Stereoselective Substitution of *trans*-2-Butene for the *S*,*S*-2-Butene in Trichloro-*S*,*S*-2-buteneplatinate(II) in Acetone

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A new complex salt [Ph_4P][$PtCl_3$(*S*,*S*-tbn[1,3-^3H])] (tbn, *trans*-2-butene) undergoes racemization and ligand isotopic exchange in acetone containing a large excess of tbn without side reactions. Both rates are expressed by the second order rate equations, $R_{(CD)}=k_{2(CD)}$[Pt][tbn] and $R_{(IE)}=k_{2(IE)}$[Pt][tbn], the k_2 values being 17.6 and $70.6\times10^{-3}M^{-1}s^{-1}$ at 8.0 °C, respectively (M=mol dm^{-3}). Individual k_2 values for the substitutions without and with inversion of configuration of coordinated tbn are calculated to be 62.0 and $8.7\times10^{-3}M^{-1}s^{-1}$, respectively, the corresponding $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values being 36.3 ± 3.1 and 37.6 ± 2.7 kJ mol^{-1}, and -138 ± 12 and -149 ± 10 J· mol^{-1} K^{-1}. Source of the stereoselectivity appears to consist in the difference in ease of formation of square pyramidal transition state on the nucleophilic attack of tbn upon the complex.

In a previous paper we have reported the kinetics of ligand isotopic exchange and epimerization of *trans*(*N*, olefin)[PtCl(L-pro)(*S*,*S*-2-butene)] in acetone in the presence of an excess of *trans*-2-butene (tbn), and found that the coordinated *S*,*S*-2-butene is replaced by tbn faster with retention than with inversion of configuration by *ca.* 10 times.[1] The substrate complex has two asymmetric sources, the L-prolinate (with two asymmetric centers, the carbon and the coordinated nitrogen) and the *S*,*S*-2-butene. In order to find the origin of the stereoselectivity, complexes having only one source of asymmetry should be needed. We have found that *trans*(*N*,olefin)[PtCl(L-pro)(*S*,*S*-2-butene[1,3-^3H])] gives [$PtCl_3$(*S*,*S*-2-butene[1,3-^3H])]$^-$ in 6 M hydrochloric acid and crystallizs as tetraphenylphosphonium salt with retention of configuration. This salt enabled us to carry out kinetic studies of the isotopic exchange and racemization in acetone.

Experimental

Materials. Tetraphenylphosphonium trichloro-*S*,*S*-2-butene[1,3-^3H]platinate(II) was prepared by treating optically active [PtCl(L-pro)(*S*,*S*-2-butene[1,3-^3H])] (0.2 g, $\Delta\varepsilon$ at 27000 cm^{-1} 1.05) with 6 M hydrochloroic acid (4 cm^3) and tetraphenylphosphonium chloride (0.23 g) for 1 h at room temperature, and cooling in a refrigerator. The precipitated product was filtered off, air dried, and recrystallized from acetone by adding petroleum ether. Yield 0.3 g (85% on platinum). The specific activity was *ca.* 2×10^4 d.p.m. per mg, and $\Delta\varepsilon$ at 23800 cm^{-1} *ca.* 0.7. The purity was examined by the ultraviolet (UV) absorption spectrum. The elemental analysis of carbon and hydrogen was carried out by use of a similarly prepared non-radioactive sample. Found: C, 48.22; H, 4.04%, Calcd C, 48.25; H, 4.05%.

trans-2-Butene of research grade (>99.3%) from Nippon Tokushu Gas Co. was used without further purification. Acetone and acetonitrile were purified by the usual method.

