Asymmetric Induction on the Reaction of Prochiral Olefins with Chloro-L-aminocarboxylato-η^2-ethyleneplatinum(II)

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(Received May 17, 1978)

Addition of a large excess of *trans*-2-butene (tbn) or 2-methyl-2-butene (mbn) to an acetone solution of *cis*- or *trans*(*N*, ethylene)[PtCl(L-am)(C_2H_4)] (L-am, 9 kinds of L-aminocarboxylate) gave first increase and then gradual decrease in CD strength in the region $\simeq$26500 cm^{-1}. The kinetic optical yield amounted to 53% whereas that at the equilibrated state was much less (up to 27% for *cis*(*N*, olefin) complexes and 6 to 12% for trans complexes). *trans*-2-Butene gives larger yields than mbn. Kinetic analysis of the growth and decay curve of the CD strength disclosed that the first fast increase in CD reflects the greater rate of substitution of the prochiral olefins for ethylene in *S*-configuration than that in *R*-configuration. The second step seems to involve the exchange of coordinated tbn or mbn catalyzed by ethylene which was made free in the first step. The mechanism of asymmetric induction has been discussed from both steric and electronic viewpoints. Asymmetry of the coordinated nitrogen seems to give a dominating effect.

Corradini, Paiaro, and Pununzi observed asymmertic coordination of *trans*-2-butene (tbn) on the reaction between *cis*[$PtCl_2$((*S*)- or (*R*)-α-methylbenzylamine)(tbn)] and free tbn, and claimed that the selectivity is thermodynamically controlled.[1] We found that the replacement of coordinated *S,S*- or *R,R*-tbn in *trans*(*N*, olefin) [PtCl(L-pro)(*S,S*- or *R,R*-tbn[^3H])] (L-pro, L-prolinate) by free tbn in acetone takes place more easily with retention than with inversion of configuration. The stereoselectivity is considered to be caused by the steric interaction between the incoming tbn and the coordinated tbn and/or L-prolinate.[2] In order to clarify the source of such a stereoselective olefin exchange, we investigated the exchange of tbn between [$PtCl_3$(*S,S*-tbn[^3H])]$^-$ and free tbn, and found that the main source of asymmetric induction is in the interaction between the coordinated and the free tbn in the square pyramidal transition state.[3] However, this complex anion gives smaller ratio of rates of olefin exchange with retention and with inversion of the configuration than *trans*(*N*, olefin) [PtCl(L-am)(*S,S*-tbn)]. This suggests the significant role of L-aminocarboxylate ligand in the stereoselective substitution. This paper deals with the kinetics of substitution reaction of tbn and 2-methyl-2-butene(mbn) for the ethylene in *trans*- and *cis*(*N*, olefin) [PtCl(L-am)(C_2H_4)] and the accompanying thermodynamic and kinetic stereoselectivity, which is dependent on the geometrical isomerism of the complex and the variety of L-aminocarboxylates.

Experimental

Materials. All the complexes [PtCl(L-am)(ethylene)] were prepared according to previously reported methods.[4,5] The following ligands were employed; *trans*(*N*, olefin) complexes: L-am's are L-prolinate (L-pro), 4-hydroxy-L-prolinate (L-hyp), allo-4-hydroxy-L-prolinate (L-ahyp), *N*-methyl-L-prolinate (*N*-me-L-pro), *N*-methyl-4-hydroxy-L-prolinate (*N*-me-L-hyp), *N*-ethyl-L-prolinate (*N*-et-L-pro), *N*-benzyl-L-prolinate (*N*-bz-L-pro), *N*-benzyl-L-valinate (*N*-bz-L-val), L-valinate (L-val) and L-alaninate (L-ala); *cis*(*N*, olefin) complex; L-am is L-pro.

allo-4-Hydroxy-L-proline was prepared from 4-hydroxy-L-proline.[6,7] The *N*-substituted L-aminocarboxylic acids, *N*-me-L-proH, *N*-me-L-hypH, *N*-et-L-proH, *N*-bz-L-proH and *N*-bz-L-valH were synthesized by the reported methods.[8,9] The new *trans*(*N*, ethylene) complexes and their tbn and mbn derivatives containing L-ahyp, *N*-me-L-hyp, *N*-et-L-pro, *N*-bz-L-val were identified by elemental analysis of C, H, and N, and ultraviolet (UV) absorption spectra in acetonitrile (AN).

