R/X exchange reactions in cis-[M(R)$_2${P(X)(NMeCH$_2$)$_2$}$_2$] (M = Pd, Pt), *via* a phosphenium intermediate

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COMMUNICATION

R/X Exchange Reactions on Pd and Pt Complexes Containing Phosphine Ligands, *cis*-[M(R)₂{P(X)(NMeCH₂)₂}₂] (M = Pd, Pt), *via* a Phosphenium Intermediate and Theoretical Approach

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R/X exchange reactions in *cis*-[M(R)₂{P(X)(NMeCH₂)₂}₂] (M = Pd, Pt; R = aryl, alkyl; X = Cl, Br) were achieved for the first time to give *cis*-[M(X)₂{P(R)(NMeCH₂)₂}₂]. DFT calculations suggested that the exchange reaction proceeds *via* a phosphenium 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 ligand(s), Pd(L)ₓ(PR₃)ᵧ (x, y ≧ 1) commonly catalyze cross-coupling reactions.[1] However, several by-products are often obtained rather than a main product, due to exchange reactions between substituents on the phosphine ligand and the transition metal.[2] 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 R¹ groups on phosphine ligands and R² groups on transition metals have been investigated.[3] Four different pathways have been proposed for the exchange mechanism: (i) oxidative addition of the R¹–P bond to the metal center (in other words, R¹ migration to the metal center) to give a 3e- or 1e-donor phosphide complex, followed by reductive elimination of R² and the phosphide phosphorus (in other words, R² migration from the metal center to the phosphide phosphorus), (ii) formation of a phosphonium ion, (iii) concerted internal or external nucleophilic attack of the R² group on the P atom coordinated to the transition metal (M) and internal attack of R¹ on the P atom coordinated to M, and (iv) formation of a hypervalent metallaphosphorane (Scheme 1). The R¹ group on the P atom is generally a simple aryl or alkyl group, while the R² group on the
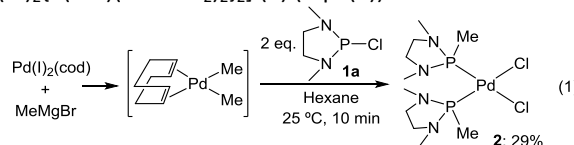
metal center is another C-based moiety, or an N- or O-based group, in most cases. Only one example of an exchange reaction involving a halogeno group has been reported by Macgregor and Grushin.[4] Exchange of the F atom on the Rh center and the Ph group on the P atom took place when a fluororhodium complex, Rh(F)(Ph₃P)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.
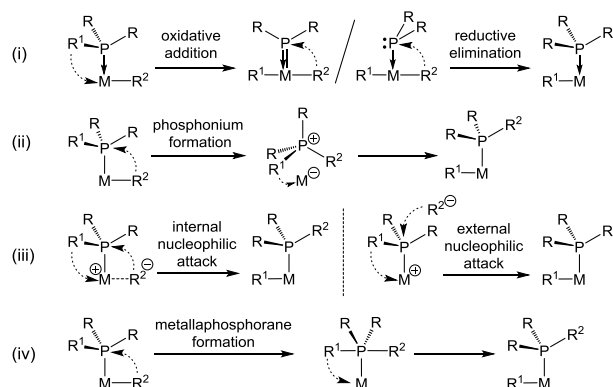
Scheme 1. Mechanisms proposed for the exchange reaction between the R¹ group on the P atom and the R² group on the metal center.

In this communication, we describe the first example of R/X (R = alkyl, aryl; X = Cl, Br) exchange reactions between X groups on P atoms and R groups on metal centers for Pd and Pt complexes, *cis*-[M(R)₂{P(X)(NMeCH₂)₂}₂]. Furthermore, the reaction mechanism was investigated by DFT calculations.

