

Thiolato-Ligand Substitution Reaction with Halide Ions of Five-Coordinate Trigonal-Bipyramidal Palladium(II) Complexes with Tris(2-(diphenylphosphino)ethyl)phosphine. Electronic and Steric Effects on the Reaction Mechanism

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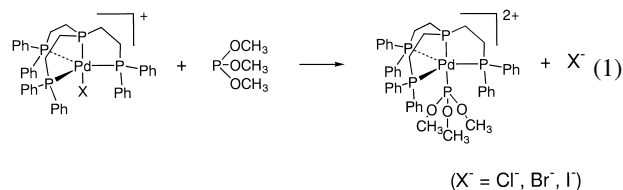
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Mononuclear and dinuclear thiolato complexes with five-coordinate trigonal-bipyramidal palladium(II), [Pd(pt or tt)(pp₃)](BF₄) and [Pd₂(pdt)(pp₃)₂](BF₄)₂ (pp₃ = tris(2-(diphenylphosphino)ethyl)phosphine, pt = 1-propanethiolate, tt = α -toluenethiolate, pdt = 1,3-propanedithiolate) have been synthesized. The solid-state structure of the dinuclear pdt complex was confirmed by an X-ray crystal structure analysis and the structures of the pt, tt, and pdt complexes in solution were characterized by ³¹P NMR spectroscopy. It is indicated from the ³¹P NMR chemical shifts of the bound pp₃ ligand that the axially coordinated thiolato ligands are strong σ and π donors compared with the halo ligands in the axial position of the corresponding trigonal-bipyramidal palladium(II) complexes, [PdX(pp₃)]⁺ (X[−] = Cl[−], Br[−], I[−]). The kinetic parameters for the one-step and successive two-step thiolato-ligand substitution reactions with halide ions in chloroform were obtained for the mononuclear and dinuclear complexes, respectively. These results have revealed that the reaction mechanism of the present thiolato-ligand substitutions is much more dissociative than that of the corresponding halo-ligand substitutions using trimethyl phosphite as the entering ligand, and that the reaction mechanism of the two-step substitution of the dinuclear thiolato complex is more dissociative than that of the mononuclear complexes. It has been concluded that the reaction mechanism of the five-coordinate trigonal-bipyramidal palladium(II) complexes with the 18-electron ground state is quite sensitive to the electronic properties of the entering and leaving ligands and the steric environment of the reaction site compared with that of four-coordinate square-planar palladium(II) complexes with the 16-electron ground state, which is generally associatively activated.

The reaction mechanism of four-coordinate square-planar palladium(II) and platinum(II) complexes has been extensively studied and an associative mechanism via the trigonal-bipyramidal 18-electron transition state has been generally proposed.^{1,2} On the other hand, five-coordinate trigonal-bipyramidal d⁸ metal complexes which have the 18-electron ground state may bring about great electronic repulsion in the associative activation state, while dissociative bond breaking may require considerably great enthalpic activation for the palladium(II) and platinum(II) complexes. Therefore, a thorough investigation is needed in order to make the above vague points clear. Furthermore, such mechanistic studies will provide further insight into the kinetic properties of the palladium(II) and platinum(II) complexes.

For a clear-cut investigation, we previously performed kinetic studies on the substitution reaction of [PdX(pp₃)]⁺ (pp₃ = tris(2-(diphenylphosphino)ethyl)phosphine; X[−] = Cl[−], Br[−], I[−]) with trimethyl phosphite in chloroform, where the axially

coordinated halide ion is replaced by monodentate phosphite to form [Pd(pp₃)(P(OCH₃)₃)]²⁺ maintaining the trigonal-bipyramidal geometry (Eq. 1).³



From the activation parameters, it was indicated that the reaction proceeds by a quite associative activation mode compared with the reaction mechanism of the square-planar palladium(II) complexes generally reported.⁴ This result was rather surprising, because it would be possible that the 18-electron ground state of the five-coordinate trigonal-bipyramidal palladium(II) complexes provides a much greater electronic repulsion with the entering ligand than the 16-electron ground state

of the four-coordinate square-planar ones, and promotes dissociation of the leaving ligand in the activation state. In our previous paper,³ we proposed that the interaction between the occupied d_{xz} and d_{yz} orbitals on the palladium(II) center and the entering electron-accepting trimethyl phosphite is of great advantage to the associative mechanism in that particular case. In addition, we also suggested that the large void volume around the substitution site surrounded by the six phenyl groups can accommodate the large volume of the entering ligand in the activation state, and shows the associative character in the activation parameters.

In order to obtain general views on the reaction mechanism of the five-coordinate trigonal-bipyramidal palladium(II) complexes, it is necessary to investigate the reaction system with a strong electronic repulsion in the activation state. In addition, steric effects of the surroundings around the reaction site should also be elucidated. From these circumstances, we have selected thiolates, such as 1-propanethiolate (pt) and α -toluenethiolate (tt), as the leaving ligands, where the thiolate sulfur atoms are expected to be relatively strong σ and π donors to increase the electron density of the palladium(II) center; we used halide ions as the entering ligands, which can cause an electronic repulsive interaction in the activation state. To investigate the steric effects, we undertook the corresponding substitution reaction by using the dinuclear trigonal-bipyramidal palladium(II) complex with a bridging dithiolato ligand, 1,3-propanedithiolate (pdt), where the substitution site is apparently blocked by the surrounding twelve phenyl groups of the bound pp_3 ligands.

