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## Mechanistic Studies on Chalcogen-Atom Replacement Reactions of Phosphine Chalcogenides and Separation of the Intermediate Phosphine

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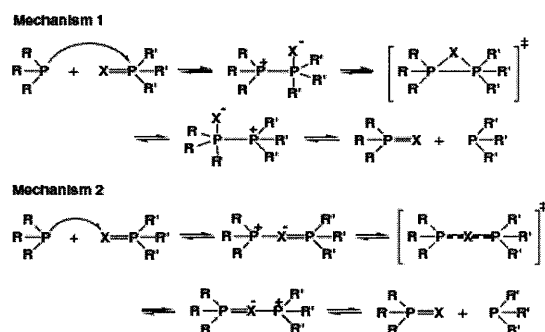
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### Background

Phosphines are effective ligands to stabilize the Pd<sup>0</sup>, therefore, phosphine-assisted Pd<sup>0</sup> complexes have been widely employed as catalysts in the coupling reactions. However, phosphines are toxic, expensive and because of their air-sensitivity, they get oxidized very easily during the catalytic reactions. Therefore it is necessary to regenerate and reuse these catalysts. On solving this problem, I have found a new catalysis of Pd<sup>0</sup> (and Pt<sup>0</sup>) for chalcogen replacement reactions of phosphine chalcogenides which is a new catalytic activity of Pd<sup>0</sup>. The mechanism of these replacement reactions has been observed to be dissociative from the kinetic investigation. On the basis of this mechanism, it is very easy to recover and reuse those phosphine catalysts which are elaborative and valuable.

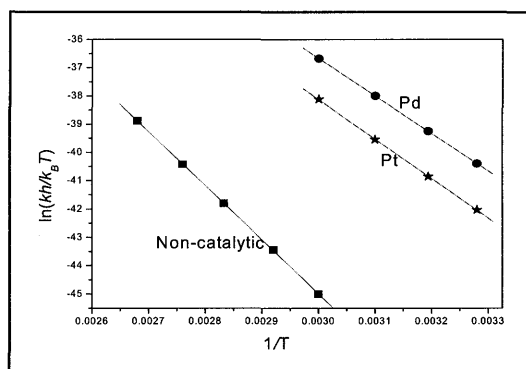
### Results

It has been observed that, phosphine-free Pd<sup>0</sup> catalysts either blocks the catalytic cycles kinetically or decomposed into inactive palladium black. To overcome these problems of phosphine ligands, we have prepared phosphine sulfides which can stabilize the Pd<sup>0</sup> thermodynamically to form air-stable Pd<sup>0</sup> catalysts even after consumption of the substrates and do not deactivate the catalytic cycle kinetically. Thus, we are able to prepare air-stable Pd<sup>0</sup>-phosphine sulfide complexes as the catalysts. 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<sup>0</sup> to give the phosphine oxides, which deactivate the Pd<sup>0</sup> catalysts by precipitation of Pd sediment. This problem can be solved by the reaction of these phosphine oxides with excess sulfur in DMF at 125°C for 2h in presence of Pd<sup>0</sup>. This is the catalytic replacement of chalcogen atoms of phosphine chalcogenides. In the absence of Pd<sup>0</sup>, this conversion can hardly proceed under the above conditions. 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. 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.



Scheme 1

From the thorough kinetic investigation, it reveals that the chalcogen atom replacement ( $R_3P=X_1 + X_2 \rightarrow R_3P=X_2 + X_1$ , where  $X_1$  and  $X_2$  are two different chalcogen)) proceeds via dissociation of  $X$  in conflict with the above theoretical investigation. For the study of the reaction mechanism, we considered the reaction of phosphine selenide with sulfur. I have taken simple monodentate triphenylphosphine selenide, which was allowed to react with excess sulfur in presence of  $[Pd(dba)_2]$  ( $dba = \text{dibenzylideneacetone}$ ). I have carried out the kinetic experiments both in presence and absence of  $Pd^0$  and found that the rate constants of chalcogen replacement reactions for both these kinds remain almost unchanged on varying the sulfur concentration. This results indicates that the rate constants does not depend on sulfur concentration ie, rate constant is zeroth order w.r.t. sulfur concentration and the mechanism may be the dissociative in nature. I have also carried out the catalytic reactions in presence of  $Pt^0$ . Activation enthalpy ( $\Delta H^\ddagger$ ) and entropy ( $\Delta S^\ddagger$ ) for both catalytic and non-catalytic reactions have been estimated (Table 1) from the Eyring plot (Figure 1). The dissociation is enthalpically promoted by the catalysis of  $Pd^0$  (and also  $Pt^0$ ). Positive  $\Delta S^\ddagger$  value also indicates the dissociative mechanism.



**Figure 1**

**Table 1:**

	$\Delta H^\ddagger$ (kJ/mol)	$\Delta S^\ddagger$ (J/mol/K)
Catalytic reaction by $Pd(0)$	$110.46 \pm 0.54$	$26 \pm 1.72$
Catalytic reaction by $Pt(0)$	$116.2 \pm 0.63$	$32 \pm 2.00$
Non-catalytic reaction	$158.5 \pm 0.60$	$102 \pm 1.73$

I have also attempted to separate the intermediate phosphine as the evidence of the dissociative mechanism. The  $p_2S_2$  complex,  $[Pd(p_2S_2)(dba)]$  was reacted with an excess of iodobenzene in DMF at  $70^\circ C$  for 48 h under  $N_2$  and the phosphine intermediate, 1,2-bis(diphenylphosphino)ethane ( $p_2$ ), was successfully separated as the chelate compound of  $Pd^{II}$  by employing the novel catalysis of  $Pd^0$ . This result gave us evidence of the dissociation of the chalcogen atom from the phosphine chalcogenides and revealed that the phosphine can be regenerated easily from the phosphine sulfide by the catalysis of  $Pd^0$ . The novel catalytic replacement and dissociation of chalcogen atom are applicable to regeneration of phosphines from their oxides via the phosphine sulfides.

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  $Pd^0$  (and also  $Pt^0$ ). 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 the regeneration and reuse of other elaborative and expensive phosphines-catalysts which gets oxidized during the coupling reaction.