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Air-Stable, Recyclable, and Regenerative Phosphine Sulfide Palladium(0) Catalysts for C−C Coupling Reaction

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Mononuclear phosphine sulfide Pd(0) complexes and a polymer-supported triphenylphosphine sulfide Pd(0) complex were prepared as new air-stable Pd(0) catalysts for C−C coupling reactions. The phosphine sulfide Pd(0) complexes are not decomposed after completion of Suzuki−Miyaura coupling, and the polymer-supported Pd(0) catalyst is practically recyclable, while phosphine Pd(0) complexes are decomposed into inactive Pd(0) black after consuming the substrates. New catalytic activity of Pd(0) that promotes chalcogen atom replacement of phosphine chalcogenides ($R_3P{=}X$, X = O, S, Se) is reported. A mechanistic study revealed that the new catalytic chalcogen replacement results from activation of the P=X bond as well as promotion of the oxidative chalcogenide formation. The intermediate phosphine was successfully trapped as a phosphine Pd(II) complex, and the P=X bond activation is applicable to regeneration of phosphine or phosphine sulfide from oxidized phosphine.

Introduction

Palladium catalysts are now quite versatile and indispensable in organic synthesis since they can catalyze the formation of various carbon−carbon and carbon−heteroatom bonds. The catalytic activity in most coupling reactions comes from the ability of Pd(0) species to activate carbon−halogen or pseudohalogen bonds by the oxidative addition that initiates the catalytic cycle.[1−4] Because phosphines have been regarded as effective ligands to stabilize the zerovalent oxidation state of palladium, phosphine-assisted reactions have been widely employed as the classical and conservative method. However, while the substrate adducts of Pd(II) formed during the catalytic cycle are relatively stable, phosphines are usually susceptible to oxidation to give inactive Pd sediment “palladium black” after the catalytic reactions are completed.[1−4] It is difficult to practically regenerate phosphines from the phosphine oxides for recycling, so that even elaborate and valuable phosphines are unavoidably discarded as phosphine oxides. Such air-sensitivity is unfavorable for application of expensive and toxic phosphines on industrial and semi-industrial scales. On the other hand, phosphine-free catalytic systems have received increasing interest for environmental and economical reasons. The problem is that the catalytic cycles are blocked by strongly bound ligands of stable phosphine-free complexes to give the low catalytic activity while weakly ligated complexes, which are likely to have high activity, are intrinsically unstable, and are liable to be decomposed into inactive palladium black. In these circumstances, we need a new ligand system that can thermodynamically stabilize the Pd(0) center but does not deactivate the catalytic cycle kinetically. It is also desirable that the new catalyst is recoverable and reusable for industrial use.

Recently, some phosphine sulfides have been employed as monodentate or bidentate ligands for some metal ions.[5−10] The sulfur−phosphorus π-bonding orbital is not so stabilized, and consequently the unoccupied π^* orbital is moderately low and can probably accept electrons from Pd(0) to stabilize the low oxidation state. On the other hand, because the phosphine sulfide group is not a strong σ-donor for Pd(II), the formation of the substrate adduct and subsequent catalytic reactions on Pd(II) are not likely to be blocked. In this work, we have provided the isolable Pd(0) complex with

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tris[2-(diphenylphosphino)ethyl]phosphine tetrasulfide (pp_3S_4) as one of the most promising catalysts, where the four phosphine sulfide groups linked by ethylene chains can stabilize the Pd(0) complex entropically as well as electronically.[11] We also report practically recyclable polymer-supported phosphine sulfide as a solid catalyst. In the course of this study, we have found new catalytic activity of Pd(0) that promotes chalcogen replacement of phosphine chalcogenides ($R_3P{=}X$, X = O, S, Se) by the P=X bond activation, which is useful for regeneration of phosphine sulfides.[12] We have also attempted to separate the intermediate phosphine as evidence of the dissociative mechanism and have applied the catalytic chalcogen dissociation to the regeneration of phosphines such as bidentate 1,2-bis(diphenylphosphino)ethane (p_2) and optically active 2,2′-bis(diphenylphosphino)-1,1′-binaphthalene (BINAP) from their oxides.

Experimental Section

Reagents. Tris[2-(diphenylphosphino)ethyl]phosphine (pp_3, Aldrich), bis[2-(diphenylphosphino)ethyl]phenylphosphine (p_3, Aldrich), 1,2-bis(diphenylphosphino)ethane (p_2, Kanto Chemical), triphenylphosphine (Ph_3P, Aldrich), (*R*)-2,2′-bis(diphenylphosphino)-1,1′-binaphthalene ((*R*)-BINAP, Aldrich), sulfur (Wako), selenium (Wako), polymer-supported triphenylphosphine (Aldrich), dibenzylideneacetone (dba, Aldrich), tetrakis(triphenylphosphine)palladium(0) (Aldrich), bis(dibenzylideneacetone)palladium ($[Pd(dba)_2]$, Kanto Chemical), trakis(acetonitrile)palladium(II) tetrafluoroborate ($[Pd(CH_3CN)_4](BF_4)_2$, Aldrich), tetra(*n*-butyl)ammonium iodide (Wako), potassium tetrachloroplatinate(II) ($K_2[PtCl_4]$, Aldrich), *trans*-bis(benzonitrile)dichloroplatinum(II) (*trans*-$[PtCl_2(NCC_6H_5)_2]$, Strem), iodobenzene (Kanto Chemical), phenylboronic acid (Sigma-Aldrich), and bis(2-butoxyethyl) ether (Wako) were used for preparation and catalytic reactions without further purification.