Results and Kinetic Analysis

Overall Progress of the Substitution Reaction between the Ethylene Complex and tbn. The change in CD pattern of *trans*(*N*, olefin) [PtCl(*N*-me-L-pro)(C_2H_4)] in the presence of a large excess of tbn is shown in Fig. 1. The change in CD strength at 26300 cm^{-1} is plotted against time in Fig. 2. The CD strength increases at the initial stage of the reaction to reach a maximum ($\Delta\varepsilon_{max}$) (first step). The UV absorption spectrum

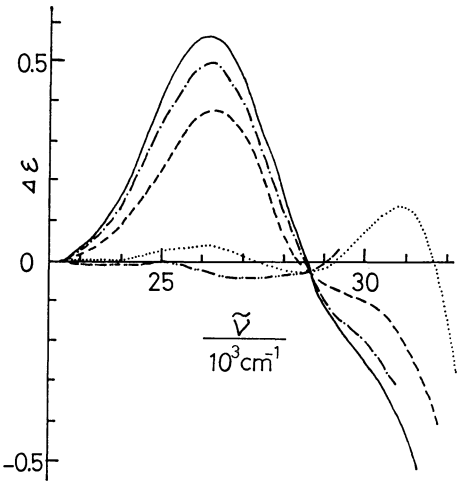

Fig. 1. Change of the CD spectrum with time on the reaction of *trans*(*N*,ethylene)[PtCl(*N*-me-L-pro)(C_2H_4)] (0.00154 mol dm^{-3}) with *trans*-2-butene (0.279 mol dm^{-3}) in acetone at −28.0 °C; dotted line: the original ethylene complex, broken line: 1 min, broken line with a dot: 2 min, solid line: 4 min, broken line with double dotts: infinite time.

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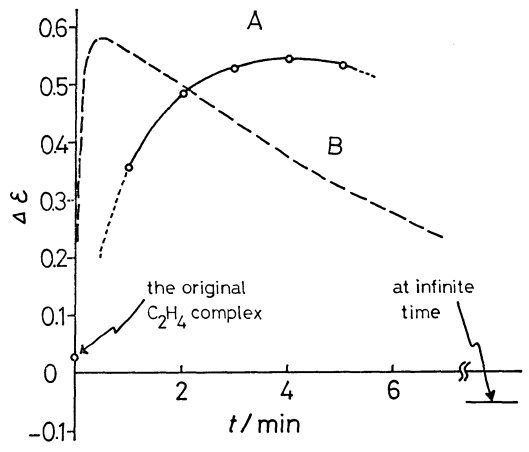

Fig. 2. Change in the CD strength with time on the reaction of *trans*(*N*,ethylene)[PtCl(*N*-me-L-pro)(C_2H_4)] with *trans*-2-butene in acetone.
A: Open circles correspond to the CD strength at the peak (26300 cm^{-1}) of the curves in Fig. 1.
B: The broken line represents the CD strength at 26300 cm^{-1} recorded continuously by the method reported in Ref. 4. ([complex]=0.00164 mol dm^{-3}, [*trans*-2-butene]=0.268 mol dm^{-3}, at 8.0 °C).

in the 32000—45000 cm^{-1} region of the original ethylene complex slightly changes simultaneously and approaches that of the tbn complex. This step should involve a stereoselective formation of the *S,S*-tbn complex by the substitution of tbn for the coordinated ethylene shown by

$$[PtCl(L\text{-am})(C_2H_4)] + tbn \rightarrow [PtCl(L\text{-am})(tbn)] + C_2H_4. \quad (1)$$

By the end of the first step, almost all the ethylene should have been replaced by tbn (*vide infra*). In the second step, the CD strength at 26300 cm^{-1} gradually decreases, while the UV absorption spectrum remains unchanged. The first step proceeds faster than the second step, and their kinetics can be studied separately. All the other ethylene complexes gave similar changes in CD and UV spectra except that for L-ala and L-val complexes, which gave change in the UV pattern but not in CD strength.

