R/X exchange reactions in cis-[M(R)2{P(X)(NMeCH2)2}]2 (M = Pd, Pt), via a phosphenium intermediate

Masumi Itazaki, Noriko Tsuchida, Yuka Shigesato, Keiko Takano and Hiroshi Nakazawa

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R/X Exchange Reactions on Pd and Pt Complexes Containing Phosphine Ligands, \( \text{cis-}[M(R)_{2}(P(X)(NMeCH_{2})_{2})_2] \) (M = Pd, Pt), via a Phosphonium Intermediate and Theoretical Approach

Masumi Itazaki, a,b Noriko Tsuchida, a,b,c Yuka Shigesato, a Keiko Takano b and Hiroshi Nakazawa *a

R/X exchange reactions in \( \text{cis-}[M(R)_{2}(P(X)(NMeCH_{2})_{2})_2] \) (M = Pd, Pt; R = ary1, alkyl; \( X = \text{Cl, Br} \)) were achieved for the first time to give \( \text{cis-}[M(X)_{2}(P(R)(NMeCH_{2})_{2})_2] \). DFT calculations suggested that the exchange reaction proceeds via a phosphonium intermediate.

Phosphine compounds in transition metal complexes play important roles in both their catalytic activity and product selectivity, and generally remain unchanged throughout catalytic reactions. For example, palladium complexes containing phosphine ligands and \( R_3P \) are often obtained rather than a main product, due to exchange reactions between substituents on the phosphine ligand and the transition metal. Therefore, a detailed investigation of exchange reactions between substituents on phosphine ligands and transition metals will provide new insight for coordination chemistry, catalytic chemistry, and organic synthesis. Exchange reactions between \( R^1 \) groups on phosphine ligands and \( R^2 \) groups on transition metals have been investigated. Four different pathways have been proposed for the exchange mechanism: (i) oxidative addition of the \( R^1 \)-P bond to the metal center (in other words, \( R^1 \) migration to the metal center) to give a 3e- or 1e-donor phosphide complex, followed by reductive elimination of \( R^2 \) and the phosphide phosphorus (in other words, \( R^2 \) migration from the metal center to the phosphide phosphorus), (ii) formation of a phosphonium ion, (iii) concerted internal or external nucleophilic attack of the \( R^2 \) group on the P atom coordinated to the transition metal (M) and internal attack of \( R^1 \) on the P atom coordinated to M, and (iv) formation of a hypervalent metallaphosphorane (Scheme 1). The \( R^1 \) group on the P atom is generally a simple aryl or alkyl group, while the \( R^2 \) group on the metal center is another C-based moiety, or an N- or O-based group, in most cases. Only one example of an exchange reaction involving a halogeno group has been reported by Macgregor and Grushin. Exchange of the F atom on the Rh center and the Ph group on the P atom took place when a fluororhodium complex, \( \text{Rh(F)(PPh}_{3})_3 \), was used. This reaction was proposed to proceed via a metallaphosphorane species by density functional theory (DFT) calculations. To the best of our knowledge, no example has yet been shown of an exchange reaction between a halogeno group on the P atom and an aryl or alkyl group on the metal center.

In this communication, we describe the first example of R/X (\( R = \text{alkyl, aryl}; X = \text{Cl, Br} \)) exchange reactions between X groups on P atoms and R groups on metal centers for Pd and Pt complexes, \( \text{cis-}[M(R)_{2}(P(X)(NMeCH_{2})_{2})_2] \). Furthermore, the reaction mechanism was investigated by DFT calculations.