Experimental

Reagents. Chloroform (Wako, Sp. Gr.) and deuterated chloroform (Aldrich, 99.8 atom% D) were dried over activated 4A Molecular Sieves, and then distilled in a vacuum line. Chloroform (Wako, ∞ pure) and deuterated chloroform (Wako, 100%) were dried over activated 4A Molecular Sieves. Tetrabutylammonium halides (Wako), Bu_4NX ($X^- = Cl^-, Br^-,$ and I^-), were dried under a vacuum. Tris(2-(diphenylphosphino)ethyl)phosphine (pp_3 , Aldrich and Strem), tetrakis(acetonitrile)palladium(II) tetrafluoroborate (Aldrich), 1-propanethiol (Hpt, Wako), α -toluenethiol (Htt, Aldrich), and 1,3-propanedithiol (H_2pdt , Wako) were used to prepare of palladium(II) complexes without further purification.

Preparation of Complexes. **[Pd(pt)(pp_3)](BF_4).** To a suspension of $[Pd(pp_3)](BF_4)_2$ (0.205 g, 0.216 mmol) in acetonitrile (20 cm^3) was added dropwise 1-propanethiol (Hpt, 0.10 g, 1.31 mmol), and then 0.1 M aqueous NaOH (1.2 cm^3). To a resultant red solution was added a small amount of ethanol and then water to give red crystals. The crystals were collected by filtration and washed with ethanol and water. Red needle crystals were obtained by recrystallization from a dichloromethane-ethanol mixture, and air-dried. Yield: 0.128 g (63%). Anal. Found: C, 56.88; H, 5.29; N, 0.00%. Calcd for $[Pd(pt)(pp_3)](BF_4)$: C, 57.56; H, 5.26; N, 0.00%. ^{31}P NMR (in $CHCl_3$): δ (relative to D_3PO_4 in external D_2O) = 30.34 (d, equatorial), 134.51 (q, axial); $J_{P-P} = 10$ Hz. UV-vis (in CH_2Cl_2): λ_{max}/nm ($\log(\epsilon/mol^{-1} kg cm^{-1})$) 551 (3.31), 409 (3.82), 315 (4.43).

[Pd(tt)(pp_3)](BF_4). Red needle crystals of the tt complex were obtained by a procedure similar to that of the pt complex by using 0.353 g (0.371 mmol) of $[Pd(pp_3)](BF_4)_2$ and 0.070 g (0.56 mmol) of α -toluenethiol (Htt). Yield: 0.291 g (81%). Anal.

Found: C, 58.10; H, 4.95; N, 0.32%. Calcd for $[Pd(tt)(pp_3)](BF_4) \cdot H_2O$: C, 58.55; H, 5.11; N, 0.00%. ^{31}P NMR (in $CHCl_3$): δ (relative to D_3PO_4 in external D_2O) 30.65 (d, equatorial), 135.57 (q, axial); $J_{P-P} = 10$ Hz.

[Pd₂(pdt)(pp_3)₂](BF_4)₂. To a suspension of $[Pd(pp_3)](BF_4)_2$ (1.036 g, 1.09 mmol) in acetonitrile (80 cm^3) was added 1,3-propanedithiol (H_2pdt , 0.0504 g, 0.466 mmol), and then 0.25 M aqueous NaOH (5 cm^3). To the resultant red solution were added dichloromethane (40 cm^3) and water (100 cm^3), and the dichloromethane phase was evaporated to dryness. The resultant red complex was recrystallized from dichloromethane by adding acetonitrile and a small amount of ethanol and water, and air-dried. Yield: 0.849 g (85%). Anal. Found: C, 55.61; H, 4.93; N, 0.00%. Calcd for $[Pd(pdt)(pp_3)_2](BF_4)_2$: C, 56.97; H, 4.95; N, 0.00%. ^{31}P NMR (in $CHCl_3$): δ (relative to D_3PO_4 in external D_2O) 30.33 (d, equatorial), 134.50 (q, axial); $J_{P-P} = 10$ Hz.

X-ray Structure Analysis. As the red crystals of the pdt complex lost the crystallizing solvent molecules when exposed to the atmosphere, one of them was sealed in a Lindemann glass-capillary tube with the mother liquor.⁶ X-ray diffraction measurements were performed on a Mac Science MXC3 diffractometer with Mo $K\alpha$ radiation. The unit-cell parameters and orientation matrix were determined by a least-squares refinement of 17 independent reflections collected in the range $18.0^\circ < 2\theta < 26.2^\circ$. Data collection was performed with the $\theta/2\theta$ scan mode with three standard reflections measured after every 100 scans, which showed no significant decay. An empirical absorption (ψ scan) correction was applied. The solution and refinement were carried out using the CRYSTAN-GM (version 6.3.3) software package.⁷ The structure was solved by the direct method using the SIR 92 program.⁸ Because of a limited data set collected from the thin plate of the crystal, only the palladium, sulfur, and phosphorus atoms were reasonably refined anisotropically. All atoms of the counter anion of the complex cation, BF_4^- , and crystallizing acetonitrile and ethanol were constrained to the appropriate positions. The hydrogen atoms were included in the calculated positions. The occupancy factor of each atom of BF_4^- was fixed to 0.5, except for B1, B2, F3, F4, and F10. The atomic scattering factors were taken from Ref. 9.