Kinetic Runs. *trans*-2-Butene boils at 0.88 °C under atmosphere and the solutions for kinetic studies should be prepared carefully as follows. *trans*-2-Butene chilled in a mixture of Dry Ice and acetone (0.1 to 2 g) was swiftly added into a stoppered Erlenmeyer flask containing a known amount (30 to 40 cm^3) of acetone, weighed, and preserved in a mixture of Dry Ice and acetone. The complex solution (to produce *ca.* 5 cm^3 of 10^{-4} to 10^{-3} M) was added to 6 to 10 small test tubes kept in a mixture of Dry Ice and acetone, and the tbn solution was added to each tube by use of a pipette wrapped with powdered Dry Ice. The tubes were stoppered and kept in a thermostat at −30 to +8 °C. They were withdrawn at appropriate intervals, placed in a liquid nitrogen bath, and tbn and the solvent evaporated off in a vacuum line at Dry Ice and room temperature, respectively. The residue consisting of pure complex was dissolved in acetonitrile (5 ml), and the UV absorption and CD spectra were recorded. A 1 ml portion of the AN solution was mixed with the liquid scintillation medium (0.108 mg of *p*-bis(5-phenyl-2-oxazolyl)benzene and 4.29 g of terphenyl per 1 dm^3; 14 cm^3) and submitted to the counting of the β-rays. The density of tbn solution in acetone differs significantly at reaction and Dry Ice–acetone temperatures, and due correction was made.

The experimental results of racemization and isotopic exchange were calculated in accordance with the first order kinetic law and the McKay formula, respectively.

Measurements. The UV absorption and CD spectra were recorded with a Hitachi 323 Spectrophotometer, and JASCO J-40 Spectrometer, respectively. The radioactivity was recorded with a Liquid Scintillation Spectrometer from Nuclear Chicago. The electrolytic conductivity was measured with a Conductoscope from Metrohm Co.

Results and Discussion

Synthesis and Spectra. The UV absorption curve (Fig. 1) is very similar to that of Zeise's salt,[2] and remains unchanged for many hours both in the absence and the presence of an excess of tbn in many kinds of solvent. Konya *et al.* gave the CD spectrum of $(+)^{\Delta\varepsilon}_{380}$-*trans*(*N*,olefin)[PtCl(L-pro)(*S*,*S*-2-butene)] in concentrated hydrochloric acid, and considered that the pattern represented the CD of [$PtCl_3$(*S*,*S*-butene)]$^-$.[3] The CD curve in Fig. 1 is very similar to theirs, and the small difference may be due to the difference in solvent, and to the presence of free L-proline in their solution, which can give outer-sphere perturbation. Since the tetraphenylphosphonium salt of this complex is sparingly soluble in hydrochloric acid, the pure salt must have been precipitated as shown in the Experimental part.

This salt is insoluble in water and methanol, rather readily soluble (to give 0.1 M solution) in acetone, acetonitrile (AN), *N*,*N*-dimethylformamide (DMF), and dichloromethane, and dissolves in dimethyl sulfoxide with gradual decomposition. The CD pattern changes very slowly in acetone, AN, and DMF. The apparent first order rate constant of the spontaneous racemization

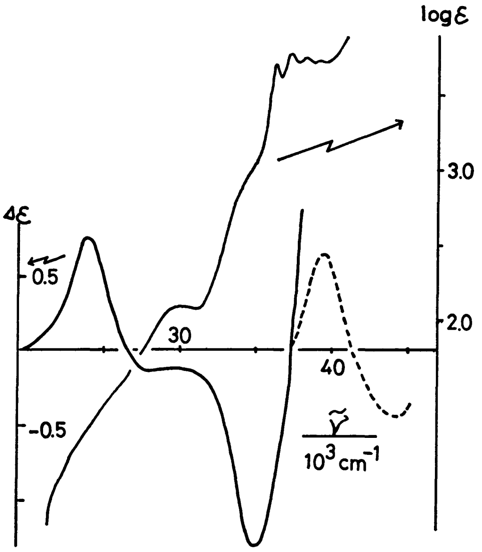

Fig. 1. Ultraviolet (UV) absorption and circular dichroism (CD) spectra of $[(C_6H_5)_4P][PtCl_3(S,S\text{-}2\text{-butene})]$ in acetonitrile (AN) at room temperature.

is $<3\times10^{-6}\,s^{-1}$ at 15 °C in acetone. Addition of water, acetic acid and alcohols enhanced whilst that of chloride retarded the spontaneous racemization. However, under the present experimental conditions, such a CD change can be ignored. Molar conductivity measurement in acetone gave a straight line on the plot *vs.* square root of concentration of this salt for $<1\times10^{-3}$ M. The degree of electrolytic dissociation of a 0.9×10^{-3} M solution (almost equal to the concentration at which the kinetic studies were made) was 0.91 at 8.0 °C.