Reaction of Pd(Me)₃(cod) (COD = 1,5-cyclooctadiene), which was prepared in situ by the reaction of Pd(I)₃(cod) with MeMgBr, with 2 equiv. of P(Cl)(NMeCH₂)₂ (1a) in hexane afforded a dichloropalladium complex, cis-[Pd(Cl)₂(P(Me)(NMeCH₂)₂) (2) (eqn (1)).

\[
\begin{align*}
\text{Pd(III)(cod)} + \text{MeMgBr} & \rightarrow \text{MeBr} + \text{Pd(Me)₃(cod)} \\
\text{MeMgBr} & \rightarrow \text{MeCl} + \text{Br}^{-} \\
\text{hexane} & \rightarrow \text{hexane} \\
\text{25 °C, 10 min} & \rightarrow \text{2 23%}
\end{align*}
\]

**Scheme 1.** Mechanisms proposed for the exchange reaction between the \( R^1 \) group on the P atom and the \( R^2 \) group on the metal center.

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We originally hypothesized that 2 was synthesized by a Me/Cl exchange reaction of the dimethylpalladium complex cis-[Pd(Me)₂(P(Cl)(NMeCH₂)₂)]. However, the corresponding Pd complex could not be obtained. Therefore, we decided to obtain the corresponding dimethyl Pt complex containing chlorophosphine ligands, cis-[Pt(Me)₂(P(Cl)(NMeCH₂)₂)] (3a), in 85% yield. Complex 3a was converted into cis-[Pt(Cl)₂(P(Me)(NMeCH₂)₂)] (4a) in 99% yield in CH₂CN at 25 °C for 3 h as a result of the exchange reaction between the Cl atoms on the P atoms and the Me groups on the Pt center (eqn (2)). This exchange reaction was required longer reaction time (24 h) when CH₂Cl₂ or CHCl₃ was used as a solvent.

The molecular structures of 2, 3a, and 4a were confirmed by single crystal X-ray diffraction. ORTEP drawings of the complexes are depicted in Fig. 1 with the atomic numbering scheme. Complexes 2 and 4a adopt typical square planar configurations: the metal centers have two Cl atoms and two methylphosphine ligands, P(Me)(NMeCH₂)₂, which are positioned cis to each other, due to the exchange reaction. In contrast, the Pt center in 3a has two methyl groups and two phosphine ligands containing a Cl atom on each P atom.

To investigate the scope and limitation of the exchange reaction, we attempted reactions of 1a with platinum complexes containing different R ligands. Complexes 3b–d were readily converted into complexes 4b–d within 30–40 min in acetonitrile (eqn (3)).

In contrast, the exchange reaction of 3e, which contained two p-CF₃(C₆H₄) ligands on the Pt center, took 3 days at 60 °C to complete, and the products were a mixture of the cis and trans isomers (eqn (4)). The difference in reactivity between 3d and 3e can be considered to originate from the decrease in δ character of the ipso carbons in 3e. Next, we examined the reaction of Pt(Me)₂(cod) with 2 equiv. of P(Br)(NMeCH₂)₂ (1b), which has Br instead of Cl in hexane, which yielded a Pt complex cis-[Pt(Me)₂(P(Br)(NMeCH₂)₂)] (3f). Complex 3f was converted into cis-[Pt(Br)₂(P(Me)(NMeCH₂)₂)] (4f) through a Me/Br exchange reaction in CH₂CN after reaction for 1 h at 25 °C (eqn (5)). The structures of 4d and 4f were studied by X-ray crystal structure analysis (Fig. 2). Although the Me/Cl exchange reaction of 3a in CH₂CN required 3 h for completion, this Me/Br exchange took just 1 h at 25 °C. The difference in the reaction time may result from the bond energies of P–Br bond energy (78 kcal/mol) is greater than the P–Cl bond energy (63 kcal/mol). Therefore, cleavage of the P–X bond is expected to be involved in the rate determining step.

The molecular structure of 3g was confirmed by single crystal X-ray diffraction (Fig. 2). The P–Cl bonds (2.101(3), 2.097(3) Å) of 3g are longer than those of the previously reported chloro–phosphine Pt complex (1.996–2.020 Å), whereas they are shorter than the P–Cl bonds of 3a (2.1595(16) Å) (Fig. 3). The stronger P–Cl bonds of 3g compared to 3a may be responsible for the lack of I/Cl exchange.
exchange for 3g, suggesting that dissociation of Cl⁻ from the phosphorus atom is a key factor for the exchange reaction.

