Kinetic Studies of the Inversion of η^2-*trans*-2-Butene in Platinum(II) Complexes Containing Various Amino Carboxylates

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Platinum(II) complexes containing *S,S-* or *R,R-trans*-2-butene and various L-amino carboxylate, *i.e. cis*(*N*, olefin)[PtCl (L-prolinate)(*S,S-trans*-2-butene)] and *trans*(*N*,olefin)[PtCl (L-am)(*S,S-* or *R,R-trans*-2-butene)], were synthesized (L-am=L-prolinate, *N*-methyl-L-prolinate, *N*-benzyl-L-prolinate, L-alaninate and L-valinate). The kinetics of the inversion reaction of the coordinated *S,S-* or *R,R-trans*-2-butene was investigated in acetone in the presence of an excess of *trans*-2-butene at 8.0 °C. Second order rate law was obeyed with respect to the concentrations of the complex and free olefin, and no solvent path was observed. In the *trans*(*N*,olefin) complexes, interactions steric around the coordinated nitrogen atoms seems to be responsible in determining the ease of inversion *via* an associative mechanism. On the other hand, smaller rate for the *cis*(*N*,olefin) complex than the corresponding trans isomer seems to be due to the trans effect.

The substitution reaction of various olefins for the η^2-*trans*-2-butene in [PtCl(L-pro)(*S,S-trans*-2-butene)] (L-pro=L-prolinate) in acetone gave a variety of rate and activation entropy,[1,2] and we pointed out the importance of the steric effect between the nucleophilic olefin and the coordinated amino carboxylate and/or olefin.[1] This paper deals with further kinetic studies of the exchange of *trans*-2-butene with inversion of configuration by use of *cis*(*N*,olefin)[PtCl(L-pro)(*S,S-trans*-2-butene)] and various *trans*(*N*,olefin)[PtCl(L-am)(*S,S-* or *R,R-trans*-2-butene)] in acetone, where L-am stands for various amino carboxylates, *i.e.* L-prolinate, *N*-methyl-L-prolinate (*N*-Me-L-pro), *N*-benzyl-L-prolinate (*N*-Bz-L-pro), L-alaninate (L-ala), and L-valinate (L-val).

Experimental

Materials. *N*-Methyl- and *N*-benzyl-L-proline were prepared from L-proline.[3] Guaranteed grade L-proline, L-alanine and L-valine and pure grade *trans*-2-butene (Nihon Tokushu Gas Co.) were used without further purification.

Preparation of the Complexes: The *trans*(*N*, olefin) complexes, *trans*(*N*, olefin)[PtCl(L-am)(olefin)] (olefin=ethylene and *trans*-2-butene) were synthesized by the reported methods.[4] The cis complex *cis*(*N*, olefin)[PtCl(L-pro)(C_2H_4)] was prepared by a new method with tin(II) chloride as a catalyst. Three mol dm^{-3} hydrochloric acid (15 cm^3) and K[$PtCl_2$(L-pro)](2 g)[5] were sealed in a 50 cm^3 flask with a rubber stopper, and nitrogen was bubbled for 30 min. A suspension of *ca.* 30 mg tin(II) chloride dihydrate in deoxygenated water (2—3 cm^3) was added with a syringe and ethylene was bubbled slowly with a vigorous stirring. Colorless crystals precipitated within 20 min. After 30 min the flask was cooled by ice, and the precipitate was filtered off, washed with water, air-dried at room temperature, and recrystallized from *N,N*-dimethylformamide (DMF) or acetonitrile (AN). Yield *ca.* 67%.
cis(*N*, olefin)[PtCl(L-pro)(*trans*-2-butene)] was obtained by replacing the coordinated ethylene by *trans*-2-butene in AN, and recrystallized from AN by adding diethyl ether.

All the *trans*-2-butene complexes were resolved by repeated fractional recrystallization until the CD spectra remained unchanged in a mixture of acetone and petroleum ether (trans complex) or of AN and diethyl ether (cis complex).

