(pp_3S_2)]$, respectively.

The equilibrium constants for the geometrical change from the five-coordinate complex to the four-coordinate one, $[PdCl(pp_3S_2)]^+ + Cl^- \rightleftarrows [PdCl_2(pp_3S_2)]$, were obtained from the reversible ^{31}P NMR spectral change in dried deuterated chloroform at low temperatures using the ratios of the signal intensities for the central P atoms of the two species. The equilibrium constants at 298 K (K^{298}) and the enthalpy and entropy changes for the geometrical change (ΔH° and ΔS°, respectively) listed in Table 1 were determined by using each temperature dependence of K as shown in Fig. 4. The positive values of ΔH° and ΔS° are attributed to the decrease in coordination number. A little

Table 1
Thermodynamic parameters for geometrical equilibrium of **1** and **2**

Complex	K^{298}/mol^{-1}	ΔH°/kJ mol^{-1}	ΔS°/J mol^{-1} K^{-1}
1	3.7×10^3	11.3 ± 0.3	106 ± 2
2	5.4×10^2	13.4 ± 0.4	97 ± 3

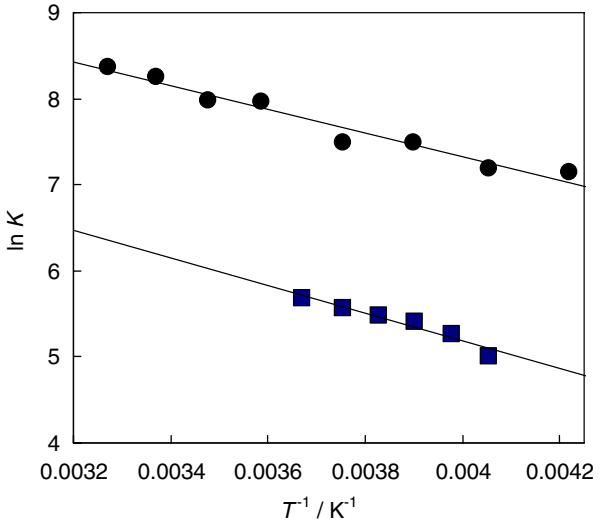


Fig. 4. Temperature dependence of ln K for the geometrical change from five- to four-coordinate structure of **1** (●) and **2** (■) in chloroform.

larger ΔH° value for **2** than that for **1** indicates that the Se atoms can enthalpically stabilize the five-coordinate structure compared with the S atoms by effective π-back donation from the occupied non-bonding d orbitals on the five-coordinate Pd(II) into the π^* orbital on the selenide Se atoms. A little smaller ΔS° value for **2** than that for **1** probably due to longer Pd–Se bond distances than Pd–S ones, which reduces entropic stabilization accompanied by the Pd–Se bond breaking. Such electronic and steric differences between the Pd–Se and Pd–S bonds in the five-coordinate complexes cause the difference in preference for the five-coordinate geometry between **1** and **2**.

The observed rate constants for the geometrical change from the five-coordinate complex to the four-coordinate one, k, were obtained from the low-temperature ^{31}P NMR line-broadening data: the values of k for **1** were given by increases in the transverse relaxation rate (ΔT_2^{-1}) of the phosphine sulfide P atoms in the four-coordinate complex using Eq. (1),

$$k = \Delta T_2^{-1}[4-\text{coordinate}]/[5-\text{coordinate}] \quad (1)$$

where [4-coordinate] and [5-coordinate] are the concentrations of the four- and five-coordinate complexes, respectively, and the k values for **2** were directly obtained from ΔT_2^{-1} for the terminal P atom in the five coordinate complex (Supplementary material). As shown in Fig. 5, each observed rate constant is proportional to the chloride ion concentration. Recently, from the kinetic results, we have proposed the preassociation mechanism for the haro-ligand

