Rapid Equilibrium between Trigonal-bipyramidal and Square-pyramidal Geometries of 1-Popanethiolato Platinum(II) Complex with Tris[2-(diphenylphosphino)ethyl]phosphine

Sen-ichi Aizawa* and Tadashi Kobayashi
Faculty of Engineering, Toyama University, 3190 Gofuku, Toyama 930-8555

(Received October 27, 2003; CL-031023)

The rapid equilibrium between five-coordinate trigonal-bipyramidal $[Pt(pt)(pp_3)]^+$ (pt = 1-propanethiolate, pp_3 = tris[2-(diphenylphosphino)ethyl]phosphine) and square-pyramidal $[PtI(pt)(pp_3)]$ with an axially coordinated I^- and dissociated terminal phosphino group was clearly observed in the presence of a large excess of I^- at low temperatures. Such a square-pyramidal intermediate is expected to be formed in the course of substitution reactions of trigonal-bipyramidal Pt(II) complexes.

The kinetic properties of four-coordinate square-planar d^8 metal complexes have been well established and the associative mechanism with the trigonal-bipyramidal 18-electron transition state or intermediate have been proposed.[1] On the other hand, though a few mechanistic studies on five-coordinate trigonal-bipyramidal d^8 metal complexes with the 18-electron ground state have been reported,[2] there is no information about structures of the transition state or intermediate, which can give us further insight into the kinetic properties of the d^8 metal complexes.

We have selected Pt(II) as the central metal, because Pt(II) complexes generally have great activation energy for each reaction step and the intermediate may be detectable. The tripodal tetradentate phosphine, tris[2-(diphenylphosphino)ethyl]phosphine (pp_3), was used for the bound ligand, which tend to form $[MX(pp_3)]$-type (M = metal ion, X = monodentate ligand) trigonal-bipyramidal complexes for d^8 metal ions.[3] In the beginning, we undertook the halo-ligand substitution reactions with halide ions, but information about the intermediate or transition state has been scarcely obtained so far. Then, the thiolato ligand, which is strong σ donor for Pt(II), was used for the bound monodentate ligand X so as not to be easily dissociated, and iodide ion, which is a relatively good π acceptor among halide ions, was used for the entering ligand in order to reduce the electronic repulsion on the Pt(II) center in the intermediate formed by the entering ligand association.

The chloro complex, $[PtCl(pp_3)]Cl$ (**1**), was prepared by a method similar to that described in the literature.[4] The single crystals were obtained from a mixture of chloroform and acetonitrile, and the crystal structure of $\mathbf{1}\cdot CH_3CN$ was determined by an X-ray crystallography.[5] The thiolato complex, $[Pt(pt)(pp_3)](BF_4)$ (pt = 1-propanethiolate) (**2**) was prepared by the reaction of $\mathbf{1}\cdot 2H_2O$ with Hpt in chloroform by addition of a 0.5 M NaOH aqueous solution after removal of Cl^- in **1** with $AgBF_4$.[6] The iodo complex, $[PtI(pp_3)]I$ (**3**), was prepared by the reaction of $\mathbf{1}\cdot 2H_2O$ with excess tetrabutylammonium iodide (NBu_4I) in chloroform.[7] Deuterated chloroform ($CDCl_3$, Aldrich) for NMR measurements was dried over activated 4A molecular sieves and deoxygenated and distilled in a vacuum line. The NMR samples for equilibrium experiments were prepared by vacuum distillation of the purified $CDCl_3$ into NMR tubes containing completely dried solid sample that were then flame-sealed after degassing. The chemical shifts of ^{31}P NMR were determined by using D_3PO_4 in external D_2O.