Kinetic Data. The absorption spectrum of the reaction mixtures was equal to that of the complex and remained unchanged during the course of the kinetic runs. The kinetic measurements were made in the concentration ranges, [complex]=0.0005 to 0.003 M and [*trans*-2-butene]=0.02 to 1.15 M (40 to 1500 times excess to the complex). The CD strength at 23800 cm^{-1} decreased with time to reach zero at infinite time, and the diagram $\ln(a_t/a_0)$ *vs.* t was straight as shown in Fig. 2. (a_t and a_0 stand for the CD strengths at time t and zero, respectively). The observed first order rate constant $k_{0(CD)}$ increased linearly with increase in free tbn concentration, and it did not change on addition of tetraphenylphosphonium chloride (Fig. 3). The decrease in specific β-activity of the recovered complex also decreased in accordance with first order rate law as shown in Fig. 2, where x's denote the specific counting rate at the times indicated by the subscripts. McKay's R was proportional to the concentration of the complex, and the observed first order rate constant $k_{0(IE)}$ increased linearly with increase in concentration of the free tbn as shown in Fig. 3.

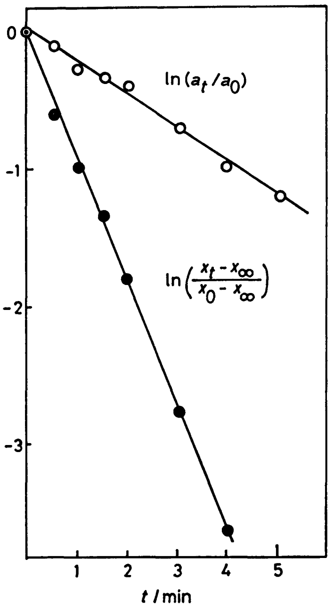

Fig. 2. The first order kinetic plots of the racemization (○) and isotopic exchange (●) of $[PtCl_3(S,S\text{-}2\text{-butene-}[^3H])]^-$ in acetone at 8.0 °C. [Complex], 8.61×10^{-4} M, [tbn], 0.218 M

Thus the rate constants obtained by both CD and β-activity measurement can be written as Eqs. 1 and 2.

$$k_{0(CD)} = k_{2(CD)}[\text{tbn}] \tag{1}$$

$$k_{0(IE)} = k_{2(IE)}[\text{tbn}] \tag{2}$$

The k_2 values are shown in Table 1.

The linear diagrams in Fig. 3 give no intercept. The spontaneous racemization was very slow, and the racemization must proceed exclusively *via* a bimolecular mechanism. When the individual second order rate constants of the substitution reaction with retention and inversion of configuration are written as $k_{2[SS]}$ and $k_{2[SR]}$, they are related to the observed k_2's by Eqs. 3 and 4.

$$k_{2(CD)} = 2k_{2[SR]} \tag{3}$$

$$k_{2(IE)} = k_{2[SR]} + k_{2[SS]} \tag{4}$$

TABLE 1. SECOND ORDER RATE CONSTANTS AND ACTIVATION PARAMETERS FOR THE SUBSTITUTION OF *trans*-2-BUTENE FOR $[PtCl_3(S,S\text{-}trans\text{-}2\text{-butene}[1,3\text{-}^3H])]^-$ IN ACETONE

$\frac{\text{Temp}}{^\circ\text{C}}$	$\frac{k_{2(CD)}}{10^{-3}\,M^{-1}\,s^{-1}}$	$\frac{k_{2(IE)}}{10^{-3}\,M^{-1}\,s^{-1}}$	$\frac{k_{2[SS]}}{10^{-3}\,M^{-1}\,s^{-1}}$	$\frac{k_{2[SR]}}{10^{-3}\,M^{-1}\,s^{-1}}$	$\frac{k_{2[SS]}}{k_{2[SR]}}$
8.0	17.3	70.6	62.0	8.7	7.2
−5.0	6.74	35.1	31.7	3.4	9.3
−20.0	2.65	11.4	10.1	1.3	7.8
$\frac{\Delta H^{\neq}}{\text{kJ mol}^{-1}}$			36.3±3.1	37.6±2.7	
$\frac{\Delta S^{\neq}}{\text{J mol}^{-1}\,\text{K}^{-1}}$			−138±12	−149±10	