The apparent optical yields in the first step (p_{max}) were calculated by[10]

$$p_{max} = (\Delta\varepsilon_{max} - \Delta\varepsilon_{vic})/(\Delta\varepsilon_{resolv} - \Delta\varepsilon_{vic}), \quad (2)$$

where $\Delta\varepsilon_{resolv}$ is the CD peak strength in the region 26000—27000 cm^{-1} of the resolved tbn complex, and $\Delta\varepsilon_{vic}$ the CD strength due to the vicinal effect of L-aminocarboxylate (L-am), which is represented by the CD strength of the ethylene complex at the same wave number. The p_{max} values for a variety of L-aminocarboxylate complexes are shown in Table 1.

The second step gives no change in UV absorption spectrum, and hence is considered to be the replacement of asymmetrically coordinated tbn by free tbn toward a thermodynamically equilibrated state:

$$[PtCl(L\text{-am})(S,S\text{-tbn})] + tbn \rightarrow [PtCl(L\text{-am})(R,R\text{-tbn})] + tbn. \quad (3)$$

The optical yields at the equilibrium were calculated by

$$p_{eq} = (\Delta\varepsilon_{eq} - \Delta\varepsilon_{vic})/(\Delta\varepsilon_{resolv} - \Delta\varepsilon_{vic}), \quad (4)$$

where $\Delta\varepsilon_{eq}$ is the CD strength in the equilibrated state. The p_{eq} values are given in Table 1.

When mbn was used in place of tbn, similar changes in UV and CD spectra were observed. Equations 2[9] and 4 are applicable to the mbn complexes, the optical yields being given in Table 1.

Kinetic Analysis of the First Step. The increase in the CD strength ($\Delta\varepsilon_t$) at $\tilde{\nu}_{max}$ (Table 1) in the first step obeyed the following first order kinetic formula 5 for all the complexes,

$$k_{obsd,i} = -\ln[(\Delta\varepsilon_t - \Delta\varepsilon_{max})/(\Delta\varepsilon_1 - \Delta\varepsilon_{max})]/t, \quad (5)$$

where $\Delta\varepsilon_1$ is the initial CD strength in this step. $k_{obsd,i}$ increases linearly with increase in free tbn concentration to give

$$Rate_i = k_{obsd,i}[complex] = k_{2,i}[tbn][complex]. \quad (6)$$

The $k_{2,i}$ values are given in Table 2. The Reaction (1) should consist of two reactions,

$$[PtCl(L\text{-am})(C_2H_4)] + tbn \xrightarrow[k_{2[ES]}]{} [PtCl(L\text{-am})(S,S\text{-tbn})] + C_2H_4$$
$$\xrightarrow[k_{2[ER]}]{} [PtCl(L\text{-am})(R,R\text{-tbn})] + C_2H_4. \quad (7)$$

The relation between $k_{2[ES]}$, $k_{2[ER]}$, the optical yield p_{max} and $k_{2,i}$ is given by

$$(1+p_{max})/(1-p_{max}) = k_{2[ES]}/k_{2[ES]}, \quad (8)$$

$$k_{2,i} = k_{2[ES]} - k_{[ER]}. \quad (9)$$

The formation rate constants of the *S,S*- and *R,R*-tbn complexes from the ethylene complex, $k_{2[ER]}$ and $k_{2[ER]}$, can be calculated by Eqs. 8 and 9. (Table 2).

