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Platinum(II)-Olefin Complexes Containing Amino Acids. III.[1] Optical Inversion and Substitution of Coordinated Olefins in Optically Active *trans(N)*-Chloro-L-prolinato-olefin-platinum(II) Complexes in Organic Solvents

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Optical inversion of coordinated 2-methyl-2-butene and *trans*-2-butene in *trans(N)*-chloro-L-prolinato-olefin-platinum(II),[1] *trans(N)*-[PtCl(L-prol)(olefin)] (nitrogen of L-prolinate ion is *trans* to the olefin), *i.e.* the interconversion between diastereoisomers (Fig. 1), has been kinetically studied in acetone by measuring the decrease in the intensity of circular dichroism (CD) in near ultraviolet region. The rate was measurable only in the presence of olefin, and can be expressed by the relation, Rate=k[complex][olefin]. The E_a and the $\Delta S^{\neq}$ values for the two complexes are 7.8±1.0 and 9.0±1.0 kcal/mol, and −44 and −39 entropy unit, respectively. The coordinated *trans*-2-butene is replaced by other olefins, 2,3-dimethyl-2-butene, 2-methyl-2-butene, *trans*-2-butene (optical inversion), and styrene, under similar conditions to give the same rate formula. The second order rate constant increases in the given order. The inversion seems to take place *via* bimolecular mechanism with excessive olefin as nucleophile. The corresponding complexes containing styrene and its *para* derivatives give such an inversion much faster in the absence of excess of olefin. With change of *para* substituents, the rate increases in the order, methoxy<methyl<hydrogen<chloro<nitro. This seems to be related with their electrondrawing ability.

Kinetics of substitution of coordinated olefins in Zeise type complexes have been studied by several authors. Cramer found that the rate of exchange between free and coordinated ethylene is greater than 70 sec^{-1} at 75°C on the basis of nuclear magnetic resonance spectroscopy.[3] Paiaro and Panunzi examined the mutarotation of diastereoisomers of olefin complexes of platinum(II) and suggested that the exchange takes place through S_N2 Smechanism.[4] Joy and Orchin[5] and Shupack and Orchin[6] measured the equilibrium constants between some platinum(II) complexes of 1-dodecene and various substituted styrenes, and discussed the relative affinity of the olefins toward the platinum(II) ion. Recently, Venanzi and his co-workers studied the formation constants of Zeise type complexes systematically in aqueous solutions containing halo complexes of platinum(II) and various olefins.[7-10]

In previous papers we reported on the preparation and characterization of platinum(II)-olefin complexes containing amino acids,[11] and also on the preparation and circular dichroism (CD) of optically active *trans*(*N*)-chloro-L-prolinato-olefinplatinum(II), *trans*(*N*)-[PtCl(L-prol)(olefin)] (nitrogen of L-prolinate ion is *trans* to the olefin).[1] These optically active olefin-platinum(II) complexes seem particularly suitable for the kinetic study of the exchange reaction of coordinated olefins, by following the change in CD spectra, due to the asymmetric coordination of olefins to platinum(II). In this paper we report on the kinetics of optical inversion and substitution of coordinated olefins in such complexes.

The inversion reaction of coordinated olefins, shown in Fig. 1, is an interconversion between (a) and (b) and involves the cleavage of both the so-called σ- and

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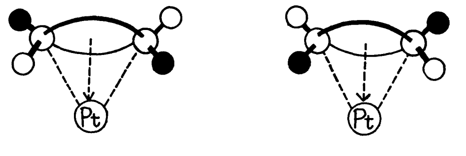

(a) (b)

Fig. 1. Enantiomeric coordination of an olefin ligand, *e.g.* *trans*-2-butene.

π-bond between the metal ion and the olefin.

The complexes of such olefins as 2-methyl-2-butene and *trans*-2-butene show no change in absorption and CD spectra in the absence of free olefin in organic solvents such as ethanol, chloroform, and acetone. When the same kind of olefin as in the complex is added, the CD spectrum changes with time and approaches a constant pattern, but the ultraviolet absorption spectrum remains unchanged. This fact indicates that only inversion reaction of the coordinated olefin takes place without involving any other reaction. When another kind of olefin is added to the solution, both ultraviolet absorption and CD spectrum change with time. The absorption pattern of the final solution suggests that an exchange of the coordinated olefin takes place with the added olefins. We have followed the change in peak height of CD spectra in near ultraviolet region of optically active $(+)^{\Delta\varepsilon}_{380}$-*trans*(*N*)-[PtCl(L-prol)(*trans*-2-butene)] and $(+)^{\Delta\varepsilon}_{380}$-*trans*(*N*)-[PtCl(L-prol)(2-methyl-2-butene)] on the addition of various olefins, and found that the rate depends on the kind of added olefin. The reaction mechanism has been discussed on the basis of the rate constants and other kinetic parameters.

