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Iodo-Ligand Substitution of $[Pd(pp_3)I]^+$ (pp_3 = Tris(2-diphenylphosphinoethyl)phosphine) by Trimethylphosphite. The First Proposition of the Associative Ligand-Substitution Mechanism of Trigonal-Bipyramidal Five-Coordinate Palladium(II) Complex

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The kinetic investigation for the iodo-ligand substitution of $[Pd(pp_3)I]^+$ (pp_3 = tris(2-diphenylphosphinoethyl)phosphine) by trimethylphosphite in $CDCl_3$ has been performed by ^{31}P NMR spectroscopy. The trigonal-bipyramidal structure of the reactant and product has been confirmed by X-ray analysis and ^{31}P NMR spectra. The associative mode in the activation process is first proposed for the trigonal-bipyramidal palladium(II) complexes.

Clarification of the reaction mechanisms for metal complexes is important to understand their properties in solution and in biological systems. From this point of view, the kinetics for ligand-substitution and solvent-exchange reactions of metal complexes have been extensively investigated. In these studies, the kinetic properties of square-planar palladium(II) and platinum(II) complexes have been well established and an associative mechanism via a trigonal-bipyramidal transition state has been generally proposed.$^{1)}$ For these complexes, the nonbonding p_z orbital perpendicular to the molecular plane is vacant. Accordingly, an electron pair of the entering ligand can attack the vacancy.$^{2)}$ On the other hand, the trigonal-bipyramidal Pd(II) and Pt(II) complexes have no vacant orbital, and consequently the lone pair of the entering ligand exclusively brings about repulsive interaction with the occupied d orbitals in the associative mechanism. Therefore, it is attractive and important to confirm the reaction mechanism and such an approach can contribute to the further understanding of the kinetic properties of Pd(II) and Pt(II) complexes.

In this work, as the simple instance, the monodentate-ligand substitution of the trigonal-bipyramidal Pd(II) complex with the tripod ligand, tris(2-diphenylphosphinoethyl)phosphine (pp_3), which tends to maintain the trigonal-bipyramidal structure for the metal ions with d^8 configuration such as Pt(II), Ni(II), and Co(I)$^{3-7)}$ has been selected. We report the kinetics for substitution of I^- in $[Pd(pp_3)I]^+$ by trimethylphosphite $P(OCH_3)_3$ and the structural characterizations of $[Pd(pp_3)I]^+$ and $[Pd(pp_3)(P(OCH_3)_3)]^{2+}$ to confirm the structure of the ground state.

The iodo complex, $[Pd(pp_3)I]I$ **1**, was prepared by the following procedure. To a solution of $[Pd(CH_3CN)_4](BF_4)_2$ in acetonitrile was added a solution of an equimolar amount of pp_3 in dichloromethane followed by concentrating the solution and keeping it in a refrigerator. The resulting pale yellow powder was treated with an excess amount of n-Bu_4NI in a dichloromethane-nitromethane solution. The deep red crystals obtained were dried in air (yield: 85%).[8)] The yellow trimethylphosphite complex $[Pd(pp_3)(P(OCH_3)_3)](BF_4)_2$ **2** was prepared by a procedure similar to that for **1** using an excess amount of $P(OCH_3)_3$ instead of n-Bu_4NI in a nitromethane-ethanol solution (yield: 58%).[9)] The crystal of **1** suitable for X-ray diffraction measurements was obtained by slow evaporation of a dichloromethane-acetonitrile-nitromethane solution, and sealed in 0.7-mm o.d. capillary tube because acetonitrile molecules in crystals are volatile to collapse the single crystals.[10)] The kinetic measurements for substitution of iodo ligand in **1** by $P(OCH_3)_3$ in $CDCl_3$ were performed with changes in ^{31}P NMR peak height under pseudo-first-order conditions in which the concentrations of **1** and $P(OCH_3)_3$ are 3.59×10^{-3} and $4.31 \times 10^{-2} - 3.35 \times 10^{-1}$ mol kg^{-1}, respectively.