Identification of Geometrical Isomers: Elemental analysis of carbon, hydrogen, and nitrogen of all the new complexes agreed with the calculated values as shown in Table 1. It was claimed that the *trans*(*N*, olefin) complexes are pale-yellow and *cis*(*N*, olefin) complexes are colorless.[4] The present new complexes seem to obey this empirical rule, when the geometrical isomerism of the prepared complexes is assigned on the basis of the route of synthesis (for the formation of the cis complexes *vide infra*). The pale-yellow and colorless [PtCl(L-pro)(*trans*-2-butene)] gave IR absorption at 350 and 340 cm^{-1}, respectively, which can be assigned to Pt-Cl stretching vibration. This correspondence is also in accord with the empirical rule.[4] The trans complexes are soluble in acetone, AN, and DMF, whereas the cis complexes are very sparingly soluble in acetone and AN and soluble in DMF. Thus the geometrical

TABLE 1. ANALYTICAL DATA OF THE NEW COMPLEXES, *trans*(*N*, olefin) [PtCl(L-am)(olefin)]

L-am	Olefin	C/%		H/%		N/%	
		Calcd	Found	Calcd	Found	Calcd	Found
L-ala	*trans*-2-Butene	22.43	22.51	3.77	3.72	3.74	3.71
L-val	Ethylene	22.43	22.46	3.77	3.83	3.74	3.76
	trans-2-Butene	26.84	26.74	4.50	4.48	3.48	3.51
N-Me-L-pro	Ethylene	24.84	24.81	3.65	3.65	3.62	3.59
	trans-2-Butene	28.95	28.84	4.37	4.48	3.38	3.35
N-Bz-L-pro	Ethylene	36.33	36.30	3.93	3.91	3.03	2.85
	trans-2-Butene	39.15	39.17	4.52	4.50	2.85	2.63
L-pro *cis*(*N*, olefin)	Ethylene	22.56	22.41	3.25	3.25	3.76	3.82
	trans-2-Butene	26.97	26.74	4.02	3.97	3.50	3.39

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isomers can be distinguished by the color of crystals, synthetic route, IR absorption, and solubility.

Kinetic Runs. The decrease in CD strength of the complexes with time was recorded in acetone by the following method. The complexes were dissolved in acetone to give *ca.* 10^{-3} mol dm^{-3} solution, cooled and mixed with cold *trans*-2-butene in acetone (10^{-2} to 1 mol dm^{-3}). The solution was placed in a cell box of a spectrometer, which had been cooled to 8.0±0.3 °C, and the decrease in CD strength at the CD peak (360—385 nm) was continuously recorded. The rate of decrease obeyed the first order kinetic law and the observed rate constant k_{obsd} is expressed by Eq. 1.

$$k_{obsd} = -\ln[(\alpha_t-\alpha_\infty)/(\alpha_0-\alpha_\infty)]/t \quad (1)$$

Where α's are the CD strength at the time denoted by the suffices. The concentrations of the complex and free olefin at 8.0 °C were calculated by taking the density of acetone into consideration.

Measurements. The CD spectra were recorded with a JASCO Model ORD/UV-5 Spectrometer with CD attachment. Visible and UV spectra and IR spectra were recorded with a Hitachi 323 and a JASCO DS-403 G, respectively, A Komatsu-Yamato Coolnics thermostat was used for keeping the temperature at 8.0 °C.