The crystallographic data are summarized in Table 1. The crystallographic details, positional and thermal parameters for all at-

Table 1. Crystallographic Data for $[Pd_2(pdt)(pp_3)_2](BF_4)_2 \cdot CH_3CN \cdot C_2H_5OH$

Formula	$C_{91}H_{99}B_2F_8NOP_8Pd_2S_2$
Fw	1921.16
Cryst syst	monoclinic
Space group	$P2_1/n$
$a/\text{\AA}$	35.26(1)
$b/\text{\AA}$	18.45(2)
$c/\text{\AA}$	13.817(5)
β/deg	91.47(3)
$V/\text{\AA}^3$	8989(9)
Z	4
$\rho_{calcd}/g cm^{-3}$	1.420
Cryst dims/mm	0.10 $\times$ 0.25 $\times$ 0.50
μ/cm^{-1}	6.358
$R,^a) R_w^b)$	0.097, 0.109

a) $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. b) $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$. $w = (\sigma(F_o)^2 + 0.001F_o^2)^{-1}$.

oms, and bond distances and angles for non-hydrogen atoms are provided as Supporting Data.

Measurements. The kinetic measurements for the substitution reactions of the pt, tt, and pdt complexes with halide ions in chloroform were carried out under the pseudo-first-order conditions where the concentrations of Bu_4NX ($\text{X}^- = \text{Cl}^-, \text{Br}^-, \text{I}^-$) were in large excess over those of the thiolato complexes (Tables S5–S9, Supporting Data). The sample preparation and kinetic measurements were performed under a nitrogen atmosphere. The absorption spectral changes were recorded on Shimadzu UV-260 FW or JASCO V-570 spectrophotometers. The temperature of the reaction solution was controlled within ± 0.1 K. The substitution reactions at various pressures were followed by using a high-pressure static vessel equipped with a le-Noble-type quartz cell.¹⁰ The substitution rates of the pt and tt complexes were sufficiently slow to obtain accurate rate constants, though about 20 min was taken up for temperature and pressure equilibration in the high pressure vessel. The ^{31}P and ^1H NMR spectra were recorded on a JEOL JNM-A400 FT-NMR spectrometer operating at 160.7 and 399.65 MHz, respectively. In order to determine the chemical shift of the ^{31}P NMR, a 3 mm o.d. NMR tube containing the sample solution was coaxially mounted in a 5 mm o.d. NMR tube containing deuterated water and phosphoric acid as a lock solvent and a reference, respectively.

Results and Discussion

Characterization. A perspective view of the pdt complex cation is displayed in Fig. 1 along with the atomic labeling for the palladium and the coordinated atoms. The selected bond distances and angles are summarized in Table 2. The complex cation has a dinuclear structure bridged by the pdt ligand. Each palladium(II) center has a trigonal-bipyramidal geometry with the thiolato sulfur atom of pdt and the central phosphorus atom of pp_3 (P_{ax}) in the axial position and the three terminal phosphorus atoms of pp_3 (P_{eq}) in the equatorial positions. The structure of the $\text{Pd}(\text{pp}_3)$ moiety is quite comparable to those of the halo complexes, $[\text{PdX}(\text{pp}_3)]^+$ ($\text{X}^- = \text{Cl}^-, \text{Br}^-, \text{I}^-$), as previously reported.³ For example, the palladium(II) ions in the pdt and halo complexes are located out of the equatorial plane defined by the three equatorial phosphorus atoms by 0.25–0.28 Å toward the axially coordinated thiolato sulfur atom or halide ions, since the chelate strain is operating in the five-membered

Table 2. Selected Bond Distances (Å) and Angles (deg) for $[\text{Pd}_2(\text{pdt})(\text{pp}_3)_2]^{2+}$

Pd(1)–S(1)	2.392(16)	Pd(2)–S(2)	2.398(15)
Pd(1)–P(1)	2.256(16)	Pd(2)–P(5)	2.240(17)
Pd(1)–P(2)	2.430(15)	Pd(2)–P(6)	2.342(17)
Pd(1)–P(3)	2.384(16)	Pd(2)–P(7)	2.359(17)
Pd(1)–P(4)	2.474(16)	Pd(2)–P(8)	2.637(18)
S(1)–Pd(1)–P(1)	176.5(6)	S(2)–Pd(2)–P(5)	166.5(7)
S(1)–Pd(1)–P(2)	97.9(6)	S(2)–Pd(2)–P(6)	90.4(6)
S(1)–Pd(1)–P(3)	93.8(6)	S(2)–Pd(2)–P(7)	94.5(6)
S(1)–Pd(1)–P(4)	96.8(6)	S(2)–Pd(2)–P(8)	110.0(6)
P(1)–Pd(1)–P(2)	85.0(6)	P(5)–Pd(2)–P(6)	83.3(6)
P(1)–Pd(1)–P(3)	83.0(6)	P(5)–Pd(2)–P(7)	83.5(7)
P(1)–Pd(1)–P(4)	83.6(6)	P(5)–Pd(2)–P(8)	83.2(6)
P(2)–Pd(1)–P(3)	123.4(6)	P(6)–Pd(2)–P(7)	142.9(6)
P(2)–Pd(1)–P(4)	116.6(6)	P(6)–Pd(2)–P(8)	104.8(6)
P(3)–Pd(1)–P(4)	116.7(6)	P(7)–Pd(2)–P(8)	107.9(6)

$\text{P}_{\text{ax}}\text{--C--C--P}_{\text{eq}}$ chelates to form small chelate bite angles ($\text{P}_{\text{ax}}\text{--Pd--P}_{\text{eq}} = 83.0\text{--}85.0^\circ$). Furthermore, the average axial and equatorial bond distances ($\text{Pd--P}_{\text{ax}} = 2.25$ Å and $\text{Pd--P}_{\text{eq}} = 2.44$ Å, respectively) are in a similar range to those of the halo complexes, indicating a strong σ interaction of the axial Pd–P bond. The average axial Pd–S bond distance (2.40 Å) is comparable to the axial Pd–Cl bond distance (2.42 Å).³ The noticeable characteristic of the pdt complex is the fact that the axial thiolato coordination sites are surrounded by twelve phenyl groups, in which the shortest C–C distance between the phenyl groups in the adjacent $\text{Pd}(\text{pp}_3)$ moieties is ca. 3.4 Å.

