Mechanism of Catalytic Chalcogen Atom Replacement of Phosphine Chalcogenides and Separation of the Intermediate Phosphine

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The reaction mechanism of the chalcogen atom replacement of phosphine chalcogenides has been revealed to be dissociative from a kinetic investigation for the reaction of phosphine selenide with sulfur. The dissociation is enthalpically promoted by the catalysis of Pd^0. For a bidentate phosphine chalcogenide, the intermediate phosphine was separated as the Pd^{II} complex by the catalysis and oxidative addition of Pd^0 complex. The novel catalytic replacement and dissociation of chalcogen atom are applicable to regeneration of phosphines from their oxides via the phosphine sulfides.

Since phosphines have been regarded as effective ligands for the Pd^0 catalysts, phosphine-assisted Pd^0 catalyses have been widely employed in various coupling reactions for organic syntheses. 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 after the catalytic reactions are completed.[1] 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. Recently, we proposed that phosphine-sulfide groups can stabilize the Pd^0 center thermodynamically to form air-stable Pd^0 catalysts even after consumption of the substrates. By way of example, we reported recyclable air-stable Pd^0 complexes with tetradentate phosphine sulfide and polymer-supported phosphine sulfide.[2] In the course of this study, we have found a new catalytic activity of Pd^0 that promotes chalcogen atom replacement of phosphine chalcogenides ($R_3P=X$, X = O, S, and Se). So far, two associative mechanisms have been proposed for the chalcogen transfer from phosphine chalcogenides to phosphines by theoretical calculations as shown in Scheme 1.[3]

Mechanism 1 involves a nucleophilic attack of the phosphine phosphorus on the phosphine-chalcogenide phosphorus
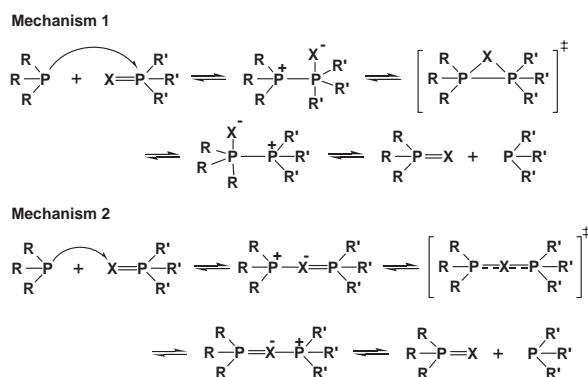
via a three-membered cyclic transition state and Mechanism 2 is an X-philic attack via a linear transition state. In the present work, however, we have revealed from kinetic experiments that the chalcogen atom replacement ($R_3P=X_1 + X_2 \rightleftarrows R_3P=X_2 + X_1$) proceeds via dissociation of X in conflict with the above theoretical investigation. We have also attempt to separate the intermediate phosphine as evidence of the dissociative mechanism and show the applicability of the catalytic dissociation to regeneration of phosphines from their oxides.

Kinetic measurements for the chalcogen atom replacement reaction 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).[4] 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.[5] Since the rates were substantially slow especially in 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 and the temperature dependence of the rate constants in Figure 1 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
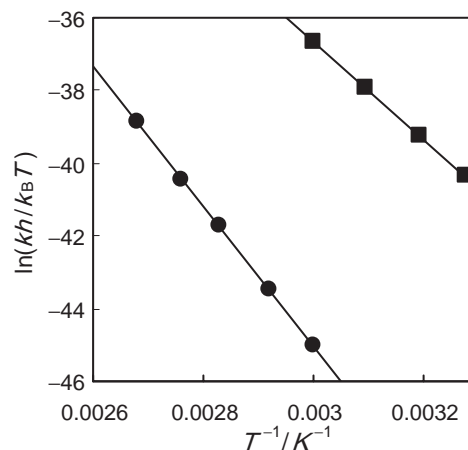

Figure 1. Temperature dependence of the rate constants for the chalcogen atom replacement reaction in the presence (■) and absence (●) of the Pd^0 catalyst.

Scheme 1.

P=X bond,[6] which is supported by the fact that the π back-donating Pt^0 center of the corresponding Pt^0 complex, $[Pt(dba)_2]$,[7] also showed similar catalytic activity.[8]

Because phosphine-sulfide groups can stabilize the Pd^0 center electronically, the phosphine-sulfide Pd^0 catalysts can be reused in air.[2] However, by a number of repetitions of the reaction, the sulfur atoms in the phosphine-sulfide groups are gradually replaced with oxygen atoms by the catalysis of Pd^0 to give the phosphine oxides, which deactivate the Pd^0 catalysts by precipitation of Pd sediment. This problem can be solved by the present catalytic replacement of chalcogen atoms. For example, though the phosphine-sulfide groups in 1,2-bis(diphenylphosphino)ethane disulfide (p_2S_2) of the substantially air-stable Pd^0 catalyst, $[Pd(p_2S_2)(dba)]$,[9] were gradually converted to phosphine oxides by heating under reflux in DMF for several hours without any substrate, the phosphine sulfide was regenerated by the addition of a large excess of sulfur to the DMF solution followed by heating at $125\,°C$ for $2\,h$ under N_2. In the absence of Pd^0, the conversion between phosphine-sulfide and phosphine-oxide groups can hardly proceed under the above conditions.