Preparation. Tris[2-(diphenylphosphino)ethyl]phosphine Tetrasulfide (pp_3S_4). To a solution containing sulfur (0.101 g, 3.15 mmol) in deoxygenated chloroform was added tris-[2-(diphenylphosphino)ethyl]phosphine, pp_3 (0.520 g, 0.775 mmol). The solution was allowed to stand at room temperature for 1 h followed by the addition of diethyl ether. The resultant colorless crystals were collected by filtration and air-dried. Yield: 0.58 g (94%). Anal. Found: C, 63.08; H, 5.30; N, 0.00. Calcd for $C_{42}H_{42}P_4S_4$: C, 63.10; H, 5.30; N, 0.00. $^{31}P\{^1H\}$ NMR ($CHCl_3$): δ (relative to D_3PO_4 in external D_2O) 44.1 (d, terminal), 54.5 (q, center); J_{P-P} = 56 Hz.

Bis[2-(diphenylphosphino)ethyl]phenylphosphine Trisulfide (p_3S_3), 1,2-Bis(diphenylphosphino)ethane Disulfide (p_2S_2), Triphenylphosphine Sulfide (Ph_3PS), (*R*)-2,2′-Bis(diphenylphosphino)-1,1′-binaphthalene Disulfide ((*R*)-BINAPS₂), and Triphenylphosphine Selenide (Ph_3PSe). These phosphine chalcogenides were prepared by a procedure similar to that reported for p_2S_2[13] using the corresponding phosphine and chalcogen.

[Pd(pp_3S_4)(dba)] (1). The tetrasulfide ligand pp_3S_4 (0.158 g, 0.198 mmol) and $[Pd(dba)_2]$ (0.104 g, 0.181 mmol) were dissolved in chloroform (5 cm^3). The reaction mixture was allowed to stand at room temperature for 1 h. The dark brown solid was precipitated by adding diethyl ether and then filtered and air-dried. Yield: 0.143 g (44%). Anal. Found: C, 44.64; H, 3.80; N, 0.00. Calcd for $C_{59}H_{56}OP_4PdS_4\cdot 5CHCl_3\cdot C_4H_{10}O$: C, 45.11; H, 3.95; N, 0.00%. $^{31}P\{^1H\}$ NMR ($CHCl_3$): δ (relative to D_3PO_4 in external D_2O) 44.2 (d, terminal), 54.6 (q, center); J_{P-P} = 56 Hz. ^1H NMR ($CDCl_3$): δ 1.21 (t, CH_3− of diethyl ether), 2.11−2.17 and 2.55−2.65 (m, $-CH_2CH_2-$ of pp_3S_4), 3.48 (q, $-CH_2-$ of diethyl ether), 7.10 (d, Ph-CH=C*H*− of dba, $^3J_{H-H}$ = 16 Hz), 7.26 (s, $CHCl_3$), 7.41−7.54 and 7.81−7.87 (m, Ph of pp_3S_4), 7.61−7.64 (m, Ph of dba), 7.75 (d, Ph-C*H*=CH− of dba, $^3J_{H-H}$ = 16 Hz).

[Pd(p_2S_2)(dba)] (2). A solution containing p_2S_2 (0.139 g, 0.300 mmol) and $[Pd(dba)_2]$ (0.174 g 0.299 mmol) in deoxygenated chloroform was stirred for 30 min at room temperature under nitrogen and then concentrated to a small volume. After the addition of diethyl ether, the mixture was kept in a refrigerator overnight. The resulting dark brown solid was filtered and washed with diethyl ether and then air-dried. Yield: 0.125 g (52%). Anal. Found: C, 57.30; H, 4.44; N, 0.00. Calcd for $C_{43}H_{38}OP_2PdS_{2M}\cdot CHCl_3$: C, 57.28; H, 4.26; N, 0.00. $^{31}P\{^1H\}$ NMR ($CHCl_3$): δ (relative to D_3PO_4 in external D_2O) 44.2 (s). ^1H NMR ($CDCl_3$): δ 2.72 (d, $-CH_2CH_2-$ of p_2S_2), 7.10 (d, Ph-CH=C*H*− of dba, $^3J_{H-H}$ = 16 Hz), 7.26 (s, $CHCl_3$), 7.40−7.43 and 7.61−7.65 (m, Ph of dba) 7.43−7.50 and 7.77−7.83 (m, Ph of p_2S_2), 7.75 (d, Ph-C*H*=CH− of dba, $^3J_{H-H}$ = 16 Hz).