Kinetic Analysis of the Second Step. The rate of decrease in the CD strength ($\Delta\varepsilon_t$) at time t is expressed by the first order kinetic formula

$$k_{obsd,d} = -\ln[(\Delta\varepsilon_t - \Delta\varepsilon_{eq})/(\Delta\varepsilon_2 - \Delta\varepsilon_{eq})]/t, \quad (10)$$

where $\Delta\varepsilon_2$ denotes the initial CD strength in this step. The $k_{obsd,d}$ is independent of the concentration of free tbn, but dependent on that of the complex:

$$k_{obsd,d} = k_{2,d}[complex]. \quad (11)$$

Since $k_{obsd,d}$ was obtained by the first order kinetic treatment with respect to the complex concentration, the rate of decrease in the CD strength is apparently proportional to the square of platinum(II) complex concentration:

$$Rate_d = k_{2,d}[complex]^2. \quad (12)$$

Such a kinetic formula is unusual for the substitution of a square planar complex, but can be accounted for by considering the catalytic action of ethylene liberated by Eq. 1 (*vide infra*). The concentration of free ethylene in the presence of a large excess of tbn should be equal to that of the initial complex, so that Eq. 12 can be rewritten as

$$Rate_d = k_{2,d}[complex][C_2H_4]. \quad (13)$$

In order to verify this, addition of a known amount of ethylene is desirable, but not practicable. Alternatively various amounts of *trans*(*N*, olefin) [PtCl(L-ala)-

TABLE 1. KINETIC AND THERMODYNANIC OPTICAL YIELDS OF *trans*(*N*, olefin)[PtCl(L-am)(olefin)] ON THE REACTION OF THE CORRESPONDING ETHYLENE COMPLEX WITH OLEFINS, ALONG WITH CIRCULAR DICHROISM DATA FOR THE COMPLEXES

L-am	$\tilde{\nu}_{max}$ / 10^{-3} cm^{-1}	$\Delta\varepsilon_{resolv}$ [a]	$\Delta\varepsilon_{vic}$ [b]	Condition [c]	$\Delta\varepsilon_{max}$	p_{max} [d] / %	$\Delta\varepsilon_{eq}$	p_{eq} [e] / %
				with *trans*-2-butene				
L-pro	27.0[g]	1.05	−0.04		0.34	35	0.09	12(*S*,*S*)
				−27.5	0.32	34		
N-me-L-pro	26.3[g]	−1.06[h]	0.03		0.59	53	−0.05	−6(*R*,*R*)
				−28.0	0.55	49		
N-et-L-pro	26.3	1.0	0		0.52	*ca.* 50	0	0
N-bz-L-pro	26.0[g]	1.00	−0.19		0.10	24	−0.20	*ca.* −1(*R*,*R*)
				DCM	0.14	28		
				15.0	0.13	27	−0.16	3(*S*,*S*)
N-bz-L-val	26.3	1.00	−0.16		0.30	40	−0.28	−10(*R*,*R*)
					0.30	40[i]		
				AN	0.29	39	−0.27	−9(*R*,*R*)
				MA	0.25	35		
L-val	26.7[g]	−1.06[h]	−0.06	−30.0	k)	0		
L-ala	27.0[g]	1.09	−0.04	−30.0	k)	0		
L-hyp	27.0	1.04	−0.01		0.38	37	0.07	8(*S*,*S*)
N-me-L-hyp	26.3	−1.06[h]	0.02		0.34	32	−0.07	−7(*R*,*R*)
L-ahyp	27.0	1.09	0.04		0.43	37	0.10	6(*S*,*S*)
L-pro[f]	27.8[g]	1.14	0.12		0.46	33		
				AN	0.52	39		
				−13.0	0.47	34	−0.16	−27(*R*,*R*)
				with 2-methyl-2-butene				
L-pro	26.3	0.67	−0.04		0.008	7	0.004	6(*S*)
L-hyp	26.3	0.67	−0.03		0.01	6	(0.002)[j]	(3)[j](*S*)
L-ahyp	26.3	0.70	0.00		0.14	19	0.05	7(*S*)
N-me-L-pro	25.6	0.74	0.04		0.09	7	0.03	*ca.* −1(*R*)
N-me-L-hyp	25.6	0.67	−0.03		−0.01	3	−0.03	0