As shown in Fig. 2, the ^{31}P NMR spectra of the pdt complex in chloroform exhibit two signals, indicating that each $\text{Pd}(\text{pp}_3)$ moiety of the dinuclear structure has C_3 symmetry with three equivalent terminal phosphorus in the equatorial position (P_{eq}) and the central phosphorus in the axial position (P_{ax}); the two $\text{Pd}(\text{pp}_3)$ moieties are also equivalent to each other in solution. Because the ^{31}P NMR spectral pattern of the pt and tt complexes in chloroform agrees with that of the pdt complex, it is obvious that the pt and tt complexes have almost the same trigonal-bipyramidal structure as that of the $\text{Pd}(\text{thiolato})(\text{pp}_3)$ moiety in the dinuclear pdt complex.

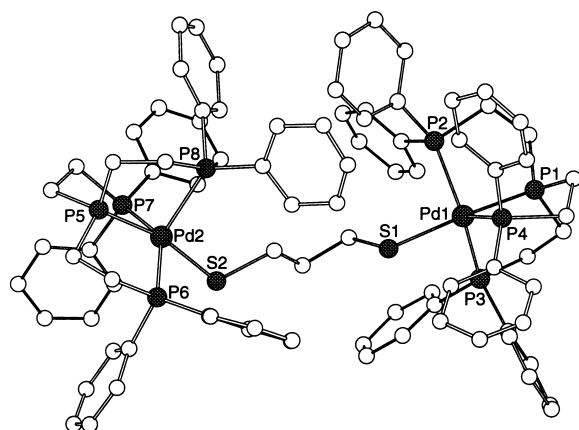


Fig. 1. Structure of the pdt complex, $[\text{Pd}_2(\text{pdt})(\text{pp}_3)_2]^{2+}$, in the crystal.

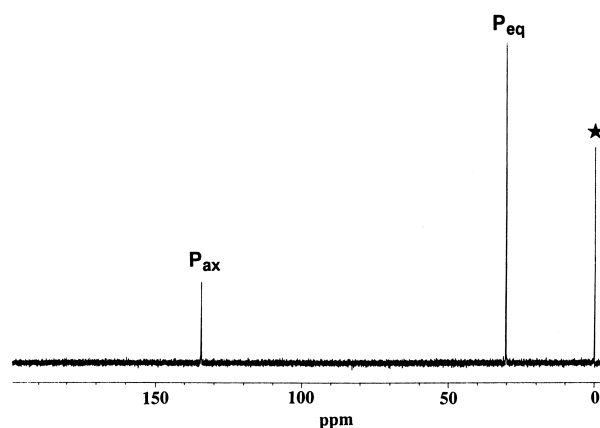


Fig. 2. ^{31}P NMR spectra of the pdt complex in chloroform. Asterisk denotes the signal for D_3PO_4 in the external D_2O .

Table 3. ^{31}P NMR Chemical Shifts for Halo and Thiolato Complexes

Complex	Chemical shift/ppm ^{a)}	
	P_{ax}	P_{eq}
$[\text{PdCl}(\text{pp}_3)]^{+ \text{b), c)}$	136.50	31.62
$[\text{PdBr}(\text{pp}_3)]^{+ \text{b), c)}$	142.57	31.76
$[\text{PdI}(\text{pp}_3)]^{+ \text{b), c)}$	147.35	31.98
$[\text{Pd}_2(\text{pdt})(\text{pp}_3)_2]^{2+ \text{d)}$	134.50	30.33
$[\text{Pd}(\text{pt})(\text{pp}_3)]^{+ \text{d)}$	134.51	30.34
$[\text{Pd}(\text{tt})(\text{pp}_3)]^{+ \text{d)}$	135.57	30.65

a) Relative to D_3PO_4 in external D_2O . b) Reference 3.
c) In dichloromethane. d) In chloroform.

In the case of the free pp_3 ligand, the ^{31}P NMR signal of the central phosphorus atom shows a greater upfield shift than that of the terminal phosphorus atoms in the diphenylphosphino groups.¹¹ However, the downfield shift of P_{ax} is much larger than that of P_{eq} . This is explained by the greater deshielding (diamagnetic contribution) and configurational nonuniformity of the valence electrons (paramagnetic contribution) on the phosphorus atoms caused by the donation of P_{ax} stronger than that of P_{eq} , which is observed in the Pd–P bond distances.^{12,13} As previously described,³ the σ donation of the axial ligand X in $[\text{PdX}(\text{pp}_3)]^+$ competes with that of P_{ax} , mainly through the d_{z^2} and p_z orbitals of the palladium(II) ion; also the π donation of the axial ligand increases the electron density in the d_{xz} and d_{yz} orbitals of the palladium(II) ion, which have π interactions with the empty d orbitals of P_{eq} . Accordingly, the strength of the σ and π donation of the axial ligand X can be separately estimated by the upfield shift of P_{ax} and P_{eq} , respectively. The chemical shifts listed in Table 3 show that the σ and π donations of the present thiolato ligands are stronger than those of the halo ligands.