The corresponding complexes containing styrene and its derivatives *trans*(*N*)-[PtCl(L-prol)(styrene)], on the other hand, show a significant change in ultraviolet absorption and CD spectrum in the absence of free olefin in organic solvents. The change is fast even at 0°C. The rate has been qualitatively examined at temperatures 0—15°C, and the influence of the substituting groups on styrene is discussed.

Results and Discussion

Optical Inversion of Coordinated Olefins in Optically Active $(+)^{\Delta\varepsilon}_{380}$-trans(N)-*[PtCl(*L*-prol)(2-methyl-2-butene)] and* $(+)^{\Delta\varepsilon}_{380}$-trans(N)-*[PtCl(*L*-prol)(*trans*-2-butene)].* The inversion reaction of olefins in both complexes was studied in acetone. Decrease in the peak height of the CD spectrum was measured on addition of the same olefin as the ligand. No change in the absorption spectrum was observed. Only the inversion reaction of coordinated olefins seemed to take place in the solution. No stereoselective coordination of the olefins was observed, when 2-methyl-2-butene and *trans*-2-butene were added to the *trans*(*N*)-[PtCl(L-prol)(ethylene)]. Thus, we can presume that neither stereoselective reaction would take place on the addition of these olefins to the solution of their complexes.

The change in CD peak height ($\Delta\varepsilon$) at 380 nm with time, when 2-methyl-2-butene (0.50M) is added to $(+)^{\Delta\varepsilon}_{380}$-*trans*(*N*)-[PtCl(L-prol)(2-methyl-2-butene)] (0.0020M) in acetone, is shown in Fig. 2. The rate of change in CD follows the first order rate law, and the apparent rate constant is given by

$$k_{\mathrm{obs}} = \ln[(\alpha_0-\alpha_\infty)/(\alpha_t-\alpha_\infty)]/(t-t_0) \qquad (1)$$

where α_0, α_t, and α_∞ denote the $\Delta\varepsilon$ values at time t_0, t, and infinite time, respectively. k_{obs} is related to the rate constant of inversion reaction, k_{inv}, by the relation $k_{\mathrm{obs}}=2k_{\mathrm{inv}}$. However, the k_{obs} values are used in the following discussion for a comparison with the rate constants of substitution reactions.

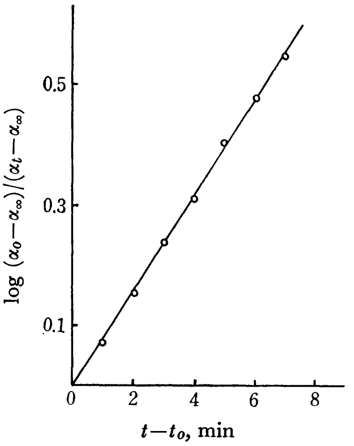

Fig. 2. CD change at 380 nm of *trans*(*N*)-[PtCl(L-prol)(2-methyl-2-butene)] with time in acetone. (23.6±0.3°C, complex (2×10^{-3}M), 2-methyl-2-butene (0.5M)).

The relationship between k_{obs} and the amount of added 2-methyl-2-butene at three temperatures is shown in Fig. 3, the concentration of the complex being kept constant at 1.9×10^{-3}M. In a given con-