Reaction of Pd(Me)₂(cod) (cod = 1,5-cyclooctadiene), which was prepared in situ by the reaction of Pd(I)₂(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] (**2**) (eqn (1)).
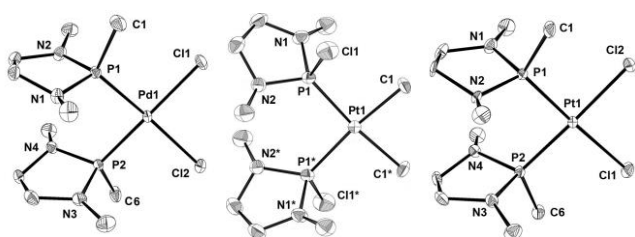
Fig. 1. ORTEP drawings of **2** (left), **3a** (center) and **4a** (right) with 30% thermal ellipsoidal plots. Hydrogen atoms are omitted for simplicity. Selected bond distances (Å): Pd1–Cl1 2.3796(12), Pd1–Cl2 2.3853(12), Pd1–P1 2.2431(12), Pd1–P2 2.2438(12) for **2**, Pt1–C1 2.132(4), Pt1–P1 2.2438(11) for **3a**, Pt1–Cl1 2.3764(19), Pt1–Cl2 2.3793(18), Pt1–P1 2.220(2), Pt1–P2 2.2244(18) for **4a**.

We originally hypothesized that **2** was synthesized by a Me/Cl exchange reaction of the dimethylpalladium complex *cis*-[Pd(Me)$_2$$\{$P(Cl)(NMeCH$_2$)$_2\}_2$]. However, the corresponding Pd complex could not be obtained. Therefore, we decided to obtain the corresponding dimethyl Pt complex containing chlorophosphine ligands, *cis*-[Pt(Me)$_2$$\{$P(Cl)(NMeCH$_2$)$_2\}_2$], as an intermediate for the Me/Cl exchange reaction. Reaction of Pt(Me)$_2$(cod) with 2 equiv. of **1a** in hexane gave the desired dimethylplatinum complex, *cis*-[Pt(Me)$_2$$\{$P(Cl)(NMeCH$_2$)$_2\}_2$] (**3a**), in 85% yield. Complex **3a** was converted into *cis*-[Pt(Cl)$_2$$\{$P(Me)(NMeCH$_2$)$_2\}_2$] (**4a**) in 99% yield in CH$_3$CN at 25 °C for 3 h as a result of the exchange reaction between the Cl atoms on the P atoms and the Me groups on the Pt center (eqn (2)). This exchange reaction was required longer reaction time (24 h) when CH$_2$Cl$_2$ or CHCl$_3$ was used as a solvent.
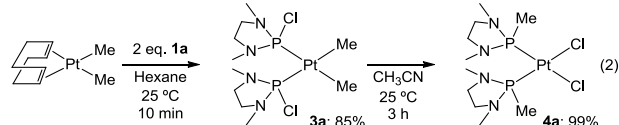
The molecular structures of **2**, **3a**, and **4a** were confirmed by single crystal X-ray diffraction. ORTEP drawings of the complexes are depicted in Fig. 1 with the atomic numbering scheme. Complexes **2** and **4a** adopt typical square planar configurations: the metal centers have two Cl atoms and two methylphosphine ligands, P(Me)(NMeCH$_2$)$_2$, 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)).
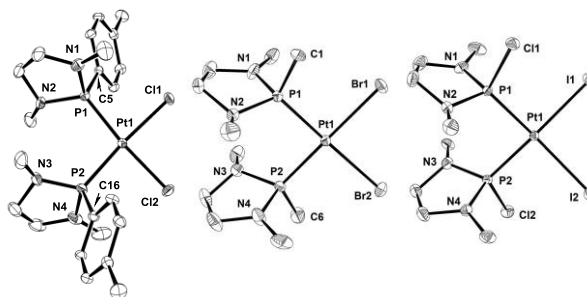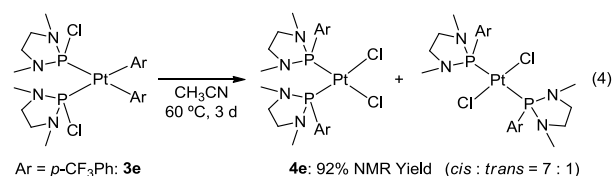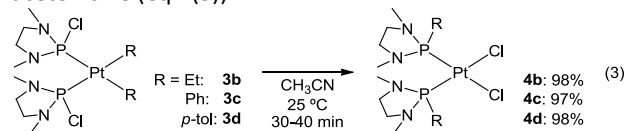

Fig. 2. ORTEP drawings of **4d** (left), **4f** (center) and **3g** (right) with 30% thermal ellipsoidal plots. Hydrogen atoms are omitted for simplicity. Selected bond distances (Å): Pt1–Cl1 2.3667(15), Pt1–Cl2 2.3724(13), Pt1–P1 2.2221(13), Pt1–P2 2.2253(15) for **4d**, Pt1–Br1 2.5175(11), Pt1–Br2 2.5031(10), Pt1–P1 2.226(2), Pt1–P2 2.225(2) for **4f**, Pt1–I1 2.6505(7), Pt1–I2 2.6492(7), Pt1–P1 2.2242(19), Pt1–P2 2.225(2) for **3g**.