a) $\Delta\varepsilon$ values for the resolved olefin complexes at $\tilde{\nu}_{max}$ in acetone. b) $\Delta\varepsilon$ values for the ethylene complexes at $\tilde{\nu}_{max}$ in acetone. c) In acetone at 8.0 °C unless otherwise stated; DCM: in dichloromethane, AN: in acetonitrile, MA: in L-menthylacetate; figures denote temperature in °C. d) From Eq. 2, always formation of (*S*,*S*)-*trans*-2-butene and (*S*)-2-methyl-2-butene complexes is preferred. e) From Eq. 4, *S* and *R* in parentheses indicate the configuration of olefin in the preferred diastereomer at the equilibrium. f) *cis*(*N*, olefin) isomers. g) Ref. 4. h) For the *R*,*R*-isomers; the other for the (*S*,*S*)-*trans*-2-butene or (*S*)-2-methyl-2-butene isomers. i) In the presence of *trans*-(*N*, ethylene) [PtCl(L-ala)(C_2H_4)] (see the text). j) Very sparingly soluble in acetone, and only an appoximate value is given. k) Not observed.

(C_2H_4)] were added to mixtures of *trans*(*N*, olefin)-[PtCl(*N*-bz-L-val)(C_2H_4)] and tbn in acetone at 8.0 °C, and the changes in the CD strength at 26300 cm^{-1} with time were measured. The rate of decrease in the CD strength in the second step is represented by

$$Rate_d = k_{2,d}[N\text{-bz-L-val complex}]([N\text{-bz-L-val complex}] + [\text{L-ala complex}]). \quad (14)$$

The L-ala complex undergoes rapid replacement of ethylene by free tbn without stereoselectivity (*cf.* Table 2). Thus the substrate complex for giving the CD change should be the *N*-bz-L-val complex alone. Under the given experimental conditions, practically all the ethylene should have been liberated from both the complexes during the first step of the reaction, and should be present as free ethylene in the reaction mixture. Thus, the term in parentheses in Eq. 14 is represented by the ethylene concentration [C_2H_4], so that Eq. 13 holds for this system. The $k_{2,d}$ values obtained from Eqs. 12 and 14 are 1.09 and 1.15 s^{-1}-mol^{-1} dm^3, respectively, for the *N*-bz-L-val complex at 8 °C, indicating the legitimacy of such a kinetic treatment.

The $k_{2,d}$ values can be compared to the k_2 values for the pure epimerization of *trans*(*N*, olefin) [PtCl-(L-am) (*S*,*S*-tbn)] in the presence of tbn under similar conditions.[4] The larger values for $k_{2,d}$ than for k_2 may be interpreted by considering the catalytic action of ethylene as in the following.

Catalytic Action of Ethylene in the Second Step. Less bulky olefins give larger values of k_2 on the substitution for tbn in *trans*(*N*, olefin) [PtCl(L-pro)(tbn)].[2] Hence, ethylene should be a more effective nucleophile than tbn towards [PtCl(L-am)(*S*,*S*- or *R*,*R*-tbn)], and the contribution of direct substitution of tbn can be ignored. Individual second order rate constants for the ethylene-

TABLE 2. INDIVIDUAL SECOND ORDER RATE CONSTANTS OF THE REACTION OF *trans*(*N*,ethylene)-[PtCl(L-am)(C_2H_4)] WITH *trans*-2-BUTENE[a]

L-am	Condition[b]	$k_{2,i}$[c]	$\frac{p_{max}}{\%}$	$k_{2[ES]}$[c]	$k_{2[ER]}$[c]	$k_{2,d}$[d]	$\frac{p_{eq}}{\%}$	$k_{2[SE]}$[d]	$k_{2[RE]}$[d]
L-pro		fast	35			6.1	12	8.3	5.1
	−27.5	(450)[g]	34	(890)	(440)				
N-me-L-pro		fast	53			1.1	−6	2.5	0.68
	−28.0	(75)[g]	49	(114)	(39)				
N-et-L-pro		10	50	15	5	slow	0		
N-bz-L-pro		8.2	24	21.2	13.0	slow	*ca.* −1		
	DCM	8.0	28	18.3	10.3	slow			
	15.0	15.3	27	36.0	20.7	0.018	<3	0.024	0.015
N-bz-L-val		fast	40			1.09	−10	2.0	0.70
		fast	40			1.15		(2.1)	(0.74)
	AN	fast	39			1.18	−9	2.1	0.77
	MA	fast	35			1.0		(1.9)	(0.66)
L-val	−30.0	not obsd	0				0		
L-ala	−30.0	not obsd	0				0		
L-hyp		fast	37			10.8	8	15.8	8.5
N-me-L-hyp		fast	32			2.4	−7	3.8	1.7
L-ahyp		fast	37			3.8	6	5.7	3.0
L-pro[e]		(20)[h]	33	(40)	(20)				
	AN	(50)[h]	39	(90)	(40)				
	−13.0	(2)[g,h]	34	(4)	(2)		−27		
L-pro[f]		fast	7			2.77	6	2.80	2.75