Kinetics of Mononuclear Complexes. The ^{31}P NMR spectra of solutions containing the pt or tt complexes and a large excess of Bu_4NX ($\text{X} = \text{Cl}^-$, Br^- , I^-) in chloroform gradually changed to those of the corresponding halo complexes. The absorption spectra of the diluted solutions (2.46×10^{-5} – $1.98 \times 10^{-4} \text{ mol kg}^{-1}$ of the pt and tt complexes and 7.13×10^{-3} – $5.32 \times 10^{-1} \text{ mol kg}^{-1}$ of Bu_4NX in chloroform) changed with isosbestic points, and finally exhibited the spectra of the corresponding halo complexes.³ The observed pseudo-first-order rate constants of the thiolato-ligand substitution reactions with halide ions (k) were determined by a least-squares analysis for the exponential time course of the absorbance at 480 nm.

The values of k were independent of the halide-ion concentration (Table S5 and Fig. S1, Supporting Data). In the case of substitution reactions of the halo complexes with neutral tri-

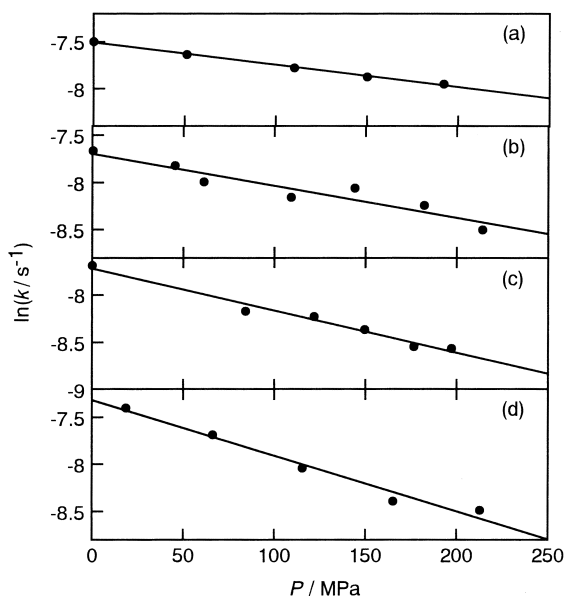


Fig. 3. Pressure dependences of $\ln k$ for the reaction of the pt complex with Cl^- (a), Br^- (b), and I^- (c) and the tt complex with I^- (d).

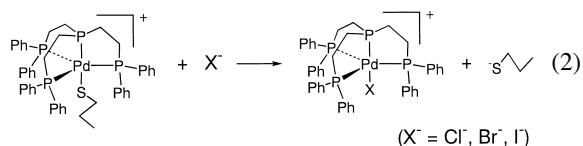
methyl phosphite, the observed rate constants were first order with respect to the entering-ligand concentration.³ Because the limiting dissociative mechanism is not consistent with the fact that the present kinetic parameters depend on the entering halide ions (vide infra), it is probable that the ion pairs of the positively charged thiolato complexes with halide ions existing in large excess are quantitatively formed in chloroform. Each temperature dependence of the first-order rate constant was fitted to the Eyring equation to give the values of the activation enthalpy ($\Delta H^\ddagger$) and activation entropy ($\Delta S^\ddagger$) (Table S6 and Fig. S2, Supporting Data). The values of the activation volume ($\Delta V^\ddagger$) were given by fitting the pressure dependence of k to $(\partial \ln k / \partial P)_T = -\Delta V^\ddagger / RT$, as shown in Fig. 3 (Table S7, Supporting Data). The activation parameters obtained for the pt and tt complexes are summarized in Table 4. If an undetectable square-planar intermediate was formed by pre-equilibrium accompanied by the dissociation of one of the terminal diphenylphosphino groups, the observed rate would be much slower than that for the square-planar complex, which has a structure corresponding to that of the square-planar intermediate, because the pre-equilibrium constant should be much smaller than unity.³ Considering the fact that the present rate constants are comparable to or larger than those of the corresponding square-planar complex, $[\text{Pd}(\text{pt})(\text{p}_3)]^+$ ($\text{p}_3 = \text{bis}(2\text{-diphenylphosphino)ethylphenylphosphine}$),¹⁴ we can reason-

Table 4. Activation Parameters for Substitution Reactions of $[\text{Pd}(\text{thiolato})(\text{pp}_3)]^+$ with Halide Ions

Thiolato ligand	Halide ion	$k^{298}/10^{-4} \text{ s}^{-1}$	$\Delta H^\ddagger/\text{kJ mol}^{-1}$	$\Delta S^\ddagger/\text{J mol}^{-1} \text{ K}^{-1}$	$\Delta V^\ddagger/\text{cm}^3 \text{ mol}^{-1}$
pt	Cl^-	3.55	70 ± 2	-77 ± 5	$6.1 \pm 0.3^{\text{a)}$
pt	Br^-	2.76	82 ± 2	-37 ± 7	$9.0 \pm 1^{\text{b)}$
pt	I^-	2.14	89 ± 1	-16 ± 2	$11.0 \pm 0.8^{\text{c)}$
tt	I^-	6.12	86 ± 2	-18 ± 8	$14.7 \pm 1.3^{\text{d)}$

a) At 302.2 K. b) At 302.7 K. c) At 303.7 K. d) At 298.2 K.