Polymer-Supported PPh₃ Sulfide Pd(0) Complex [−CH-{C₆H₄P(S)Ph₂}CH₂−]₂{Pd(dba)}₀.₄₂ (3). To a solution of sulfur (0.100 g, 3.12 mmol) in toluene (10 cm^3) was added 0.819 g (2.84 mmol of the phosphine unit) of polymer-supported triphenylphosphine (Aldrich). The suspension was allowed to stand at room temperature for 1 h, and the reacted polymer was collected by filtration and air-dried. $^{31}P\{^1H\}$ NMR (solid): δ (relative to external $NH_4H_2PO_4$) 42.4.

The obtained polymer-supported triphenylphosphine sulfide was added to a solution of $[Pd(dba)_2]$ (0.408 g, 0.71 mmol) in a mixture of toluene (10 cm^3) and chloroform (3 cm^3). The suspension was stirred for 6 h under N_2. The resultant dark brown solid was collected by filtration and air-dried. Anal. Found: C, 73.61; H, 5.35; N, 0.00; S, 6.80; Pd, 4.71. Calcd for [(−CH{$C_6H_4P(S)Ph_2$}CH_2−)12:24 AM 9/22/2009$_2${Pd-(dba)}$_{0.42}$(C_7H_8)$_{1.5}$($CHCl_3$)&Qj;$_{0.2}$]$_n$: C, 73.44; H, 5.55; N, 0.00; S, 6.78; Pd, 4.72. $^{31}P\{^1H\}$ NMR (solid): δ (relative to external $NH_4H_2PO_4$) 42.0.

[Pd((*R*)-binapS₂)(dba)]. The (*R*)-BINAPS₂ complex was prepared by a procedure similar to that for **2** using (*R*)-BINAPS₂ instead of S_2P_2. Anal. Found: C, 53.81; H, 3.92; N, 0.00. Calcd for $C_{61}H_{46}OP_2PdS_2\cdot 3.5CHCl_3\cdot C_4H_{10}O$: C, 54.15; H, 3.95; N, 0.00. $^{31}P\{^1H\}$ NMR ($CHCl_3$): δ (relative to D_3PO_4 in external D_2O) 42.5 (s). ^1H NMR ($CDCl_3$): δ 1.21 (t, CH_3- of diethyl ether), 3.48 (q, $-CH_2-$ of diethyl ether), 7.10 (d, Ph−CH=C*H*− of dba, $^3J_{H-H}$ = 16 Hz), 7.26 (s, $CHCl_3$), 7.20−7.80 (m, binap), 7.40−7.43 and 7.61−7.64 (m, Ph of dba), 7.75 (d, Ph−C*H*=CH− of dba, $^3J_{H-H}$ = 16 Hz).

[PdI₂(P₂)] and [PdI₂((*R*)-binap)]. These diiodo complexes were prepared by a similar procedure to that described in the literature[14] using $[Pd(CH_3CN)_4](BF_4)_2$, the bidentate phosphine, and $[N(n\text{-}Bu)_4]I$ (Supporting Information).

General Procedure for the C−C Coupling Reaction. The Suzuki−Miyaura coupling reaction of iodobenzene (5.7 g, 27 mmol) with phenylboronic acid (4.1 g, 27 mmol) in DMF (2.5 cm^3) was carried out in air and under N_2 at 125 °C in the presence of the Pd(0) catalyst (0.011 mmol) and K_2CO_3 (3.5 g, 25 mmol) as a base. The yields were calculated by the ^1H NMR intensity of the *ortho* protons of formed biphenyl 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. For the polymer-supported catalyst, Pd(0) content was adjusted to 0.011 mmol. To check the recyclability of the catalyst, the residue containing the polymer-supported catalyst was filtered after completion of the reaction, washed with DMF,

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and air-dried. The reaction was repeated under the same conditions by using the residual catalyst.

Kinetics. Kinetic measurements for the chalcogen atom replacement reaction were carried out by monitoring the reaction of triphenylphosphine selenide (0.0212 mol kg^{-1}) with excess sulfur (0.212−0.636 mol kg^{-1}) in DMF in the presence (0.0106 mol kg^{-1}) and absence of [Pd(dba)$_2$]. Since the ^{31}P NMR signal intensities of phosphine selenide and sulfide were proportional to their concentrations, the rate constants were obtained by the initial slope method following change in the concentrations of the phosphine chalcogenides, which were calculated from the initial concentrations and the ratio of the ^{31}P NMR signal intensities. The reaction temperature was changed from 305 to 333 K for the catalytic reaction and from 333 to 373 K for the noncatalytic reaction at fixed concentrations of phosphine selenide (0.0212 mol kg^{-1}) and sulfur (0.212 mol kg^{-1}). Under the same concentrations, the reaction rate was also checked in chloroform at 333 K. The temperature dependence of the rate constant was obtained under the same conditions as those for the catalytic reaction using the corresponding Pt(0) complex [Pt(dba)$_2$].[15]