2.2437(11) Å  
2.2437(11) Å

Fig. 3. Selected bond distances for 3g (left) and 3a (right).

For the Me/Cl exchange reaction of 3a to 4a shown in Eq. 2, there are three possible pathways, i.e., (1) “path A” via metallaphosphorane complexes 6a and 7a as intermediates or transition states (TSs), (2) “path B”, an oxidative addition and reductive elimination path via five-coordinated metal complexes, and (3) “path C” via phosphene complexes 10a and 12a as intermediates or transition states (see Scheme 2). All structures depicted in this scheme show only the connectivity and do not show the geometrical relationship.

path A: via metallaphosphorane

path B: oxidative addition and reductive elimination

path C: via phosphene

Scheme 2. Possible reaction pathway for Me/Cl exchange.

To elucidate the mechanism of the Me/Cl exchange process of cis-[Pt(Me)₂(P(Cl)(MeCH₂))₂] (3a), DFT (B3PW91) calculations were performed with two different basis sets, considering solvent effects by IEFPCM (solvent: acetonitrile). The basis sets used were SDD ECP plus the corresponding basis set for Pt, 6-31+G* for chlorine, and 6-31G* for the other atoms, denoted as BS1; and SDD ECP plus the corresponding basis set for Pt, 6-311+G* for chlorine, and 6-31G* for the other atoms, denoted as BS2.

The stationary points for the metallaphosphorane complexes were not found for path A. Computational details and results are described in the Supporting Information (SI) (see Figs. S1 and S2).

For path B, geometry optimization was carried out for the metal complexes derived from 3a and 5a. Supposing that oxidative addition of one of the P–Cl bonds in 3a generates [Pt(Cl)(Me)₂(PR₃)(P(Cl)R₃)] with the PR₃ and Cl ligands in cis positions, five five-coordinated isomers (Aₘₐₓ=Eₜₐₜ) are conceivable (see Fig. S3). After optimization of these five complexes, Aₘₐₓ=Eₜₐₜ were obtained (see Fig. S3). Aₘₐₓ and Bₘₐₓ have a dissociated Cl atom, which is not the case for stable complexes. Cₘₐₓ and Dₘₐₓ have the phosphide ligand at the top of the pyramidal structure. In both cases, the phosphide ligand serves as a 1e-donor ligand. Cₘₐₓ and Dₘₐₓ contain two Me ligands in cis and trans positions, respectively. Eₘₐₓ has almost the same geometry as that of Cₘₐₓ. Thus, two types of optimized geometries, Cₘₐₓ and Dₘₐₓ, were obtained for five-coordinated complex 8a. Dₘₐₓ was much more unstable than the reactant 3a, by 10.23 kcal/mol. Cₘₐₓ was less stable but comparable in energy to 3a. The energy difference between them was only 2.14 kcal/mol. Therefore, the most plausible intermediate out of the five five-coordinated metal complexes derived from 3a was Cₘₐₓ. We then performed a search for the transition state (TS) involved in the transfer of Cl from the phosphine to Pt. However, the TS was not found (see Figs. S5 and S8). Similar results were obtained for 9a, (see Figs. S4, S6, and S8). Thus, the Me/Cl exchange reaction does not take place via path B.