ably expect one-step substitution, as previously proposed (Eq. 2).³



As we reported previously, the halo-ligand substitution reactions of the same type of the trigonal-bipyramidal palladium(II) complexes, $[\text{PdX}(\text{pp}_3)]^+$ ($\text{X} = \text{Cl}^-, \text{Br}^-, \text{I}^-$), proceed by a surprisingly associative activation mode, showing large negative values of $\Delta S^\ddagger$ (-89 – $-198 \text{ J K}^{-1} \text{ mol}^{-1}$) and $\Delta V^\ddagger$ (-22.6 – $-25.5 \text{ cm}^3 \text{ mol}^{-1}$), probably due to the electron-accepting ability of the entering phosphite.³ As shown in Table 4, the present substitution mechanism is obviously much more dissociative, showing large $\Delta H^\ddagger$, less negative $\Delta S^\ddagger$, and considerably large positive $\Delta V^\ddagger$ values compared with the previous case. Considering that the axially coordinated thiolato sulfur atom is a fairly strong σ and π donor to the orbitals on the palladium(II) center (vide supra), the change in the reaction mechanism is mainly attributed to an electronic repulsion between the shielded metal center and the entering anion. This is supported by the fact that the steric difference in the axial thiolato ligands, pt and tt, does not vary the reaction mechanism, except for a slight deviation of the $\Delta V^\ddagger$ value. It may be concluded that the reaction mechanism of the five-coordinate trigonal-bipyramidal palladium(II) complexes with the 18-electron system is quite variable with the electronic repulsion in the transition state, while four-coordinate square-planar ones with empty p_z orbital are generally activated in the associative mode to form an 18-electron transition state. On the other hand, enhancement of the dissociative character from Cl^- to I^- is ascribed to an increase in the size of the entering halide ion, because a greater steric hindrance promotes the dissociation of the leaving ligand (vide infra).

Kinetics of Dinuclear Complex. The absorption spectral change of the reaction solution containing the pdt complex ($6.0 \times 10^{-5} \text{ mol kg}^{-1}$) and a large excess of Bu_4NI ($2.4 \times 10^{-2} \text{ mol kg}^{-1}$) in chloroform is shown in Fig. 4. Though the final spectrum agreed with that of the iodo complex,³ the isosbestic point at ca. 375 nm was gradually shifted to ca. 340 nm. As shown in Fig. 5, the absorbance at 365 nm first decreased and, subsequently increased; each absorbance change for the first several minutes and after the elapse of ca. 1 h can be fitted to an exponential curve. From these facts, the reaction of the pdt complex with I^- can be regarded as successive substitution. In the initial stage of the reaction, the ^1H NMR signals for the methylene protons of the bridging pdt ligand ($\delta = 1.7$ for the terminal $-\text{CH}_2\text{S}-$ and 1.4 for the central $-\text{CH}_2-$) were overlapped by large signals of the excess Bu_4NI (Fig. 6a). As the reaction proceeded, the signals assigned to the methylene protons of the pendant pdt ligand ($\delta = 2.1$ – 2.3 for the free $-\text{CH}_2\text{S}^-$ and 1.8–1.9 for the bound $-\text{CH}_2\text{S}-$) increased (Fig. 6b), followed by a subsequent decrease with increasing signals for the free pdt ligand ($\delta = 3.1$ for the terminal $-\text{CH}_2\text{S}^-$ and 2.3 for the central $-\text{CH}_2-$) (Fig. 6e). This ^1H NMR spectral change, which is consistent with the successive two-step substitution, was also observed in the case of a solution containing

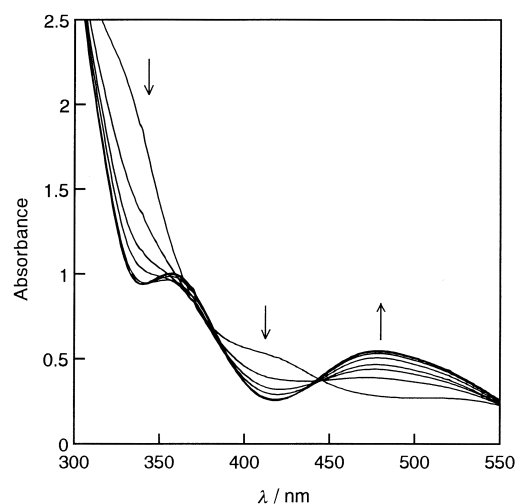
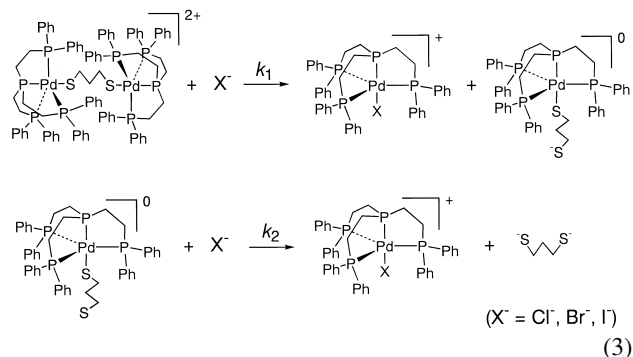


Fig. 4. Absorption spectral change of chloroform solution containing $[\text{Pd}_2(\text{pdt})(\text{pp}_3)_2]^{2+}$ and excess I^- at 0, 520, 1040, 1560, 3161, 6239, 12477, and 24028 s after the temperature equilibration. The direction of the change is denoted by arrows.

excess Bu_4NCl and Bu_4NBr instead of Bu_4NI . On the basis of the above absorption and NMR spectral behaviors, the pseudo-first-order rate constants for the two-step substitution reactions (Eq. 3) were obtained by using chloroform solutions containing the pdt complex (6.03 – $6.33 \times 10^{-5} \text{ mol kg}^{-1}$) and a large excess of Bu_4NX ($\text{X}^- = \text{Cl}^-, \text{Br}^-, \text{I}^-$) at various concentrations (3.45 – $36.1 \times 10^{-2} \text{ mol kg}^{-1}$).