The ^{31}P NMR spectrum of **2** in completely deoxygenated and dried $CDCl_3$ exhibits two sharp signals coupled with ^{195}Pt assigned to the three equivalent terminal phosphorus atoms in the equatorial position and the central phosphorus atom in the axial position for the trigonal-bipyramidal geometry with C_3 symmetry.[6] On the other hand, the ^{31}P NMR spectrum of the $CDCl_3$ solution of **2** containing a large excess of NBu_4I was extremely broadened at room temperature, and reversibly changed with temperature as shown in Figure 1. Three sets of signals other than the signals of **2** were clearly observed at the lower temperature. By comparison with ^{31}P NMR spectra of the square-planar oxidized complex obtained from **2**, $[Pt(pt)(pp_3O)]BF_4$ (**4** in Figure 2),[8] and free pp_3 ligand,[9] the two signals at 44.0

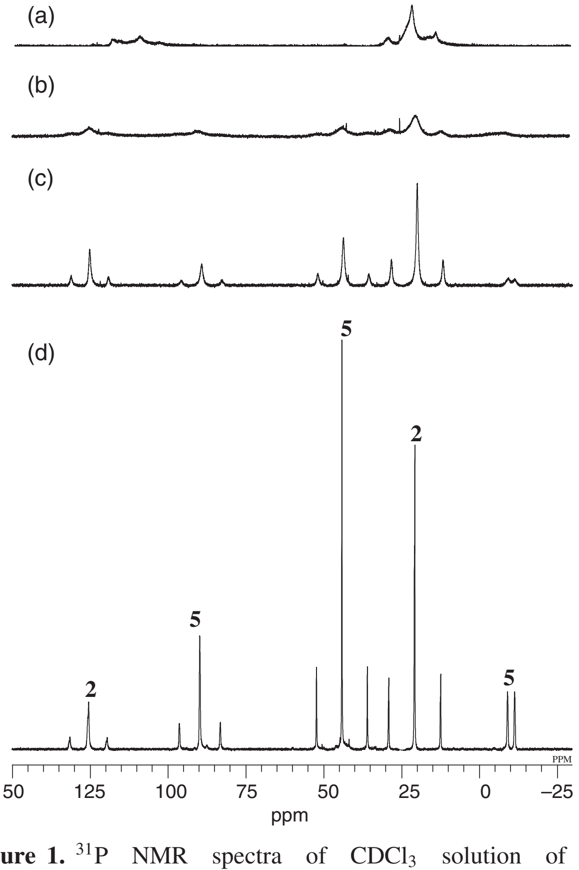

Figure 1. ^{31}P NMR spectra of $CDCl_3$ solution of **2** ($2.2 \times 10^{-2}\,mol\,kg^{-1}$) containing a large excess of NBu_4I ($4.1 \times 10^{-1}\,mol\,kg^{-1}$) at various temperature (298.3(a), 250.0(b), 236.9(c), and 206.7(d) K). **2** and **5** denote the signals for the corresponding complexes.

and 89.6 ppm coupled with ^{195}Pt ($J_{\text{P-Pt}} = 1322$ and 1058 Hz, respectively) are reasonably assigned respectively to the two terminal and central phosphorus atoms on the square-planar geometry of Pt(II) and a pair of signals at −9.1 and −11.4 ppm corresponds to the free terminal phosphorus atom. Considering that the relative strength of these signals increases with an increase of the concentration of I^-, the above finding is attributable to the formation of the square-pyramidal Pt(II) complex with one dissociated terminal phosphorus atom and apically coordinated I^- (**5** in Figure 2). Coordination of the pt ligand in the square-plane is confirmed by the values of $J_{\text{P-Pt}}$ for the coordinated terminal and central phosphorus atoms of **5** that are in good agreement with those of **4** but entirely different from those of $[\mathrm{PtI(pp_3O)}]^+$ (**6** in Figure 2)[10] with I^- in the square plane (see below). Because the two isomeric structures, one with the iodo ligand and free $\mathrm{Ph_2PCH_2CH_2}$– group on the same side of the Pt(II) square plane and the other on the opposite side, are possible for **5**, we can assume that the two NMR resonance lines observed in the region of the free diphenylphosphino group are due to the two different steric surroundings.