Conversion from Phosphine Oxide to Phosphine Sulfide. The phosphine sulfide complex [Pd(pp$_3$S$_4$)(dba)] (0.029 mmol) was heated in DMF (10 cm^3) under reflux for 6 h, and the formation of phosphine oxide groups was confirmed by ^{31}P NMR measurements. The solution was reacted with excess sulfur (29 mmol) at 125 °C for 2 h under N$_2$, and conversion to phosphine sulfide was checked by ^{31}P NMR measurements. Similarly, phosphine sulfide groups of p$_3$S$_3$ and p$_2$S$_2$ were also partially converted to phosphine oxide ones, and phosphino groups of (*R*)-BINAP were partially oxidized in the presence of 1/10 equiv of Pd(0) complex [Pd(dba)$_2$]. Conversion from phosphine oxide groups to phosphine sulfide ones was carried out under the same conditions as described for pp$_3$S$_4$.

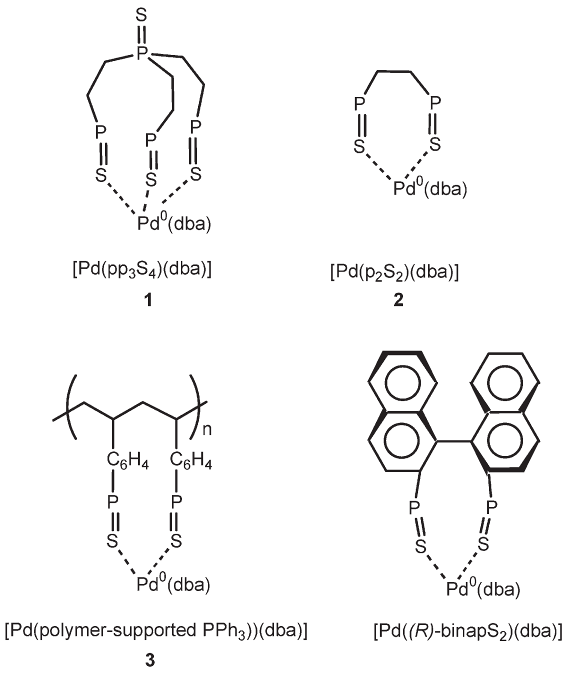
Conversion from Phosphine Sulfide to Phosphine. The p$_2$S$_2$ complex [Pd(p$_2$S$_2$)(dba)] (0.0803 g, 0.10 mmol) was reacted with an excess of iodobenzene (2.04 g, 10 mmol) in DMF (10 cm^3) at 70 °C for 48 h under N$_2$. The reaction solution was separated by chromatography with an SiO$_2$ column by elution with chloroform. The yellow eluate was concentrated to dryness, and the yellow complex was recrystallized from chloroform and characterized by ^{31}P NMR. Only the yellow complex was formed by the successive addition of 2 equiv of [Pd(dba)$_2$] at 70 °C and isolated by adding ethanol without column separation. Conversion from BINAPS$_2$ to BINAP was carried out by a similar procedure using [Pd((*R*)-binapS$_2$)(dba)] instead of [Pd(p$_2$S$_2$)(dba)]. The purple complex was isolated by column separation with SiO$_2$ as described above and characterized by ^{31}P NMR spectroscopy.

Measurements. ^{31}P and ^{1}H NMR spectra for solutions were recorded on a JEOL JNM-A400 FT-NMR spectrometer operating at 160.70 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 as a lock solvent and phosphoric acid as a reference. Solid state ^{31}P NMR spectra were recorded on a Bruker AVANCE-600 NMR spectrometer operating at 242.94 MHz by using ammonium dihydrogen phosphate as a reference. Inductively coupled plasma (ICP) analyses were carried out using a Perkin-Elmer Optima 2000XL.

Results and Discussion

C−C Coupling Reaction. The air-stable Pd(0) complexes **1**, **2**, **3**, and [Pd((*R*)-binapS$_2$)(dba)] were prepared by the reactions of [Pd(dba)$_2$] with phosphine sulfides pp$_3$S$_4$, and p$_2$S$_2$, polymer-supported PPh$_3$, and (*R*)-BINAPS$_2$, respectively. The coordination of dba and phosphine sulfide ligands and the compositions were confirmed by ^{31}P and ^{1}H NMR and elementary analysis. All the diphenylphosphine sulfide groups for each complex are regarded as equivalent from the ^{31}P NMR spectra, and the dba ligand is assumed to be coordinated with the double bonds as proposed in the literature.[15] The schematic structures are shown in Scheme 1. The catalytic activity for Suzuki−Miyaura coupling reaction of **1** was compared with that of [Pd(PPh$_3$)$_4$] by using iodobenzene and phenylboronic acid as the substrates at high temperature (125 °C) to confirm the stability of the catalyst. The phosphine sulfide complex **1** exhibited almost the same catalytic activity under N$_2$ and in air, which was comparable to that for [Pd(PPh$_3$)$_4$] under N$_2$, while [Pd(PPh$_3$)$_4$] was decomposed and deactivated during long-time reaction at high temperature in air (Figure 1).