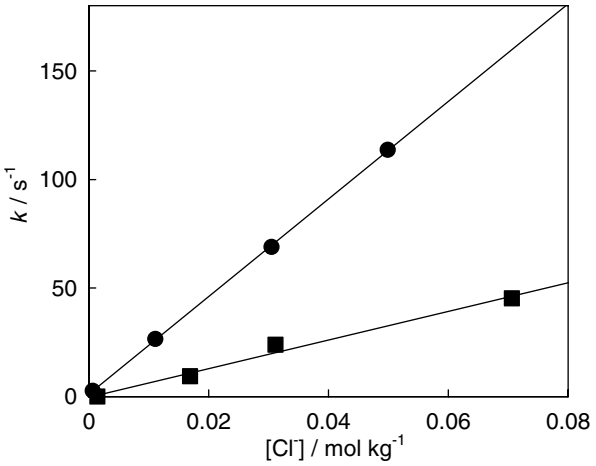
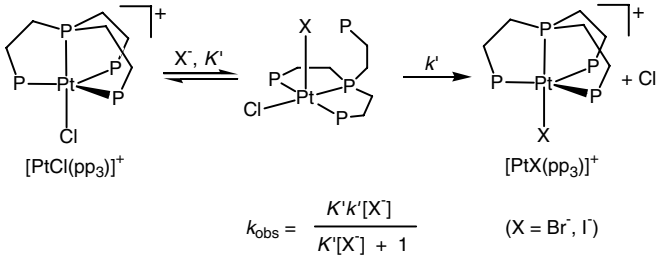
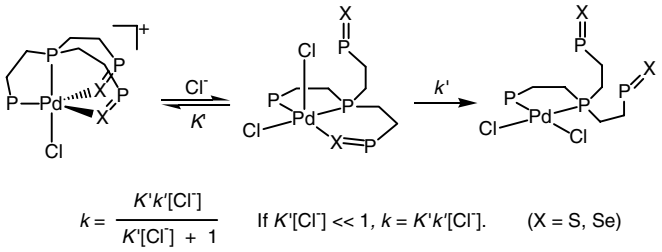


Fig. 5. Dependence of k (246.7 K) for the geometrical change form five- to four-coordinate structure of **1** (●) and **2** (■) on chloride ion concentration in chloroform.



Scheme 2.

substitution reaction of the five-coordinate trigonal-bipyramidal $[PtCl(pp_3)]^+$ in chloroform as shown in Scheme 2 [12]. It may be possible that the present geometrical change for the five-coordinate Pd(II) complexes take a similar reaction mechanism (Scheme 3) where the pre-equilibrium constant (K') is small enough ($K'[Cl^-] \ll 1$) to give the linear concentration dependence, $k = K'k'[Cl^-]$, as shown in Fig. 5. As above described, the thermodynamic study revealed that the selenide coordination of **2** stabilizes the five-coordinate species $[PdCl(pp_3Se_2)]^+$ compared with the sulfide coordination of **1**. This fact is consistent with the smaller K', and consequently, the smaller k of **2**.



Scheme 3.

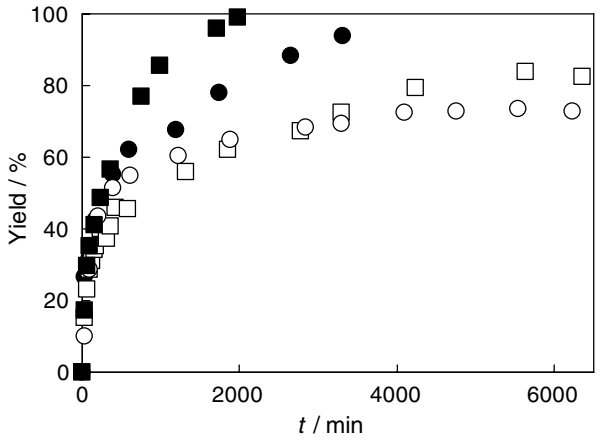


Fig. 6. Change in the yield of biphenyl with time in Suzuki coupling reaction catalyzed by **1** (●), **2** (■), [PdCl(pp$_3$)]Cl (○), and [PdCl(p$_3$)]Cl (□).

3.3. C–C coupling reaction

In order to clarify the electronic effect of the phosphine chalcogenides on the Pd-catalyzed C–C coupling reactions, we adopted Suzuki coupling that is one of the most widespread coupling reactions. The catalytic activities of **1** and **2** were compared to those of the phosphine complexes, [PdCl(pp$_3$)]Cl and [PdCl(p$_3$)]Cl, using iodobenzene and phenylboronic acid as the substrates under the same condition.

Palladium-catalyzed C–C coupling reactions usually start from formation of the catalytically active Pd(0) species by prereduction of Pd(II). Because the Pd(0) species is formed again after the reductive elimination of substrates and prior to the next oxidative addition in the catalytic cycle, stability of the Pd(0) species is very important for retention of the catalytic activity. As shown in Fig. 6, difference in the retentive ability, **2** > **1** > [PdCl(pp$_3$ or p$_3$)]Cl, were observed in the present Suzuki coupling reaction. Considering the π accepting ability of the selenide Se atom superior to the sulfide S atom, as mentioned above, and strong σ donating ability of the phosphine P atom, the retentive ability is consistent with the electron-accepting ability of the ligands, which stabilizes the electron-rich Pd(0) center. Furthermore, it is probable that the formation of the substrate adduct and subsequent transmetallation of the Pd(II) species are not blocked by coordination of the phosphine chalcogenide groups because they can be easily dissociated from the Pd(II) center to open the coordination sites as observed in the rapid geometrical equilibrium.

Appendix A. Supplementary data

The thermodynamic and kinetic data for **1** and **2** are available from the author upon request. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.10.020.

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