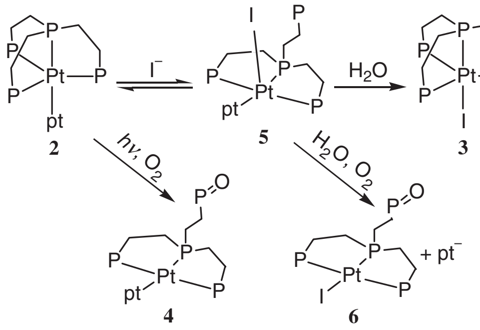

Figure 2. Reaction mechanism for the substitution and oxidation reactions of **2**. The positive charges of the cationic complexes are omitted.

By addition of a small amount of water to the equilibrated solution, the substitution reaction of pt ligand with I^- proceeded to give the five-coordinate trigonal-bipyramidal iodo complex **3** (Figure 2). This fact indicates that the re-coordination of the free $\mathrm{Ph_2CH_2CH_2}$– group accompanies the release of the thiolato ligand bound to Pt(II) into the moist chloroform because of the greater solvation energy for pt^- compared with dry chloroform. Formation of the square-pyramidal intermediate **5** with one pendant $\mathrm{Ph_2PCH_2CH_2}$– group in the course of the pt ligand substitution reaction of **2** with I^- is consistent with the fact that one terminal phosphino group of coordinated $\mathrm{pp_3}$ was partially oxidized during the substitution reaction under air (**6** in Figure 2). The equilibrium constant and enthalpy and entropy changes for the formation of **5** in $\mathrm{CDCl_3}$ were obtained by using the change in ratio of the ^{31}P NMR intensity with temperature as follows: $K^{298} = 7.5 \times 10^{-1}\,\mathrm{mol^{-1}\,kg}$; $\Delta H^\circ = -10 \pm 2.4\,\mathrm{kJ\,mol^{-1}}$; $\Delta S^\circ = -36 \pm 10\,\mathrm{kJ\,K^{-1}\,mol^{-1}}$. These thermodynamic parameters reveal that **5** is enthalpically a little stable but entropically unstable compared with **2** by coordination of free I^-. The observed chemical exchange rate constant at 298 K was estimated to be $1.3 \times 10^4\,\mathrm{s^{-1}}$ by using the ^{31}P NMR line-broadening data of **2** in the temperature range from 219.5 to 234.9 K.[11] This exchange rate is extremely faster than the usual substitution rates for Pt(II) complexes. Expecting that such a rapid pre-equilibrium is included in the substitution process of the trigonal-bipyramidal Pt(II) complexes (Eq 1), the observed rate constants can be given by $k_{\text{obs}} = kK[\mathrm{Y}]/(K[\mathrm{Y}] + 1)$ under the pseudo-first-order conditions with a large excess of Y.

$$[\mathrm{PtX(pp_3)}]^+ + \mathrm{Y} \overset{K}{\rightleftharpoons} \{\mathrm{PtXY(pp_3)}\} \overset{k}{\rightarrow} [\mathrm{PtY(pp_3)}]^+ + \mathrm{X} \quad (1)$$

In other words, it is possible that the pre-equilibrium constant K and rate constant k are obtained from the dependence of k_{obs} on [Y].

This work was supported by a grant from Kurita Water and Environment Foundation and Grant-in-Aid for Scientific Research (No. 15550104) from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

References

1 R. G. Wilkins, in "Kinetics and Mechanism of Reaction of Transition Metal Complexes," 2nd ed., VCH, Weinheim (1991), Chap. 4; B. J. Cross, "Mechanisms of Inorganic and Organometallic Reactions," ed. by M. V. Twigg, Plenum, New York (1988), Chap. 5; Z. Lin and M. B. Hall, *Inorg. Chem.*, **30**, 646 (1991).

2 S. Aizawa, T. Iida, and S. Funahashi, *Inorg. Chem.*, **35**, 5163 (1996); S. Aizawa, T. Iida, Y. Sone, T. Kawamoto, S. Funahashi, S. Yamada, and M. Nakamura, *Bull. Chem. Soc. Jpn.*, **75**, 91 (2002).