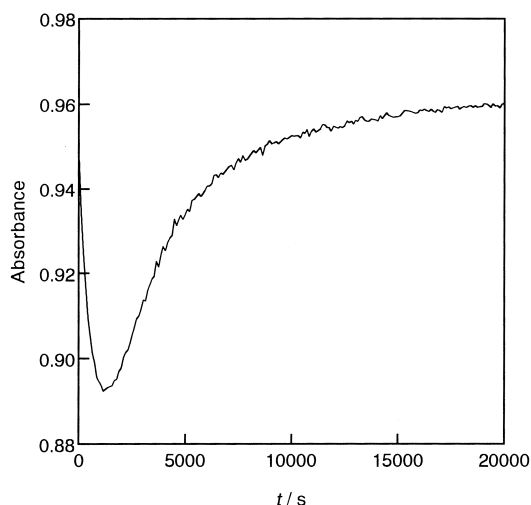


The rate constant for the first-step reaction (k_1) with I^- was obtained from the exponential time course for the first several minutes at 350 nm, where the absorbance change for the second step was quite small, and that for the second step (k_2) was obtained from the sufficiently large absorbance change at 478 nm after a sufficient elapse of time. The values of k_1 and k_2 for the substitution reactions with Cl^- and Br^- were similarly obtained by using the large absorbance change at 350 nm.

The rate constants for the first and second steps were independent of the entering-halide-ion concentration in chloroform (Table S8 and Fig. S3, Supporting Data), as observed for the substitution reaction of the pt and tt complexes. The activation parameters for the two steps were obtained from the temperature dependence of the k_1 and k_2 values, as listed in Table 5. Comparing the activation parameters between the pt and pdt complexes, it is obvious that the reaction mechanism of the di-

Table 5. Activation Parameters for Successive Substitution Reactions of $[\text{Pd}_2(\text{pdt})(\text{pp}_3)_2]^{2+}$ with Halide Ions

Halide ion	First step			Second step		
	$k^{298}/10^{-4} \text{ s}^{-1}$	$\Delta H^\ddagger/\text{kJ mol}^{-1}$	$\Delta S^\ddagger/\text{J mol}^{-1} \text{ K}^{-1}$	$k^{298}/10^{-4} \text{ s}^{-1}$	$\Delta H^\ddagger/\text{kJ mol}^{-1}$	$\Delta S^\ddagger/\text{J mol}^{-1} \text{ K}^{-1}$
Cl^-	16.9	96 ± 5	24 ± 18	5.69	130 ± 1.3	129 ± 4.4
Br^-	29.5	97 ± 16	32 ± 15	2.90	126 ± 2.6	110 ± 9
I^-	5.90	115 ± 5	79 ± 18	4.14	93.7 ± 1.5	4.6 ± 4.9

Fig. 5. Absorbance change of chloroform solution containing $[\text{Pd}_2(\text{pdt})(\text{pp}_3)_2]^{2+}$ and excess I^- at 365 nm.

nuclear pdt complex is more dissociative than that of the mononuclear pt complex, showing large $\Delta H^\ddagger$ and positive $\Delta S^\ddagger$ values. In the initial state of the first step, the substitution site is surrounded by the twelve phenyl groups, as shown in the crystal structure, where the entering ligand is apparently blocked. Consequently, the leaving ligand dissociation is required to reach the activation state. In fact, the dissociative character is enhanced by an increase in the size of the entering ion. In addition, the mutual steric repulsion between the phenyl groups in the two palladium(II) terminals also promotes dissociation of the palladium(II)–sulfur bond. In the case of the second step, an assumption that the negative charge of the pendant thiolate group in the intermediate interferes with the approach of the entering halide ion is consistent with the fact that the dissociative character is enhanced compared with the reaction of the positive mononuclear pt complex, and is promoted by an increase in the charge density of the entering halide ion.

Conclusion

We have newly prepared mononuclear and dinuclear five-coordinate trigonal-bipyramidal thiolato palladium(II) complexes, $[\text{PdX}(\text{pp}_3)]^+$ ($\text{X} = \text{pt}, \text{tt}$) and $[\text{Pd}_2(\text{pdt})(\text{pp}_3)_2]^{2+}$, for the purpose of mechanistic studies. These complexes were characterized by X-ray crystal structure analysis and ^{31}P NMR spectroscopy. The activation parameters of the thiolato-ligand substitution reactions with halide ions in chloroform were obtained for the one-step substitution of the mononuclear complexes, and for the successive two-step substitution of the dinuclear complex. A comparison between the present results and those for the halo-ligand substitution reaction with trimethyl