In contrast, the exchange reaction of **3e**, which contained two *p*-CF$_3$(C$_6$H$_4$) 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)).[5] 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)(NMeCH$_2$)$_2$ (**1b**), which has Br instead of Cl, in hexane, which yielded a Pt complex *cis*-[Pt(Me)$_2$$\{$P(Br)(NMeCH$_2$)$_2\}_2$] (**3f**). Complex **3f** was converted into *cis*-[Pt(Br)$_2$$\{$P(Me)(NMeCH$_2$)$_2\}_2$] (**4f**) through a Me/Br exchange reaction in CH$_3$CN after reaction for 1 h at 25 °C (eqn (5)). The structures of **4d** and **4f** were studied by X-ray crystal structure analysis (Fig. 2). Although the Me/Cl exchange reaction of **3a** in CH$_3$CN required 3 h for completion, this Me/Br exchange took just 1 h at 25 °C. The difference in the reaction time may result from the bond energies of P–X. The P–Cl bond energy (78 kcal/mol) is greater than the P–Br bond energy (63 kcal/mol).[6] Therefore, cleavage of the P–X bond is expected to be involved in the rate determining step.
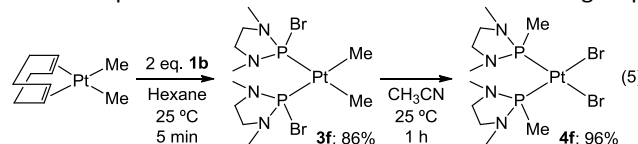
In order to examine I/Cl exchange, *cis*-[Pt(I)$_2$$\{$P(Cl)(NMeCH$_2$)$_2\}_2$] (**3g**) was prepared in 62% yield *via* reaction of Pt(I)$_2$(cod) with 2 equiv. of **1a** in CH$_2$Cl$_2$ (eqn (6)). The CH$_3$CN solution of **3g** did not undergo an I/Cl exchange reaction.
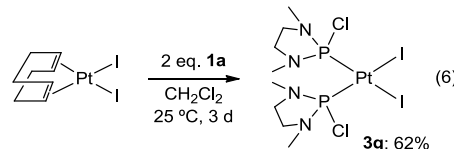
The molecular structure of **3g** was confirmed by single crystal X-ray diffraction (Fig. 2). The P–Cl bonds (2.101(3), 2.097(3) Å) of **3g** are longer than those of the previously reported chloro–phosphine Pt complex (1.996–2.020 Å),[7] whereas they are shorter than the P–Cl bonds of **3a** (2.1595(16) Å) (Fig. 3). The stronger P–Cl bonds of **3g** compared to **3a** may be responsible for the lack of I/Cl

exchange for **3g**, suggesting that dissociation of Cl⁻ from the phosphorus atom is a key factor for the exchange reaction.
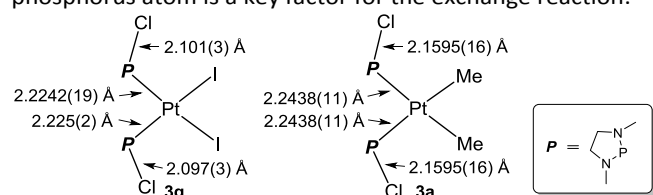

Fig. 3. Selected bond distances for **3g** (left) and **3a** (right).