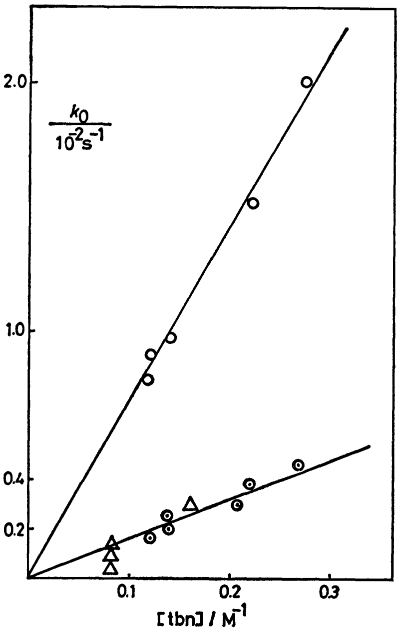

Fig. 3. Dependence of the observed first order rate constants of the racemization (○) and isotopic exchange (●) of $[PtCl_3(S,S\text{-}2\text{-butene}[^3H])]^-$ upon the concentration of free tbn in acetone at 8 °C. (△0.0034 M Ph_4PCl added.)

On the basis of the observed k_2's, $k_{2[SR]}$, and $k_{2[SS]}$ were calculated as shown in Table 1. The activation parameters are also included in the same table.

Dynamic Stereoselectivity. The ratio $k_{2[SS]}/k_{2[SR]}$ is *ca.* 8 in the present temperature range. The activation parameters involve rather large experimental errors, but the difference in k_2's must consist in the $\Delta S^{\ne}$ term. It is generally believed that the substitution of such square planar complexes proceed *via* S_N2 mechanism, and the ease of nucleophilic attack by the incoming ligand is the rate-determining step. The two kinds of substitution with retention and inversion of configuration should have very similar transition states and the approach of tbn resulting in retention of configuration must be slightly easier than that resulting in inversion. Such a difference must be of a steric origin, and very naturally reflected in the $\Delta S^{\ne}$ rather than in the $\Delta H^{\ne}$ value.

So far as the substitution reaction proceeds *via* an associative mechanism, the transition state should be either a trigonal bipyramid or a square pyramid. Some trigonal bipyramidal complexes have been isolated as crystals (*e.g.* $[PtCl_2(C_2H_4)(phen)]$[4] and $[Ir^ICl(C_2H_4)_4]$[5]), and π-accepting ligands are claimed to stabilize trigonal bipyramidal structure.[6] Hence the present substitution reaction may have a square pyramidal transition state (Fig. 4), which undergoes internal rearrangement to give a trigonal bipyramidal intermediate. Even a simple molecular model study discloses that the approach of tbn as shown in Fig. 4A involves less steric hindrance than that as shown in Fig. 4B. The stereoselctivity of the present substitution is slightly smaller than that in the substitution of tbn for *trans*(*N*, olefin)[PtCl(L-pro)(*S*,*S*-2-butene)], but very near to it. Similar difference to that shown in Fig. 4 may be encountered in the substitution of the L-prolinato complex, and we can conclude that the main source of selectivity in this complex should be in the asymmetrically coordinated *trans*-2-butene.

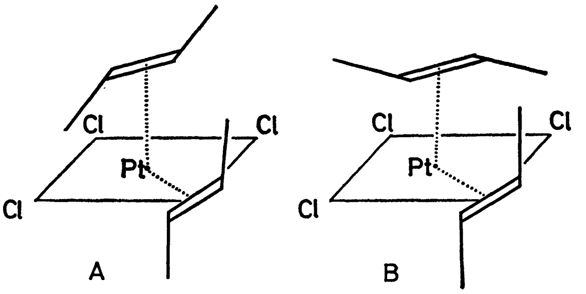

Fig. 4. Plausible transition state on the nucleophilic attack of tbn upon $[PtCl_3(S,S\text{-}2\text{-butene})]^-$.

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