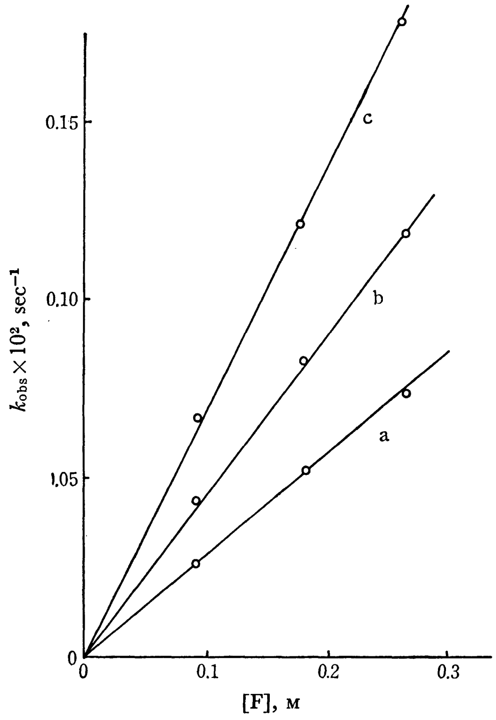

Fig. 3. Relationship between k_{obs} and the concentration of added 2-methyl-2-butene. (*trans*(*N*)-[PtCl(L-prol)(2-methyl-2-butene)] (1.90×10^{-3}M)). a, 3.7±0.3°C; b, 13.2±0.3°C; c, 21.6±0.3°C.

centration range, k_{obs} is proportional to the amount of added olefin. The lines showing the proportionality pass the origin. This coincides with the observation that the CD spectrum does not change in the absence of excessive olefin. Thus the apparent rate is given by

$$\text{Rate} = k_{obs}[\text{complex}] = k[\text{F}][\text{complex}] \qquad (2)$$

where [F] is the concentration of added olefin.

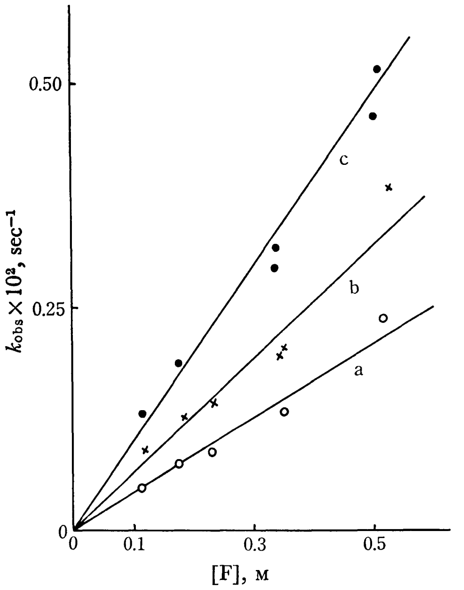

Fig. 4. Relationship between k_{obs} and the concentration of added *trans*-2-butene. (*trans*(*N*)-[PtCl(L-prol)(*trans*-2-butene)] (1.50×10^{-3}M)). a, 8.1±0.3°C; b, 17.0±0.3°C; c, 23.6±0.3°C.

The CD strength of the corresponding *trans*-2-butene complex also decreases in a similar way. In the relationship between k_{obs} and the amount of added *trans*-2-butene complex shown in Fig. 4, the fluctuation in individual plots is slightly greater than that in Fig. 3. This is due to the inaccuracies involved on the addition of the olefin to the sample solution, since *trans*-2-butene is a gas at room temperature (bp +0.88°C).

The Arrhenius plots of the results for the two complexes are given in Fig. 5, and the kinetic parameters summarized in Table 1.

In general, substitution reactions of square planar complexes obey the formula

$$\text{Rate} = -\text{d}[\text{substrate}]/\text{d}t = [\text{substrate}](k_1 + k_2[\text{Y}]) \qquad (3)$$

where [Y] stands for the concentration of the nucleophile substituting for the ligand. The k_1 and k_2 term represent the solvent path and the reagent path, respectively. Both paths are believed to proceed *via* S_N2 reaction mechanism. Our rate formula (Eq. (2)) corresponds to Eq. 3 where k_1 is equal to zero.

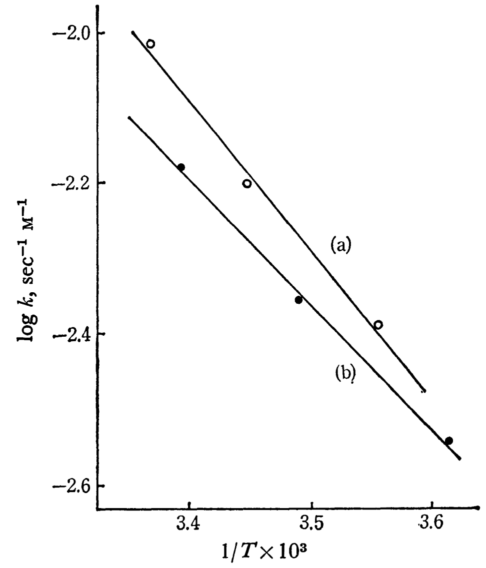

Fig. 5. Arrhenius plots for the interconversion reaction of *trans*-2-butene(a) and 2-methyl-2-butene(b) complex.