Scheme 1



Phenyl groups are omitted.

Furthermore, after keeping the completely reacted solution in air for several additional hours without residual unreacted substrates, the brown solution for **1** maintained catalytic activity for another addition of the substrates. To the contrary, [Pd(PPh$_3$)$_4$] gradually decomposed into inactive palladium black in air after consuming the substrates to give the almost colorless supernatant. This fact indicates that the Pd(0) in **1** is stabilized by the phosphine sulfide groups, while [Pd(PPh$_3$)$_4$] itself is air-sensitive unless forming the Pd(II) substrate adduct by oxidative addition. We have also prepared the polymer-supported phosphine sulfide Pd(0) complex **3** as a readily recyclable C−C coupling catalyst. **3** used in air was filtered from the completely reacted solution and then reused in air again. The recycled **3** was not deactivated by repetition of this procedure at least several times (Figure 2).

Chalcogen-Replacement Reaction. While phosphines are known to be susceptible to oxidation in air, we found in this work that the oxidation is catalyzed by Pd(0). As shown in Figure 3, PPh$_3$ was completely oxidized in a DMF solution of

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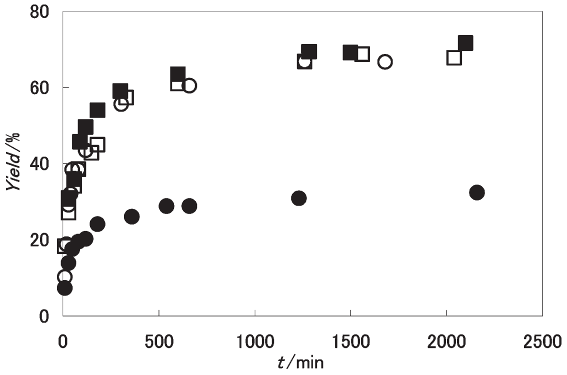

Figure 1. Change in the yield of biphenyl with time in the Suzuki coupling reaction catalyzed by **1** (■, in air; □, under N_2) and $[Pd(PPh_3)_4]$ (● in air; ○, under N_2).

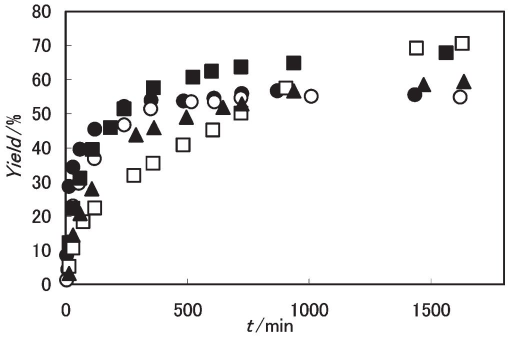

Figure 2. Change in the yield of biphenyl with time in the Suzuki coupling reaction catalyzed by **3** (●, freshly prepared; ○, recycled once; ■, recycled twice; □, recycled three times; ▲, recycled four times) in air.

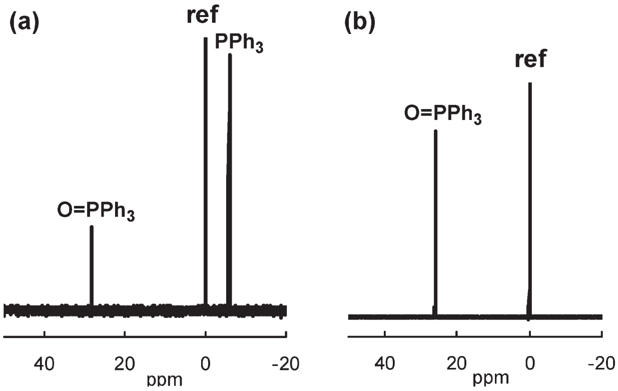

Figure 3. ^{31}P NMR spectra of DMF solutions of PPh_3 (0.171 mol kg^{-1}) (a) and $[Pd(PPh_3)_4]$ (0.043 mol kg^{-1}) (b) allowed to stand at room temperature for 4 days and 2 h, respectively. **ref** denotes the signal for D_3PO_4 in the outer D_2O.