a) The error in k_2 values is ±5 on the last figures of individual data on 70% confidence level unless otherwise stated. b) *Cf.* footnote c in Table 1. c) In 10^{-3} s^{-1} mol^{-1} dm^3. d) In s^{-1} mol^{-1} dm^3. e) Reaction of *cis*(*N*,ethylene) isomer. f) Reactions with 2-methyl-2-butene. g) Only from one datum. h) *Cf.* footnote, j in Table 1.

catalyzed epimerization

$$[PtCl(L\text{-am})(S,S\text{-tbn})] + C_2H_4 \underset{k_{2[ES]}}{\overset{k_{2[SE]}}{\rightleftharpoons}} [PtCl[(L\text{-am})(C_2H_4)] + \text{tbn}, \quad (15)$$

$$[PtCl(L\text{-am})(R,R\text{-tbn})] + C_2H_4 \underset{k_{2[ER]}}{\overset{k_{2[RE]}}{\rightleftharpoons}} [PtCl[(L\text{-am})(C_2H_4)] + \text{tbn}, \quad (15)$$

are written as follows:

$$d[S]/dt = k_{2[ES]}[E][tbn] - k_{2[SE]}[S][C_2H_4], \quad (16)$$

$$d[E]/dt = k_{2[SE]}[S][C_2H_4] - (k_{2[ES]}+k_{2[ER]})[E][tbn] + k_{2[RE]}[R][C_2H_4], \quad (17)$$

$$d[R]/dt = k_{2[ER]}[E][tbn] - k_{2[RE]}[R][C_2H_4], \quad (18)$$

$$[C] = [S] + [E] + [R], \quad (19)$$

where [E], [S], and [R] represent the concentrations of the ethylene, *S*,*S*-tbn and *R*,*R*-tbn complexes containing a given L-am, respectively; [C] is their total. Under the present experimental conditions where the free tbn overwhelms the initial ethylene complex and the first step has reached completion, the ethylene complex should be present only as an intermediate in Eq. 15, and a steady state treatment can be applied to Eq. 17, *i.e.* $d[E]/dt=0$. Hence the rate of decrease of [S] can be written by

$$-d[S]/dt = (k_{2[SE]}k_{2[ER]}[S] - k_{2[RE]}k_{2[ES]}[R]) \times [C_2H_4]/(k_{2[ES]}+k_{2[ER]}). \quad (20)$$

Integrating, we get

$$-\ln\left\{\frac{[S]-(k_{2[RE]}k_{2[ES]}[R]/k_{2[SE]}k_{2[ER]})}{[S]+[R]}\right\}\Big/t = (k_{2[SE]}k_{2[ER]} + k_{2[RE]}k_{2[ES]})[C_2H_4]/(k_{2[ES]}+k_{2[ER]}) \quad (21)$$

In the equilibrated state, the left side of Eq. 20 should be zero, and we obtain

$$K_{RS} = [S]_\infty/[R]_\infty = k_{2[RE]}k_{2[ES]}/k_{2[SE]}k_{2[ER]}. \quad (22)$$

Expressing [S], [R], $[S]_\infty$, and $[R]_\infty$ in Eqs. 21 and 22 in terms of $\Delta\varepsilon_t$, $\Delta\varepsilon_2$, and $\Delta\varepsilon_\infty$, we have

$$-\ln\{(\Delta\varepsilon_t-\Delta\varepsilon_\infty)/(\Delta\varepsilon_2-\Delta\varepsilon_\infty)\}/t = (k_{2[SE]}k_{2[ER]}+k_{2[RE]}k_{2[ES]})[C_2H_4]/(k_{2[ES]}k_{2[ER]}). \quad (23)$$