The small E_a and the big absolute value of $\Delta S^{\neq}$ given in Table 1 indicate that the inversion of coordinated olefins would take place through S_N 2reaction mechanism. A probable intermediate state is shown in Fig. 6. Since proline has a large pyrolidine ring, the olefin could approach the complex only from one side of the complex plane. The very big negative values of $\Delta S^{\neq}$ seem to reflect this limited possibility in the formation of the intermediate state with coordination number five.

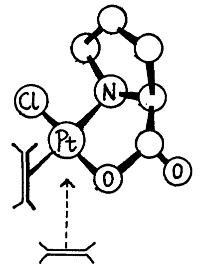

Fig. 6. Probable intermediate state.

Negligible contribution of the solvent path to the inversion reaction could be understood by considering the fact that acetone is a very weak nucleophile towards platinum(II).[12]

Substitution Reaction of Optically Active $(+)^{\Delta\varepsilon}_{380}$-trans*(N)-[PtCl(L-prol)(*trans-*2-butene)]*. In order to examine the steric effect of the nucleophile, we have examined

TABLE 1. ACTIVATION PARAMETERS FOR THE INVERSION REACTION OF OLEFINS IN *trans*(*N*)-[PtCl(L-prol)(2-methyl-2butene)] AND *trans*(*N*)-[PtCl(L-prol)(*trans*-2-butene)] IN ACETONE

Complex	T, °C	$k \times 10^3$(sec^{-1}M^{-1})	E_a,kcal/mol	$\Delta S^{\neq}$, e.u.
trans(*N*)-[PtCl(L-prol)(2-methyl-2-butene)]	13.2	4.44±0.02	7.8	−44
trans(*N*)-[PtCl(L-prol)(*trans*-2-butene)]	17.0	6.3 ±0.1	9.0	−39

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[12] R. G. Pearson, H. B. Gray, and F. Basolo, *J. Amer. Chem. Soc.*, **82**, 787 (1960).

the replacement of coordinated *trans*-2-butene in $(+)^{\Delta\varepsilon}_{380}$-*trans*($N$)-[PtCl(L-prol)(*trans*-2-butene)] by various olefins including styrene, 2-methyl-2-butene, and 2,3-dimethyl-2-butene. Although the reaction products were not isolated crystalline, change in absorption spectra indicated that substitution reaction took place as follows.

$$\textit{trans}(N)\text{-[PtCl(L-prol)}(\textit{trans}\text{-2-butene})] + \text{olefin} \rightleftharpoons \textit{trans}(N)\text{-[PtCl(L-prol)(olefin)]} + \textit{trans}\text{-2-butene} \quad (4)$$

The substitution reactions were best followed by measuring the change in CD, since it is much more marked than the change in absorption spectra on the substitution reaction.

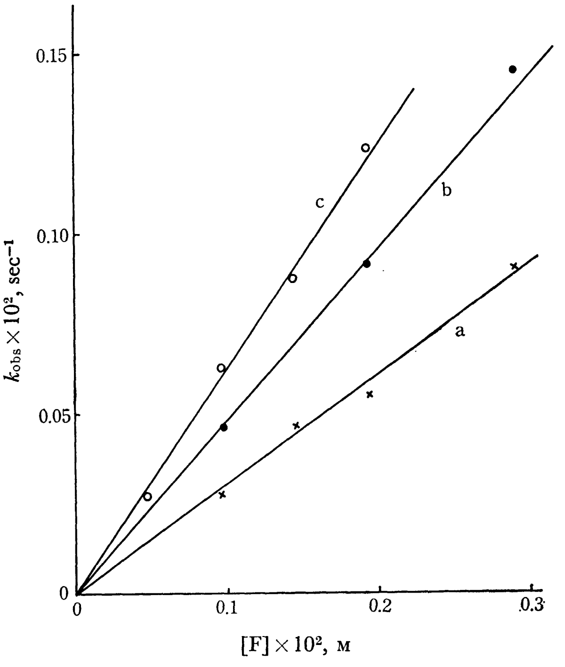

Fig. 7. Relationship between k_{obs} and the concentration of added styrene. (*trans*(N)-[PtCl(L-prol)(*trans*-2-butene)] (1.50×10^{-3}M)). a, 8.1±0.3°C; b, 17.0±0.3°C; c, 23.6±0.3°C.