$[Pd(PPh_3)_4]$ at room temperature in 2 h by dissolved oxygen, although only ca. 20% of free PPh_3 was oxidized by keeping the solution for 4 days under the same conditions. This catalysis leads to a serious problem in the phosphine-assisted palladium-catalyzed reactions. Furthermore, chalcogen-replacement reactions of phosphine chalcogenides were also revealed to be catalyzed by Pd(0). For example, the sulfur atoms in free pp_3S_4 are hardly replaced by oxygen atoms, but those in **1** were partially replaced to give some phosphine oxide groups at high temperature (Figure 4a). Such a replacement reaction of phosphine sulfide groups is possible during the prolonged or repeated catalytic reaction using **1** or **3**. However, pp_3S_4 was readily regenerated from the partially oxygenated ligand in **1** by the reaction with excess sulfur in DMF at 125 °C for 2 h (Figure 4b), while the conversion from phosphine oxide to phosphine sulfide does not proceed at all without Pd(0) even by reflux in DMF. Similarly, p_3S_3 and p_2S_2 were also regenerated from the partially oxygenated ligands in the presence of Pd(0) (Figure S1), and this new catalytic reaction is applicable to recycling phosphine sulfide Pd(0) catalysts.

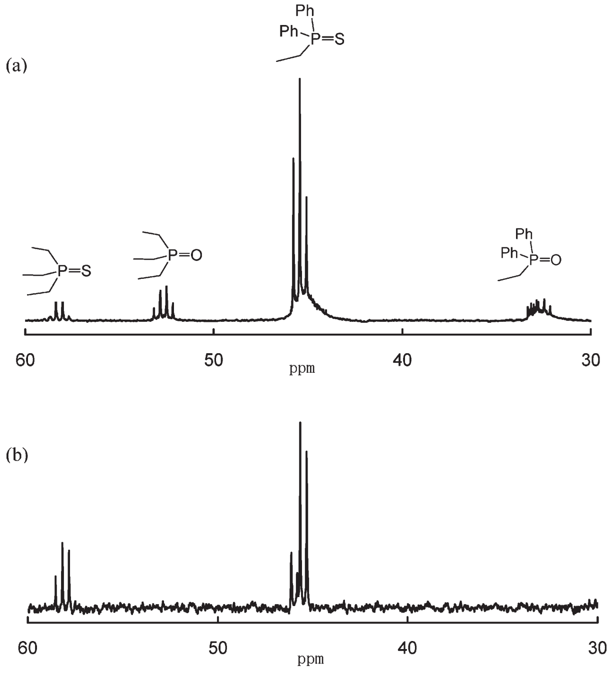

Figure 4. ^{31}P NMR spectra of **1** (0.029 mmol) heated in DMF (10 cm^3) under reflux for 6 h (a) and the subsequently reacted solution with excess sulfur (29 mmol) at 125 °C for 2 h (b).

Reaction Mechanism. So far, a few chalcogen transfer reactions from phosphine chalcogenides to phosphines were reported,[16,17] and two associative mechanisms have been proposed for the chalcogen transfer by means of theoretical calculations, as shown in Scheme 2.[18] Mechanism 1 involves a nucleophilic attack of the phosphine phosphorus on the phosphine-chalcogenide phosphorus via a three-membered cyclic transition state, and mechanism 2 is an X-philic attack via a linear transition state.

In the present system, however, the chalcogen replacement proceeds without phosphine nucleophile. In order to elucidate the reaction mechanism of the replacement, we undertook kinetic experiments. Kinetic measurements were carried out by monitoring the reaction of triphenylphosphine selenide with excess sulfur in DMF in the presence and absence of $[Pd(dba)_2]$ (dba = dibenzylideneacetone). By following an increase in the ^{31}P NMR signal intensity of phosphine sulfide formed, it was confirmed that the observed rates are first-order with respect to the phosphine-selenide concentration. Since the rates were considerably slow especially in

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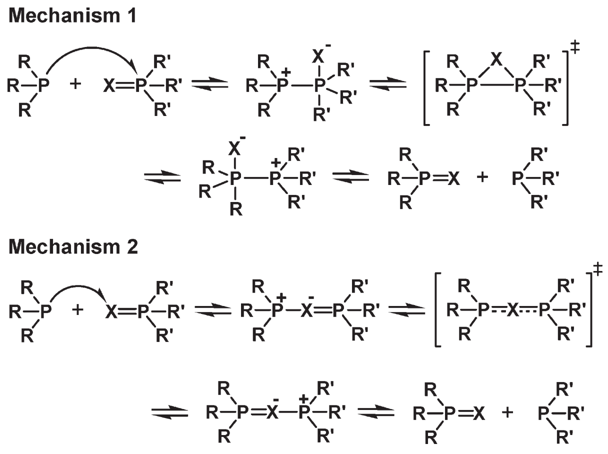
Scheme 2



the absence of Pd(0), the rate constants were obtained by the initial slope method. The observed rate constants were independent of the sulfur concentration (Figure S2), and the temperature dependence of the rate constants in Figure 5 gave the activation parameters $\Delta H^{\ddagger} = 110 \pm 1$ kJ mol^{-1} and $\Delta S^{\ddagger} = 26 \pm 2$ J mol^{-1} K^{-1} in the presence of Pd(0) and $\Delta H^{\ddagger} = 159 \pm 1$ kJ mol^{-1} and $\Delta S^{\ddagger} = 103 \pm 2$ J mol^{-1} K^{-1} in the absence of Pd(0).