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. The p_2S_2 complex, $[Pd(p_2S_2)(dba)]$,[9] was reacted with an excess of iodobenzene in DMF at $125\,°C$ for $48\,h$ under N_2. About one third of p_2S_2 was converted to p_2, which is coordinated to Pd^{II} showing a ^{31}P NMR singlet at 65.9 ppm. The Pd^{II} complex was separated chromatographically with an SiO_2 column. The ^{31}P NMR spectrum of the isolated Pd^{II} complex in chloroform was in agreement with that of $[PdI_2(p_2)]$[10] exactly, showing the singlet at 61.9 ppm. The formation of iodo Pd^{II} complex is attributed to oxidative addition of the Pd^0 complex with iodobenzene followed by disproportionation.[11] Almost quantitative formation of p_2 from p_2S_2 and isolation as the Pd^{II} complex was achieved without the chromatographic separation by the subsequent addition of two equiv of $[Pd(dba)_2]$, which acts as a catalyst and a source of $[PdI_2(p_2)]$. This result gave us evidence of the dissociation of the chalcogen atom from the phosphine chalcogenide and revealed that the phosphine can be regenerated easily from the phosphine sulfide by the catalysis of Pd^0 and its oxidative addition.[12]

We can conclude that the chalcogen atom replacement of phosphine chalcogenides proceeds by dissociation of the chalcogen atoms, which is enthalpically promoted by the catalytic interaction of Pd^0. Taking advantage of this catalysis, it is possible to regenerate phosphines from phosphine oxides via phosphine sulfide formation. This catalytic conversion will be significant especially for elaborate and valuable phosphines.[13]

References and Notes
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3 M. Kullberg, J. Stawinski, *J. Organomet. Chem.* **2005**, *690*, 2571.

4 The concentrations of triphenylphosphine selenide, sulfur, and $[Pd(dba)_2]$ were 0.0212, 0.212–0.636, and 0.0106 or $0\,mol\,kg^{-1}$, respectively. The reaction temperature was changed from 305 to 333 K for the catalytic reaction and from 333 to 373 K for the considerably slow noncatalytic reaction. The catalytic reaction rate was unchanged in chloroform.

5 It was confirmed that the ^{31}P NMR signal intensity is proportional to the phosphine-chalcogenide concentration.

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

7 W. J. Cherwinski, B. F. G. Johnson, J. Lewis, *J. Chem. Soc., Dalton Trans.* **1974**, 1405.

8 By similar 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.

9 The phosphine sulfide Pd^0 complexes, $[Pd(p_2S_2)(dba)]$, was obtained by the reaction of p_2S_2 with equimolar $[Pd(dba)_2]$ in chloroform at room temperature followed by the addition of diethyl ether. $^{31}P\{^1H\}$ NMR ($CHCl_3$): δ (relative to D_3PO_4 in external D_2O) 44.2 (s). ^1H NMR ($CHCl_3$): δ 1.25 (t, CH_3- of diethyl ether, $^3J_{H-H} = 2.8$ Hz), 2.72 (d, $-CH_2CH_2-$ of p_2S_2), 3.72 (q, $-CH_2-$ of diethyl ether, $^3J_{H-H} = 2.8$ Hz), 7.10 (d, Ph–CH=CH– 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 pp_3S_4), 7.75 (d, Ph–CH=CH– of dba, $^3J_{H-H} = 16$ Hz). The catalytic activity for the cross-coupling reactions is comparable to or better than that of commonly used $[Pd(PPh_3)_4]$, which is unstable under aerobic conditions.

10 W. Oberhauser, C. Bachmann, T. Stampfl, R. Haid, P. Brüggeller, *Polyhedron* **1997**, *16*, 2827.

11 The phosphine oxide was mainly formed without iodobenzene because p_2 was not trapped by Pd^{II} and consequently oxidized. When the Pd^{II} complex such as $[Pd(CH_3CN)_4](BF_4)_2$ was used to trap the phosphine instead of adding iodobenzene, the conversion from p_2S_2 to p_2 was hardly observed probably due to the formation of the Pd^{II} complex with p_2S_2 prior to the catalytic reaction of p_2S_2 with Pd^0.

12 It is difficult to obtain pure phosphine directly from the phosphine oxide because the P=O bond is much stronger than the P=S bond and the interaction between the phosphine-oxide group and Pd^0 is extremely weak.

13 The regeneration of valuable optically active diphosphines, 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP) derivatives, is under investigation and will be successful retaining optical purity.

14 Supporting Information is also available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chemlett/index.html.