All the reactions obeyed the second order rate expression with regard to both the concentration of the complex and that of added olefin (Eq. (2)). The relationship between the k_{obs} and the concentration of styrene at three temperatures is shown in Fig. 7. 2-Methyl-2-butene and 2,3-dimethyl-2-butene give similar diagrams on the substitution reaction. All the straight lines have zero intercepts. The rate constants and the activation parameters are given in Table 2.

The rate constants increase in the order
2,3-dimethyl-2-butene < 2-methyl-2-butene < *trans*-2-butene(optical inversion) < styrene.

We also see that the activation energies are almost equal to one another in the given substitution reactions, and the order of increase in the rate constant is the same as the order of decrease in $-\Delta S^{\neq}$ values. The order of increase in nucleophilicity of the olefins seems to be the reverse of that for the increase in the rate constant, since methyl is more electron pushing than phenyl, and the increase in number of methyl group will certainly result in the increase in electron density on the C=C bond of the olefins. Thus, a steric effect seems to be more responsible for determining the rate of the substitution reaction of such prolinato olefin complexes. A decrease in the number of substituting groups on the carbon atoms of C=C double bond would make it easier for the olefin to approach the complex as shown in Fig. 6.

Observation on the Change in CD of trans(N)-*L-Prolinatoplatinum(II) Complexes Containing Styrene and Its Derivatives.* The CD strength of the optically active complexes *trans*(N)-[PtCl(L-prol)(*p*-X-styrene)] (X=methoxy, methyl, chloro, nitro, and hydrogen) decreases with time in acetone, and becomes constant within 5 to 10 min at room temperature in the absence of excessive styrenes as shown in Fig. 8. The rate increases with the progress of reaction. The absorp-

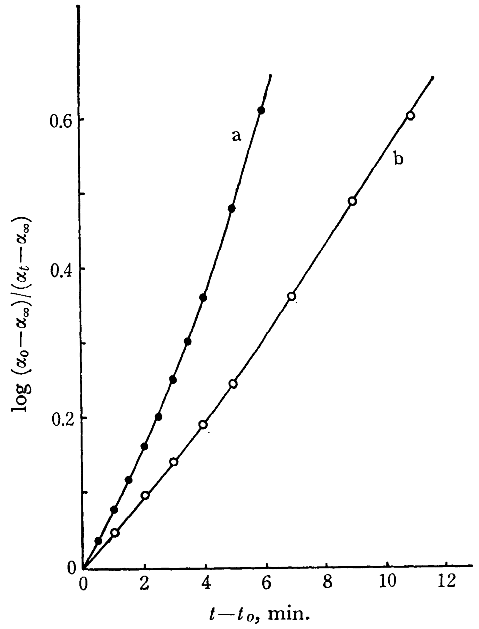

Fig. 8. CD change at 380 nm with time of *trans*(N)-[PtCl(L-prol)(styrene)] (1.326×10^{-3}M)(a) and *trans*(N)-[PtCl(L-prol)(*p*-methoxystyrene)] (1.455×10^{-3}M) (b) in acetone. (17.1±0.3°C).

Table 2 Rate constants and activation parameters for the substitution reactions of *trans*(N)-[PtCl(L-prol)(*trans*-2-butene)] with various olefins in acetone

Olefin	$k \times 10^3$(sec^{-1}M^{-1})						E_a, kcal/mol	$\Delta S^{\neq}$, e.u.
	T, °C 8.1	17.0	23.6	31.5	39.5	Error		
Styrene	303	480	621	—	—	±20	8.2	−34
trans-2-Butene	4.1	6.3	9.7	—	—	±1.0	9.0	−39
2-Methyl-2-butene	3.41	5.35	7.29	—	—	±0.20	8.6	−41
2,3-Dimethyl-2-butene	—	—	0.220	0.325	0.463	±0.020	8.6	−46

TABLE 3. RESULTS OF MICROANALYSIS

	C(%)		H(%)		N(%)	
	Found	Calcd	Found	Calcd	Found	Calcd
trans(*N*)-[PtCl(L-prol)(*p*-methoxystyrene)]	35.02	35.19	3.85	3.59	2.98	2.93
trans(*N*)-[PtCl(L-prol)(*p*-methylstyrene)]	35.96	36.41	3.92	3.71	2.95	3.03
trans(*N*)-[PtCl(L-prol)(*p*-chlorostyrene)]	32.67	32.37	3.22	2.93	2.81	2.90
trans(*N*)-[PtCl(L-prol)(*p*-ntrostyrene)]	31.56	31.68	3.07	2.87	5.51	5.68

tion spectra of these complexes change simultaneously and seem to approach a constant pattern in a few hours at room temperature. Thus the following solvolytic equilibrium might be involved.