The sulfur-concentration independency of the observed rate constants and the positive $\Delta S^{\ddagger}$ values indicate dissociative activation. The smaller positive $\Delta S^{\ddagger}$ value in the presence of Pd(0) is attributed to the interaction between the phosphine chalcogenide and Pd(0) in the activation state in which the P=X bond breaking is promoted enthalpically. The catalytic activation may be caused by π back-donation from Pd(0) to the π^* orbital of the P=X bond,[19] which is supported by the fact that the π back-donating Pt(0) center of the corresponding Pt(0) complex, [Pt(dba)$_2$],[15] also showed similar catalytic activity. By the kinetic experiments, the sulfur-concentration independency of the observed rate constant and the activation parameters, $\Delta H^{\ddagger} = 116 \pm 1$ kJ mol^{-1} and $\Delta S^{\ddagger} = 32 \pm 2$ J mol^{-1} K^{-1}, similar to those for the Pd(0) catalysis were obtained for the Pt(0) complex (Figure S3). Because the catalytic reaction rate was unchanged in chloroform, it seems that DMF solvent does not participate in the activation. Considering that oxidation of phosphine, that is, phosphine chalcogenide formation, was also promoted by Pd(0) as mentioned above, acceleration of the chalcogen-atom replacement results from the catalytic P=X bond cleavage and also formation by Pd(0). The π back-donation from Pd(0) to the phosphine P atom can increase electron density on the P atom to promote the oxidative chalcogenide formation as well as the activation of the P=X bond.

Isolation of Phosphine Intermediate. When **1** was reacted with relatively labile [PtCl$_2$(NCC$_6$H$_5$)$_2$] in DMF at 95 °C for several hours, the ^{31}P NMR signals for phosphino groups coordinated to Pt(II) and Pd(II) formed by oxidation of Pd(0) were observed (Figure S4).[20] Such a P=S bond cleavage was not observed for a DMF solution containing pp$_3$S$_4$ and [PtCl$_2$(NCC$_6$H$_5$)$_2$] without Pd(0). The phosphine intermediate 1,2-bis(diphenylphosphino)ethane (p$_2$) can be successfully separated as the chelate compound of Pd(II) by employing the novel catalysis of Pd(0) as follows. The p$_2$S$_2$ complex **2** was reacted with an excess of iodobenzene in DMF at 70 °C for 48 h under N$_2$ (see Experimental Section). About one-third of p$_2$S$_2$ was converted to p$_2$, which is coordinated to Pd(II), showing a ^{31}P NMR singlet at 65.9 ppm (Figure 6a). The yellow Pd(II) complex was separated by chromatography with an SiO$_2$ column. The ^{31}P NMR spectrum of the isolated Pd(II) complex in chloroform was in agreement with that of [PdI$_2$(p$_2$)][12] exactly, showing the singlet at 61.9 ppm (Figure 6b). The formation of the iodo Pd(II) complex is attributed to oxidative addition of the Pd(0) complex to iodobenzene followed by disproportionation (Scheme 3a). The phosphine oxide was mainly formed without iodobenzene because oxidative addition of Pd(0) did not proceed, and consequently p$_2$ was not trapped by Pd(II) and finally oxidized (Scheme 3b). When a Pd(II) complex such as [Pd(CH$_3$CN)$_4$](BF$_4$)$_2$ was used to trap the phosphine

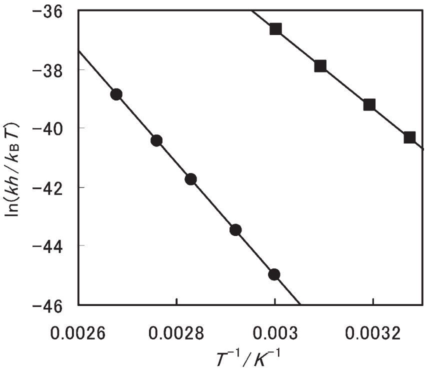


Figure 5. Temperature dependence of the rate constants for the chalcogen replacement reaction in the presence (■) and absence (●) of Pd(0).