Results and Discussion

Preparation of cis(N,*olefin*)[*PtCl*(L-*pro*)(trans-*2-butene*)]. *cis*(*N*, olefin)-complexes of platinum(II) containing prochiral olefin have been known only for the type [$PtCl_2$(*S*- or *R*-α-methylbenzylamine)(*S,S*- or *R,R*-*trans*-2-butene)].[6] We have succeeded in preparing *cis*(*N*, olefin)[PtCl(L-pro)(*trans*-2-butene)] by the substitution of *trans*-2-butene for the ethylene in *cis*(*N*,olefin)[PtCl(L-pro)(C_2H_4)] in AN. Several *cis*(*N*,olefin)[PtCl(am)-(C_2H_4)] had been prepared by the reaction of amino carboxylate with $[PtCl_4]^{2-}$ followed by the action of concentrated hydrochloric acid and ethylene in aqueous solution. However, the corresponding L-prolinate complex was not obtained by this method.[4]

We have found that tin(II) chloride was a useful catalyst for the synthesis of *cis*(*N*,olefin)[PtCl(L-pro)-(C_2H_4)]. Belluco *et al.* studied the mechanism of the catalytic action of tin(II) chloride in the substitution of aquo-soluble olefins for the chloride in $[PtCl_4]^{2-}$ in hydrochloric acid.[7] They considered the formation of some reactive intermediates containing $SnCl_3^-$ ligand. In the present synthesis, $[PtCl_3$(L-proH)$]^-$ (L-proH is coordinated as a unidentate on nitrogen) may have been formed from $[PtCl_2$(L-pro)$]^-$,[5] and reacted with tin(II) chloride in deoxygenated concentrated hydrochloric acid solution, to give *cis*-$[PtCl_2$(L-proH)(C_2H_4)$]^-$ *via* similar intermediates containing $SnCl_3^-$. This *cis* complex must be in equilibrium with *cis*(*N*,olefin)-[PtCl(L-pro)(C_2H_4)] in aqueous solution and the less soluble latter complex was precipitated as colorless crystals. The corresponding L-alaninato complex *cis*(*N*, olefin)[PtCl(L-ala)(C_2H_4)] was not obtained by this method, presumably because of its solubility in aqueous solution.

UV Absorption and CD Spectra. Spectral data of UV absorption of all the trans complexes give d-d transition absorption around 25000 cm^{-1}, whereas the cis complexes at *ca.* 28000 cm^{-1} (Table 2). The CD maxima of all the trans complexes in this region are 26.0—27.0×10^3 cm^{-1}, and that of the cis complex is at 27.8×10^3 cm^{-1}. The diastereoisomers with plus CD in this region are assigned to *S,S*- and those with minus CD to *R,R*-configuration of coordinated *trans*-2-butene, in accordance with Scott and Wrixon's empirical rule.[8]

Table 2. The UV absorption spectral data of *trans*- and *cis*(*N*, olefin) [PtCl(L-am)(olefin)] in ethanol

	Olefin	Absorption maxima/10^3 cm^{-1} (logε)		
trans-Complex	C_2H_4	*ca.* 25* (1.6—1.8)	*ca.* 33.5 (≈3)	37—38 (3.2—3.3)
	trans-2-Butene	*ca.* 25* (1.5)	35—36* (≈3)	*ca.* 39* (3.1—3.3)
cis-Complex	C_2H_4	*ca.* 28* (1.5)	*ca.* 35* (2.9)	*ca.* 38 (3.3)
	trans-2-Butene	*ca.* 28* (1.5)	*ca.* 33.5* (2.4)	*ca.* 39* (3.3)

* shoulder

Table 3. The Δε values of CD maxima in d-d region of the completely resolved *trans* (*N*, olefin)[PtCl(L-am)(*S,S*- or *R,R*-*trans*-2-butene)] and that of the corresponding ethylene complexes in ethanol

L-am	ν (CD max) 10^{3}cm^{-1}	Δε(C_4H_8) (a,c)	Δε(C_2H_4) (b,c)	δΔε[d]	C_4H_8[e]
L-ala	27.0	+1.13	0	+1.13	*S,S*
L-val	26.7	−1.0	0	−1.0	*R,R*
L-pro	27.0	+1.05	−0.05	+1.10	*S,S*
N-Me-L-pro	26.3	−1.06	+0.02	−1.08	*R,R*
N-Bz-L-pro	26.0	+1.00	−0.19	+1.19	*S,S*
L-pro[f]	27.8	+1.14	+0.12	+1.02	*S,S*

a) Δε value of the *trans*-2-butene complex b) Δε value of the ethylene complex, c) at the CD maxima of the *trans*-2-butene complexes at *ca.* 27000 cm^{-1}, d) Δε (*trans*-2-butene complex)-Δε(C_2H_4 complex), e) absolute configuration of coordinated *trans*-2-butene, f) *cis* (*N*, olefin)[PtCl(L-pro)(olefin)].