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* phosphenium 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.).
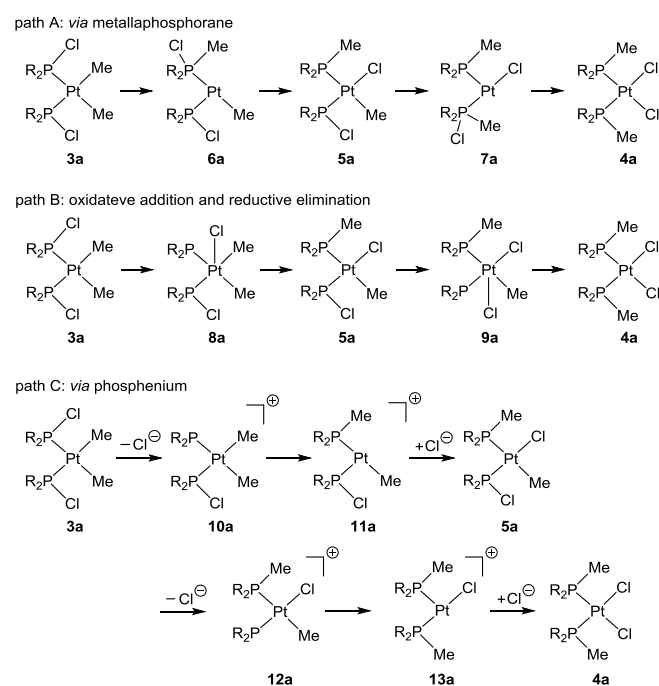
Scheme 2. Possible reaction pathway for Me/Cl exchange.

To elucidate the mechanism of the Me/Cl exchange process of *cis*-[Pt(Me)₂{P(Cl)(NMeCH₂)₂}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 6-311G* 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(PR₂)(PClR₂)] with the PR₂ and Cl ligands in *cis* positions, five five-coordinated isomers (A_{init}–E_{init}) are conceivable (see Fig. S3). After optimization of these five complexes, A_{opt}–E_{opt} were obtained (see Fig. S3). A_{opt} and B_{opt} have a dissociated Cl atom, which is not the case for stable complexes. C_{opt} and D_{opt} have the phosphide ligand at the top of the pyramidal structure. In both cases, the phosphide ligand serves as a 1e-donor ligand. C_{opt} and D_{opt} contain two Me ligands in *cis* and *trans* positions, respectively. E_{opt} has almost the same geometry as that of C_{opt}. Thus, two types of optimized geometries, C_{opt} and D_{opt}, were obtained for five-coordinated complex **8a**. D_{opt} was much more unstable than the reactant **3a**, by 10.23 kcal/mol. C_{opt} 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 C_{opt}. 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 phosphenium complex *via* heterolytic cleavage of the P–Cl bond. The phosphenium 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
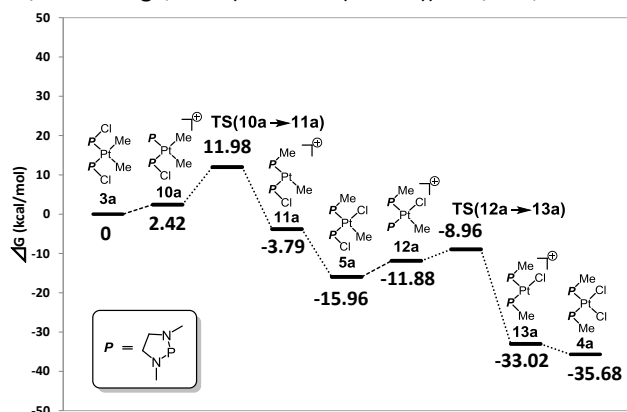

Fig. 4. Gibbs free energy profile for path C based on the B3PW91/BS2 calculations.

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 phosphenium complex.

The energy diagram shown in Fig. 4 suggests that some modification causing destabilization of the phosphenium intermediate leads to faster formation of the R/X exchange product. We previously reported that a phosphenium complex was stabilized by an *N,N'*-chelating ligand on the phosphenium phosphorus.[8] Therefore, a faster Me/Cl exchange reaction is expected for *cis*-[Pt(Me)$_2$\{P(Cl)(NMe$_2$)$_2$\}$_2$] (**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(Cl)(NMe$_2$)$_2$ 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)(NMe$_2$)$_2$\}$_2$] (**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 phosphenium intermediate.
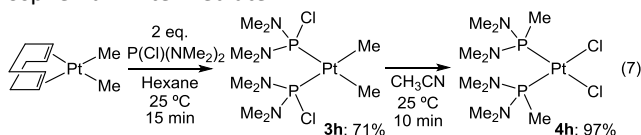
In summary, we developed an unprecedented R/X exchange reaction on Pt and Pd complexes with phosphine ligands, *cis*-[M(R)$_2$\{P(X)(NMeCH$_2$)$_2$\}$_2$] (M = Pd, Pt; R = alkyl, aryl; X = Cl, Br). This exchange reaction took place through a phosphenium intermediate, which was supported by DFT calculations.

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