3 R. B. King, R. N. Kapoor, M. S. Saran, and P. N. Kapoor, *Inorg. Chem.*, **10**, 1851 (1971); C. A. Ghilardi, S. Midollini, and L. Sacconi, *Inorg. Chem.*, **14**, 1790 (1975); A. Orlandini and L. Sacconi, *Inorg. Chem.*, **15**, 78 (1976); W. H. Hohman, D. J. Kountz, and D. W. Meek, *Inorg. Chem.*, **25**, 616 (1986).

4 D. Fernández, M. I. G.-Seijo, T. Kégl, G. Petöcz, L. Kollár, and M. E. G.-Fernández, *Inorg. Chem.*, **41**, 4435 (2002).

5 Because the crystal structure of $\mathbf{1}\cdot6\mathrm{H_2O}$ was reported recently in Reference 4, the crystallographic data of $\mathbf{1}\cdot\mathrm{CH_3CN}$ are omitted here.

6 Yield 86%. Anal. Found: C, 51.69; H, 4.70; N, 0.00%. Calcd for $\mathrm{C_{45}H_{49}BF_4P_4SPt\cdot H_2O}$: C, 51.68; H, 4.92; N, 0.00%. $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR ($\mathrm{CHCl_3}$): σ 20.2 (s, 3P, terminal, $J_{\text{P-Pt}} = 1325$ Hz), 126.3 (s, 1P, center, $J_{\text{P-Pt}} = 970$ Hz).

7 Yield 84%. Anal. Found: C, 44.50; H, 3.73; N, 0.00%. Calcd for $\mathrm{C_{42}H_{42}P_4I_2Pt}$: C, 45.06; H, 3.78; N, 0.00%. $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR ($\mathrm{CHCl_3}$): σ 18.5 (s, 3P, terminal, $J_{\text{P-Pt}} = 1286$ Hz), 129.4 (s, 1P, center, $J_{\text{P-Pt}} = 1191$ Hz).

8 **4** was prepared by photolysis of one terminal phosphorus atom of **2** under air. $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR ($\mathrm{CHCl_3}$): σ 32.3 (d, 1P, oxide, $J_{\text{P-P}} = 37$ Hz), 44.6 (s, 2P, terminal, $J_{\text{P-Pt}} = 1324$ Hz), 91.7 (d, 1P, center, $J_{\text{P-Pt}} = 1061$ Hz) (unpublished results).

9 $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR ($\mathrm{CHCl_3}$): $\sigma - 13.0$ (d, 3P, terminal), −17.5 (q, 1P, center); $J_{\text{P-P}} = 26$ Hz.

10 $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR ($\mathrm{CHCl_3}$): σ 32.2 (d, 1P, oxide, $J_{\text{P-P}} = 37$ Hz), 42.2 (s, 2P, terminal, $J_{\text{P-Pt}} = 1217$ Hz), 95.0 (d, 1P, center, $J_{\text{P-Pt}} = 1400$ Hz) (unpublished results).

11 The observed chemical exchange rate constant (k_{ex}) is expressed by $k_{\text{ex}} = \pi(\Delta\nu_{\text{obs}} - \Delta\nu_{\text{ref}}) = k_{\text{B}}T/h\ \exp(-\Delta H^{\ddagger}/RT + \Delta S^{\ddagger}/R)$, where $\Delta\nu_{\text{obs}}$ and $\Delta\nu_{\text{ref}}$ are the half-height widths of the NMR signal of **2** in the present and absent of excess I^-, respectively. The values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were determined to be $34.0 \pm 4.7\,\mathrm{kJ\,mol^{-1}}$ and $-50 \pm 21\,\mathrm{J\,mol^{-1}\,K^{-1}}$, respectively, under the conditions in Figure 1.

Published on the web (Advance View) March 1, 2004; DOI 10.1246/cl.2004.384