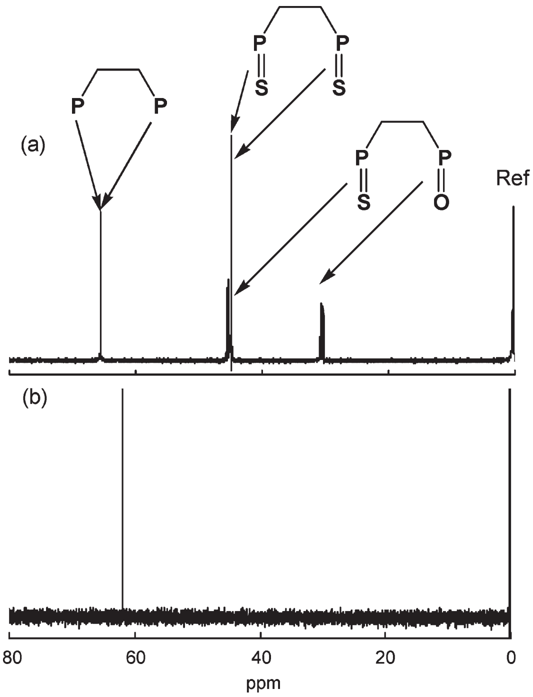


Figure 6. ^{31}P NMR spectrum of the DMF solution of [Pd(p$_2$S$_2$)(dba)] reacted with an excess of iodobenzene at 70 °C for 48 h under N$_2$ (a) and chloroform solution of isolated yellow Pd(II) complex (b).

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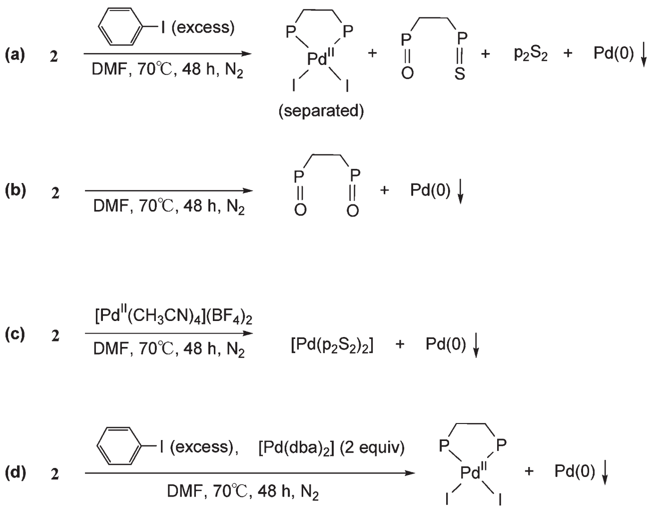
(19) Dobado, J. A.; Martínez-García, H.; Molina, J. M.; Sundberg, M. R. *J. Am. Chem. Soc.* **1998**, *120*, 8461.

(20) Aizawa, S.; Saito, K.; Kawamoto, T.; Matsumoto, E. *Inorg. Chem.* **2006**, *45*, 4859.

Scheme 3



instead of adding iodobenzene, the conversion from p_2S_2 to p_2 was hardly observed due to the formation of the Pd(II) complex with p_2S_2[13] prior to the catalytic reaction of p_2S_2 with Pd(0) (Scheme 3c). Almost quantitative formation of p_2 from p_2S_2 and isolation as the Pd(II) complex was achieved without chromatographic separation by the subsequent addition of [Pd(dba)$_2$], which acts as a catalyst and a source of [PdI$_2$(p$_2$)] (Scheme 3d). This result gave us evidence of the dissociation of chalcogen from the phosphine chalcogenide and revealed that the phosphine can be regenerated easily from the phosphine sulfide by P=S bond activation by Pd(0) and its oxidative addition.

Regeneration Reaction. As an example of application of this palladium-assisted P=X bond activation, regeneration of optically active BINAP was performed. Partially oxidized (*R*)-BINAP was easily converted to (*R*)-BINAPS$_2$ in a similar manner to that described for the other oxygenated phosphine sulfides (see Experimental Section). Regeneration of (*R*)-BINAP was successful by the reaction of [Pd((*R*)-binapS$_2$)(dba)] with excess iodobenzene, as in the case of regeneration of p_2. The ^{31}P NMR spectrum of the isolated purple complex is in good agreement with that of [PdI$_2$(binap)], showing a singlet at 17.8 ppm. It is confirmed that the optical purity of (*R*)-BINAP was completely retained during this regeneration procedure, because the CD intensity of the isolated complex normalized by the absorbance was in good agreement with that for [PdI$_2$((*R*)-binap)] separately prepared from (*R*)-BINAP ligand (Figure S5). These facts suggest that the new palladium(0)-promoted P=X bond activation is widely applicable to regeneration of phosphine or phosphine sulfide ligands.

Conclusions

Air-stable phosphine sulfide palladium(0) complexes **1**−**3** and [Pd((*R*)-binapS$_2$)(dba)] were prepared. High thermal stability of **1** and good recyclability of **3** were shown for Suzuki−Miyaura coupling in air. A mechanistic study revealed that the new catalytic chalcogen-atom replacement results from activation of the P=X bond as well as promotion of the oxidative chalcogenide formation. The intermediate phosphine was successfully trapped as a phosphine Pd(II) complex. The palladium(0)-promoted P=X bond activation is applicable to regeneration of phosphine or phosphine sulfide from oxidized phosphine.

Supporting Information Available: Preparation procedures, ^{31}P NMR for chalcogen-replacement reactions, kinetic data, and CD spectrum of the isolated binap complex. This material is available free of charge via the Internet at http://pubs.acs.org.