$$trans(N)\text{-}[\mathrm{PtCl}(\textsc{l}\text{-prol})(p\text{-X-styrene})] + \text{solvent} \rightleftharpoons trans(N)\text{-}[\mathrm{PtCl}(\textsc{l}\text{-prol})(\text{solvent})] + p\text{-X-styrene} \qquad (5)$$

The decrease in CD strength can be presumed to proceed *via* two routes, the solvent path and the reagent path, as in most square planar complexes. If the inversion reaction were accompanied by the solvolysis, the styrene liberated on solvolysis would operate as nucleophile and bring about an increase in the rate of CD change with the progress of reaction. Preliminary experiments showed that the CD strength of optically active styrene complexes decreased rapidly when a very small amount (*e.g.* 1% to the complex in molar ratio) of styrene was added to the complex solution.

The final pattern of the absorption spectrum should correspond to that of the equilibrated state of Eq. (5). However, the absorption spectrum of the product is unknown. Thus, we analyzed the initial part of the curves in Fig. 8 by use of Eq. (1), as in other olefin complexes in order to find the effect of substituents on styrene. The k_{obs} values increase almost linearly with the increase in the initial concentration of the complex, and are too great to enable kinetic treatment. It is seen, however, that the apparent rate constant k_{obs} increases in the sequence

p-methoxystyrene<*p*-methylstyrene<styrene<*p*-chlorostyrene<*p*-nitrostyrene

The order of such an increase is in accord with that of electrondrawing ability of the substituents on the *para* position. The stronger the attraction of electrons by substituent, the smaller the electron density on the C=C double bond in the side chain. The smaller electron density on the C=C double bond may result in a decrease in the σ-donating ability and an increase in the π-accepting ability of the olefin ligand.[5,6] The rate for the present reactions should have both nonzero k_1 and k_2 term (Eq. 3), although their values were not obtained separately. Thus the true mechanism of the reaction remains uncertain. However, the above sequence of the styrene derivatives suggests that the racemization is closely related to the strength of the metal-olefin σ-bond.

Experimental

Material. $(+)\text{-}^{\Delta\varepsilon}_{380}$*trans*(*N*)-[PtCl(L-prol)(2-methyl-2-butene)] and $(+)^{\Delta\varepsilon}_{380}$-*trans*(*N*)-[PtCl(L-prol)(*trans*-2-butene)] were prepared as described previously.[1] 2-Methyl-2-butene, *trans*-2-butene, styrene, and 2,3-dimethyl-2-butene are of extra-pure grade (Tokyo Kasei Co.) and used without further purification. Derivatives of styrene (*p*-methoxy, *p*-methyl, *p*-chloro, and *p*-nitrostyrene) were prepared by the method of Walling and Wolfstirn.[13] The complexes were synthesized as in the case of styrene.[1] Commercial acetone of spectrograde was used as solvent without purification. The results of microanalysis are shown in Table 3.

Equipments. Circular dichroism was measured with a JASCO Model ORD/UV-5 Spectrometer with CD attachment and a cell jacket to keep the temperature constant within ±0.3°C (Komatsu-Yamato Coolnics). A Takara Thermister Type SPD-1D thermometer was calibrated with Toa's standard thermometer and the unit was placed inside the CD cell. Absorption spectra were recorded with a Hitachi 124 Spectrometer.

Procedure. Inversion reaction of coordinated olefins in $(+)^{\Delta\varepsilon}_{380}$-*trans*(*N*)-[PtCl(L-prol)(olefin)] (olefin = 2-methyl-2-butene, *trans*-2-butene). To a thermostated acetone solution of the complex ($\simeq 10^{-3}$M) was added a certain amount ($\simeq 10^{-1}$M) of olefin with a micro syringe. The solution was kept in the cell box of the spectrometer which had also been thermostated. The $\Delta\varepsilon$ value at 380 nm was continuously recorded.

The complexes of styrene and its derivatives were dissolved in acetone and the decrease in CD was measured at 380 nm, the temperature being controlled within ±0.3°C.

We are grateful to the Ministry of Education for a Grant-in-aid for our studies on optically active complexes.

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13) C. Walling and K. B. Wolfstirn, *J. Amer. Chem. Soc.*, **69**, 852 (1947).