Table 3 gives the CD strength of all the completely resolved complexes at the peak of the *trans*-2-butene complexes in the d-d transition band region. These complexes are the diastereoisomers first crystallized on fractional crystallization. It also shows the difference in CD strength between the *trans*-2-butene- and the ethylene complexes at the wave length mentioned above. The δΔε is almost equal for all the complexes, suggesting that the contribution of asymmetrically coordinated *trans*-2-butene to the CD strength is not affected by the variety of the coordinated amino carboxylates.

Kinetics of the Inversion of trans-*2-Butene.* When *trans*-2-butene was added to the *trans*- and *cis*(*N*,olefin)-[PtCl(L-am)(*S,S*- or *R,R*-*trans*-2-butene)] complexes in acetone at 8.0 °C, the UV absorption remained unchanged for at least two days, whereas the CD strength at the peak in 360—385 nm region decreased obeying Eq. 1. This reaction should be the substitution with inversion of *trans*-2-butene ligand, *i.e.* the epimerization of the complex on the substitution.

The k_{obs} increased linearly with increase in free *trans*-2-butene concentration to give Eq. 2.

$$k_{obsd} = k_2[\textit{trans}\text{-2-butene}] \quad (2)$$

The k_2 is related to the rate constant of the inversion reaction, k_2^{inv}, by the relation $k_2=2k_2^{inv}$. However, the k_2 values are used in the following discussion. By use of *cis*-2-butene in place of *trans*-2-butene as nucleophile the same relation holds. Absence of intercept on the k_{obsd} *vs.* free ligand concentration diagram indicates no participation of the solvent molecule in the rate determining process.

trans(N,*olefin*) *Complexes*: The second order rate constant decreases in the following sequence as the amino carboxylate was changed. (Table 4).

Table 4. Rate constants of the epimerization reaction of *trans*(*N*, olefin)[PtCl(L-am)(*S,S*- or *R,R-trans*-2-butene)] in acetone at 8.0 °C

L-am	Config.[a]	Added olefin	$k_2/10^{-3}$ s^{-1} mol^{-1} dm^3
L-ala	*S,S*	*trans*-2-Butene	30 ± 3
L-val	*R,R*	*trans*-2-Butene	39 ± 4
L-pro	*S,S*	*trans*-2-Butene	9.7 ± 0.6[b,c]
L-pro	*R,R*	*trans*-2-Butene	7.6 ± 0.3
L-pro	*S,S*	*cis*-2-Butene	350 ±13[b,d]
N-Me-L-pro	*R,R*	*trans*-2-Butene	0.54± 0.01
N-Me-L-pro	*R,R*	*cis*-2-Butene	26 ± 5[d]
N-Bz-L-pro	*R,R*	*trans*-2-Butene	<0.01
L-pro[e]	*S,S*	*trans*-2-Butene	<0.3

a) Configuration of coordinated *trans*-2-butene. b) Ref. 1. c) The datum was obtained by the different method (see Ref. 1). d) The rate is not epimerization, but substitution rate. e) *cis*(*N*, olefin)[PtCl(L-pro)(*S,S-trans*-2-butene)].

$$\text{L-val, L-ala} > \text{L-pro} > \textit{N}\text{-Me-L-pro} > \textit{N}\text{-Bz-L-pro} \quad (3)$$

No appreciable difference is seen between the rate for the L-alaninato and L-valinato complex, indicating little influence of the substituents on the asymmetric carbon atoms. Hence, the discussion is to be made among complexes containing various substituents on the coordinated nitrogen atom.