The molecular structures of **1** in the crystal of **1**$\cdot CH_3CN$ are shown in Fig. 1.[11)] Two sets of formula units exist in the unit cell and each complex cation has the trigonal-bipyramidal geometry. The average axial Pd-P bond distance (2.23 Å) is notably shorter than the average equatorial bond distance (2.41 Å). This is attributed to the strong σ-bonding of the axial Pd-P bonds in the trigonal-bipyramidal geometry. The iodide counter ions are located on the opposite side of the iodo ligand of each complex cation probably to reduce the electrostatic repulsion. The ^{31}P NMR spectra of **1** in $CDCl_3$ show two peaks (t-P(1) and c-P(1) in Fig. 2) corresponding to three terminal diphenylphosphino groups and the central phosphorus atom in pp_3 ligand, respectively. The phosphite complex **2** exhibits a singlet (t-P(2) in Fig. 2) corresponding to the terminal diphenylphosphino groups and two doublets (b-P(2) and c-P(2) in Fig. 2) corresponding to the bound $P(OCH_3)_3$ and the central phosphorus atom, respectively. The doublets result from coupling with the phosphorus atoms trans to each other. The unexpected upfield shift for the bound $P(OCH_3)_3$ compared with the free ligand is attributable to the shielding by the six surrounding phenyl groups of the terminal diphenylphosphino groups. These ^{31}P NMR spectra indicate that **1** and **2** maintain the trigonal-bipyramidal geometry (at least C_3 symmetry) in solution as observed in the crystal of **1**$\cdot CH_3CN$.

The typical change in ^{31}P NMR spectra under the proceeding of the substitution reaction of **1** with $P(OCH_3)_3$ is shown in Fig. 2. The peaks for **1** decreased as the peaks for **2** increased, and finally disappeared. The observed rate constants, k_{obs}, for the substitution under the pseudo-first-order conditions were obtained from the increase in peak height for the terminal phosphino groups in **2**. The plot of k_{obs}

values versus the concentration of $P(OCH_3)_3$ gives a straight line with negligible intercept showing the first-order dependence of k_{obs} on the entering-ligand concentration. From the temperature dependence of the second-order rate constant, k, in the range of 254.9–289.4 K according to the Eyring plot, the activation parameters were obtained as follows: $k^{298} = 1.2 \times 10^{-2}$ kg mol^{-1} s^{-1}, $\Delta H^{\ddagger} = 57.7 \pm 4.1$ kJ mol^{-1}, and $\Delta S^{\ddagger} = -89 \pm 15$ J mol^{-1} K^{-1}. A large negative value of $\Delta S^{\ddagger}$ is comparable to or more negative than those for the ligand substitution or exchange of the square-planar Pd(II) complexes which mainly range from -20 to -90 J mol^{-1} K^{-1}.12) This strongly suggests that an associative activation mode is operative in the transition state for the substitution.

The crystal structure and ^{31}P NMR spectra for **1** indicate that the substitution site is surrounded by bulky diphenylphosphino groups with steric hindrance to the entering-ligand attack. The central Pd(II) has no vacant electron orbital which can accommodate a lone pair. Moreover, the occupied d orbitals and negatively charged

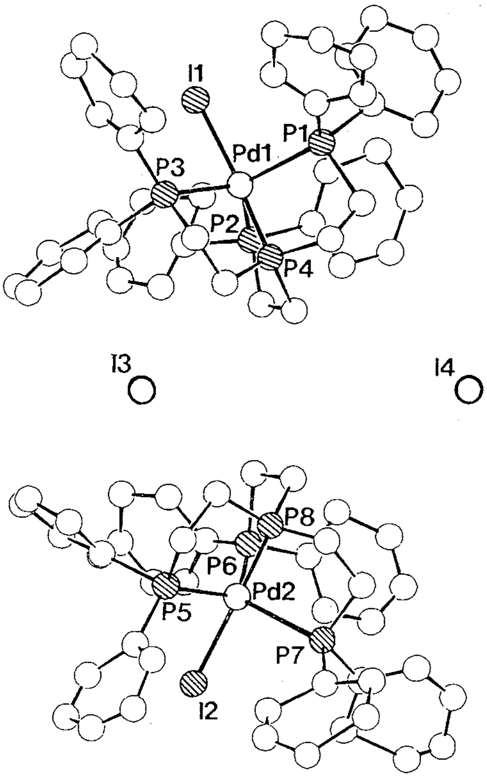

Fig. 1. Perspective drawing of **1** in the crystal of **1**•CH_3CN. Two acetonitrile molecules are omitted.