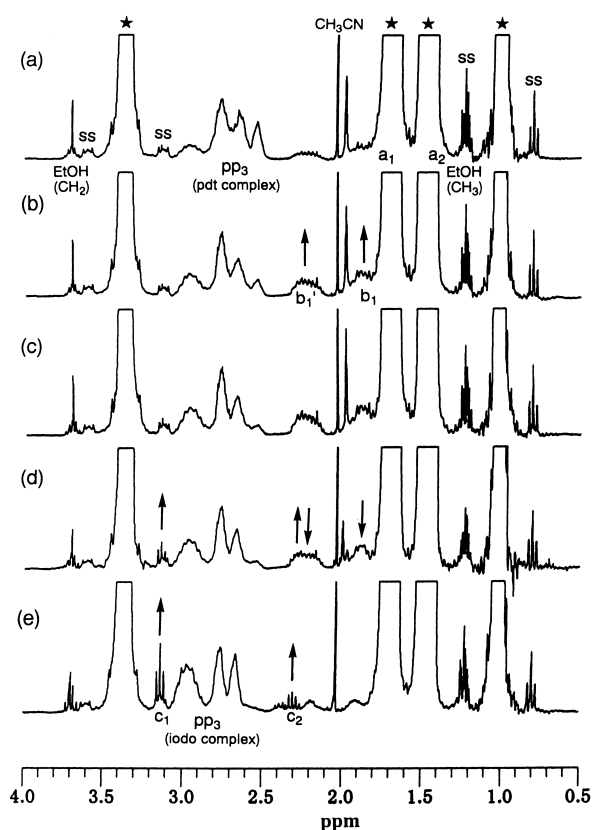


Fig. 6. ^1H NMR spectral change of chloroform solution containing $[\text{Pd}_2(\text{pdt})(\text{pp}_3)_2]^{2+}$ ($7.1 \times 10^{-3} \text{ mol kg}^{-1}$) and excess I^- ($5.0 \times 10^{-1} \text{ mol kg}^{-1}$) at 5 (a), 20 (b), 45 (c), 120 (d), and 1200 (e) min after preparation of the sample solution. Asterisks and ss's denote the signals for the excess Bu_4NI and their spinning side bands, respectively. The chemical shifts for the terminal and central methylenes of the bridging pdt are shown by a_1 and a_2 , respectively. The signals for the free and bound terminal methylenes of the pendant pdt are denoted by b_1' and b_1 , respectively, and the signal for the central methylene is overlapped by the signals of the excess Bu_4NI . The signals for the terminal and central methylenes of the free pdt are denoted by c_1 and c_2 , respectively. The signals for ethanol and acetonitrile are due to the solvent molecules contained in the crystals of the pdt complex.

phosphite³ indicates that an increase in the electronic repulsion and steric hindrance in the activation state changes the reaction mechanism sensitively to the dissociative mode of the reaction. This phenomenon is a clear difference between the five-coordinate trigonal-bipyramidal palladium(II) complexes with the 18-electron ground state and four-coordinate square-planar ones with the 16-electron ground state, which is activated asso-

ciatively. Therefore, the fine tuning of the reaction mechanism will be possible by controlling the electronic and steric environments in the case of the five-coordinate trigonal-bipyramidal palladium(II) complexes.

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Supporting Data

X-ray crystallographic data (Table S1), atomic coordinates and isotropic thermal parameters (Table S2), anisotropic thermal parameters (Table S3), bond distances and angles (Table S4), entering-ligand concentration (Table S5 and Fig. S1), temperature (Table S6 and Fig. S2), and pressure (Table S7) dependences of the substitution rate constants for the mononuclear pt and tt complexes, entering-ligand concentration (Table S8 and Fig. S3) and temperature (Table S9 and Fig. S4) dependences of the successive substitution rate constants for the dinuclear pdt complex (in total 20 pages) are deposited as Document No.75004 at the Office of the Editor of Bull. Chem. Soc. Jpn. and are also available from the author upon request. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 174601.

References

- 1 R. G. Wilkins, "Kinetics and Mechanism of Reaction of Transition Metal Complexes," 2nd ed, VCH, Weinheim (1991), Chap. 4; R. J. Cross, "Mechanisms of Inorganic and Organometallic Reactions," ed by M. V. Twigg, Plenum, New York (1988), Chap. 5.
- 2 Z. Lin and M. B. Hall, *Inorg. Chem.*, **30**, 646 (1991).
- 3 S. Aizawa, T. Iida, and S. Funahashi, *Inorg. Chem.*, **35**, 5163 (1996).
- 4 M. Kotowski and R. van Eldik, "Inorganic High Pressure Chemistry," ed by R. van Eldik, Elsevier, Amsterdam (1986), Chap. 4.
- 5 S. Aizawa and S. Funahashi, *Anal. Sci.*, **12**, 27 (1996).
- 6 It was confirmed by ^1H NMR measurements of the freshly prepared crystals dissolved in deuterated chloroform that acetonitrile and ethanol molecules were contained in the crystals. The signals of the solvent molecules for the air-dried powdery sample were apparently decreased.
- 7 Programs for X-ray crystal structure determination, MAC Science, Yokohama (1994).
- 8 A. Altomare, G. Cascarano, C. Giacovazzo, and A. Guagliardi, *J. Appl. Crystallogr.*, **26**, 343 (1993).
- 9 "International Tables for X-ray Crystallography," Kynoch, Birmingham (1974), Vol. IV.
- 10 W. J. le Noble and R. Schlott, *Rev. Sci. Instrum.*, **47**, 770 (1976).
- 11 ^{31}P NMR (in CHCl_3): δ (relative to D_3PO_4 in D_2O) -17.48 (q, central), -12.99 (d, terminal); $J_{\text{P-P}} = 27$ Hz.
- 12 C. J. Jameson and H. S. Gutowsky, *J. Chem. Phys.*, **40**, 1714 (1964).
- 13 N. F. Ramsey, *Phys. Rev.*, **77**, 567 (1950).
- 14 The substitution rate constants at 298.1 K for the reaction of $[\text{Pd}(\text{pt})(\text{p}_3)]^+$ with Br^- and Cl^- are $1.68 \times 10^{-4} \text{ s}^{-1}$ and $7.22 \times 10^{-4} \text{ s}^{-1}$ in the same conditions as those in this work, respectively (unpublished results).