The difference among k_2 values can be interpreted either by the electronic or the steric effect brought about by the amino carboxylates. The most important electronic effect affecting the rate of substitution reaction around square planar complexes is the trans effect. Various factors can give influence upon this effect, but the basicity of the nitrogen atom should be looked upon as predominating in the present complexes. L-Proline has larger pK_a (10.64 at 25 °C) than L-alanine and L-valine (9.64 and 9.72, respectively), and the L-prolinato complex gives much smaller k_2 than the L-alaninato- and L-valinato complexes do. On the other hand, *N*-methyl-L-proline can be expected to be more basic than *N*-benzyl-L-proline (because pK_a of methylamine and benzylamine are 10.68 and *ca.* 9.6, respectively at 25 °C), but the k_2 value of *N*-methyl-L-prolinato complex is larger than that of *N*-benzyl-L-prolinato complex. Thus no regular relationship is observed between the basicity of the amino nitrogen and the second order rate constant, suggesting that the electronic effect is not very important in determining the ease of inversion of *trans*-2-butene.

Parametrization of steric effect is far more difficult. We will use the overall bulkiness of ligands around the platinum(II) ion as influencing the ease of formation of the transition state with coordination number 5 containing two moles of *trans*-2-butene. The k_2 values do not differ much by use of a pair of diastereomers containing *R,R*- and *S,S-trans*-2-butene. Thus, our tentative representation of the overall bulkiness by molecular model studies would not be very inappropriate. Studies with molecular models indicate that the bulkiness of the coordinated amino carboxylate around the platinum(II) ion increases in the sequence of Fig. 1. This sequence is equal to the sequence (3). Thus, presence of bulky substituents on the nitrogen atom may hinder the formation of the transition state with coordination number 5, to result in slower substitution of the olefin.

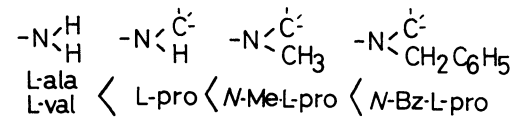

Fig. 1. Sequence of the bulkiness of the coordinated amino nitrogen.

Moreover, Table 4 includes the rate of substitution of *cis*-2-butene for the coordinated *trans*-2-butene. *cis*-2-Butene is not prochiral and its substitution always brings about decrease in CD strength,[1] so that the rate indicates the ease of substitution. When the L-prolinato and the *N*-methyl-L-prolinato complexes are compared, the ratio of their k_2 values is almost equal for both the substitution of *cis*-2-butene and the inversion of *trans*-2-butene. This fact suggests that the bulkiness of the coordinated amino carboxylate affects the rate of the substitution of *cis*-2-butene in a similar manner.

cis(N,*olefin*) *Complex*: Studies with molecular models suggest no significant difference in overall bulkiness around the platinum(II) ion between the *cis*(*N*,olefin)- and the *trans*(*N*,olefin)-L-prolinato complexes. On the other hand, a significant difference in electronic effect is expected, since the pK_a value of the carboxylate oxygen (1.99 at 25 °C) is far smaller than that of the nitrogen (*loc. cit.*). Such a difference is reflected in the frequency of Pt–Cl streching vibration; *i.e.* the *cis*(*N*,-olefin) complex with nitrogen trans to chloride gives an IR absorption peak at 340 cm^{-1}, whereas *trans*(*N*,olefin) with the oxygen trans to chloride at 350 cm^{-1}. Thus a basic ligand at the trans position seems to make the Pt–Cl bond loose. The nature of metal–ligand bond between Pt(II) and η^2-olefin should be significantly different from that between Pt(II) and chloride. However, the ease of exchange of olefins in [PtCl(L-am)(olefin)] seems to be mainly governed by the strength of σ-bond between Pt(II) and olefin.[2] *trans*-2 Butene–Pt(II) bond can be made loose by the trans influence of basic nitrogen in the *trans*(*N*,olefin) complex, so that the k_2 value becomes greater than that of the *cis*(*N*,olefin) complex.

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