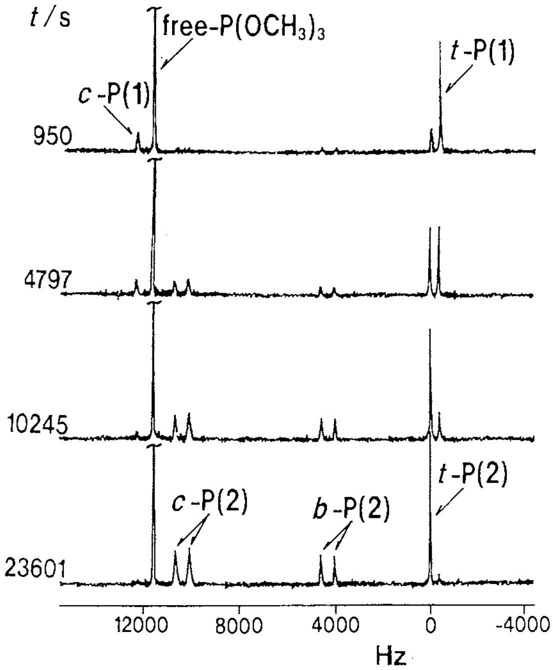

Fig. 2. Change in 109.26-MHz ^{31}P NMR spectrum accompanying the substitution of I^- in **1** by $P(OCH_3)_3$ in $CDCl_3$ at 273.7 K. Initial concentrations: [complex **1**] = 3.59×10^{-3} mol kg^{-1}, [$P(OCH_3)_3$] = 4.31×10^{-2} mol kg^{-1}. The peaks labeled *t*-P(1 or 2) and *c*-P(1 or 2) are respectively from the terminal and central phosphorus atoms of pp_3 ligand in **1** or **2**. The labeling *b*-P(2) denotes the phosphorus atom of bound $P(OCH_3)_3$ in **2**.

iodo group have only the repulsive interaction with the lone pair of the entering ligand. Taking these facts into consideration, the associative transition state is regarded as somewhat surprising. It is probable that the energy for the bond-breaking of the axially coordinated iodo group is greater than that for the electronic repulsion between d orbitals and the lone pair of the entering phosphite ligand because of the strong axial bonds. Furthermore, the π–accepting ability of the phosphorus atom in trimethylphosphite may also stabilize the associative transition state.

Kinetic studies with different combinations of σ-donor and π-acceptor for the leaving and entering ligands are now in progress. The comparison of these results will clarify the primary factor in determining the reaction mechanism for the trigonal-bipyramidal Pd(II) complexes.

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8) Anal. Found: C, 46.68; H, 3.90; N, 0.26%. Calcd for $PdI_2P_4C_{42}H_{42}$: C, 48.93; H, 4.11.
9) Anal. Found: C, 49.57; H, 4.98. Calcd for $PdP_5F_8O_3B_2C_{45}H_{51}$: C, 50.29; H, 4.78.
10) One acetonitrile molecule was found in each formula unit by the X-ray analysis for the sealed sample while the elemental analysis for the air-dried sample did not show the corresponding nitrogen content.
11) Crystallographic data for **1**$\cdot CH_3CN$: formula, $PdI_2P_4NC_{44}H_{45}$; fw = 1072.0; space group, $P2_1$; a = 10.853(4), b = 39.69(2), c = 10.430(2) Å, β = 106.14(2)°; V = 4315(27) $Å^3$; Z = 4; D_{calcd} = 1.65 g cm^{-3}; μ = 18.82 cm^{-1}; radiation, Mo Kα (λ = 0.71073 Å); unique obsd data, 4256; R = 0.067, R_W = 0.077.
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