On the other hand, all of the stationary points along the reaction pathway were found for path C. The energy profile of the reaction based on the B3PW91/BS2 calculations is shown in Fig. 4. The route has 7 local minima and two TSs. Complexes 3a, 4a, and 5a are neutral complexes, and the others are cationic complexes. The energy of the isolated Cl anion is added to each of the cationic complexes. The first step (3a → 10a) is the formation of the phosphene complex via heterolytic cleavage of the P–Cl bond. The phosphene complex 10a and the reactant 3a are comparable in energy (the energy difference is only 2.42 kcal/mol). Although the TS for P–Cl bond cleavage has not yet been found, scanning on the potential energy surface (PES) of P–Cl bond dissociation showed that the maximum value of the dissociation energy is 11.35 kcal/mol and Cl⁻ elimination can occur at room temperature (see Fig. S9). A methyl group transfers from the central metal to the P atom in the second step (10a → 11a), for which the activation energy is 9.56 (= 11.98 − 2.42) kcal/mol. Molecular orbital analysis was carried out to elucidate the character of the interaction between the leaving group and the atomic site or bond to which the former moves during the reaction. The Me group transfer is attributed to the donor-acceptor interaction between the σ orbital on the Me–Pt bond (HOMO-1) and the empty π orbital on the P atom (LUMO) (see Fig. S11). The third step (11a → 5a) is the process of Cl⁻ coordination to Pt. Complex 5a is more stable than the reactant 3a by 15.96 kcal/mol. One Me/Cl exchange reaction is completed in the first half of the reaction (steps 3a to 5a). The second half of the reaction (steps 5a to 4a) is quite similar to the first half.

As for the first half of the reaction, the TS for Cl⁻ elimination in the second half of the reaction was not found. However, the PES for P–Cl bond dissociation showed that Cl⁻ elimination is possible at room temperature, as for the first half of the
reaction (see Fig. S10). The activation energy for the second Me/Cl exchange, 2.92 (≈ −8.96 − (−11.88)) kcal/mol, is lower than that of the first (9.56 kcal/mol). The orbital involved in the Me-transfer reaction was stabilized from 12a to 13a, in contrast to 10a to 11a (see the orbital energies in Fig. S12). These results are consistent with the difference in activation energies between TS(10a → 11a) and TS(12a → 13a). The final product (4a) is more stable than 3a and 5a by 35.68 and 19.72 kcal/mol, respectively. All steps in the reaction are exothermic after the formation of 11a, and all the activation energies are low enough for the reaction to proceed at room temperature. Therefore, it is concluded that the most plausible pathway for the Me/Cl exchange reaction is path C via the phosphinenium complex.

The energy diagram shown in Fig. 4 suggests that some modification causing destabilization of the phosphinenium intermediate leads to faster formation of the R/X exchange product. We previously reported that a complex was stabilized by an N,N′-chelating ligand on the phosphinenium phosphorus. Therefore, a faster Me/Cl exchange reaction is expected for cis-[Pt(Me)2(P(NEt2)(NMMe2))] (3h), which contains no chelating ligands, than for 3a which does contain N,N′-chelating ligands. We prepared 3h and examined the Me/Cl exchange reaction (eqn 7). Reaction of Pt(Me)2(cod) with P(NEt2)(NMMe2) generated 3h in 71% yield. The Me/Cl exchange reaction proceeded successfully for 3h in acetonitrile, forming dichloroplatinum complex cis-[Pt(Cl)2(P(Me)(NMMe2))] (4h) within 10 min (eqn 7). The exchange reaction for 3h is much faster than that for 3a (3 h). These results support the hypothesis that the exchange reaction proceeds via the phosphinenium intermediate.

In summary, we developed an unprecedented R/X exchange reaction on Pt and Pd complexes with phosphine ligands, cis-[M(R)2(P(X)(NMMe2))] (M = Pd, Pt; R = alkyl, aryl; X = Cl, Br). This exchange reaction took place through a phosphinenium intermediate, which was supported by DFT calculations.

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Notes and references
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5 Previously we reported that reaction of cis-[Pt(Cl)(Me)(cod)] with 2 equiv. of P(NEt2)3(NMeCH2)2 afforded a similar complex [Pt(Cl)(Me)(P(NEt2)3(NMeCH2)2)] as the cis/trans mixture. M. Itazaki, Y. Shigesato, H. Nakazawa, C. R. Chim., 2010, 13, 943.