This corresponds to the experimental kinetic formula Eq. 13, $k_{2,d}$ being written as

$$k_{2,d} = (k_{2[SE]}k_{2[ER]}+k_{2[RE]}k_{2[ES]})/(k_{2[ES]}/k_{2[ER]}). \quad (24)$$

From Eqs. 8, 16, 22, and 24, individual rate constants were calculated by use of the following equations:

$$k_{2[SE]} = (1-p_{eq})k_{2,d}/(1-p_{max}), \quad (25)$$

$$k_{2[RE]} = (1+p_{eq})k_{2,d}/(1+p_{max}). \quad (26)$$

The data for tbn and mbn complexes are given in Table 2.

Discussion

Stereoselectivity in the Equilibrium State. The p_{eq} value for the tbn complexes in the equilibrium state (end point of the second step) can be reckoned as to

reflect the difference of stability between the *S,S*- and the *R,R*-tbn complexes. The stability should be directly related to the structure of both isomers. Table 1 indicates that the *cis*(*N*, olefin) complex gives a rather large negative p_{eq}. Molecular models of the two optical isomers of *cis*(*N*, olefin) [PtCl(L-pro)(tbn)] suggest that the coordinated *S,S*-tbn is subject to a larger steric hindrance than *R,R*-tbn is, giving a large negative p_{eq} value (favorable for *R,R*-configuration).

trans(*N*, tbn)-Complexes with various L-aminocarboxylates containing asymmetric nitrogens give larger $|p_{eq}|$ values than those without asymmetric nitrogens. Molecular model studies cannot account for such a selectivity. An indirect influence coming from solvent molecules does not seem significant, since similar optical yields were observed for the *N*-bz-L-pro and *N*-bz-L-val complex in different solvents (Table 1). There can be an electronic effect from the asymmetric nitrogen to the coordinated tbn through platinum(II) d-orbitals. We studied the CD spectra of *trans*(*N*, olefin)[PtCl(L-am)(*S,S*-tbn)], and suggested an electronic perturbation from asymmetric nitrogen upon coordinated tbn.[11] However, the L-pro, L-hyp, and L-ahyp complexes give positive, and the *N*-me-L-pro, *N*-me-L-hyp and *N*-bz-L-val complexes negative signs. The reason for such a difference cannot be understood at the present stage.

A similar trend in p_{eq} values is observed for the mbn complexes, the signs being the same as those for the tbn complexes. However, the figures for the mbn complexes are smaller than those for the tbn complexes with given L-aminocarboxylates.

Asymmetric Induction on the Substitution of tbn. The *S,S*-tbn complexes are formed from the corresponding ethylene complexes more readily than the *R,R*-tbn complexes. The extent can be represented by the p_{max} values. The complexes containing asymmetric nitrogens give p_{max} values from 20 to 55%, while the L-ala and L-val complexes without asymmetric nitrogens fail to give appreciable optical yields. Thus the asymmetric induction should be governed by the symmetry of the coordinated amino nitrogen. The energy diagram for the forward process of Eq. 7 can be written as shown in Fig. 3. The $\delta\Delta G^*$ is expressed by

$$-\delta\Delta G^* = RT\ln[(1+p_{max})/(1-p_{max})] = RT\ln(k_{2[ES]}/k_{2[ER]}). \quad (29)$$

The sign of p_{max} is not always equal to that of p_{eq} for a given complex. The sequence of magnitude of p_{max}'s of the complexes containing various aminocarboxylates is neither parallel to that of p_{eq}'s. The difference between $k_{2[ES]}$ and $k_{2[ER]}$ for a given complex cannot be interpreted by the difference in stability between the *S,S*- and *R,R*-tbn complexes. The transition state on the substitution reaction should be considered.

Substitution reactions of square-planar complexes are understood to proceed *via* five coordinated transition states. The kinetic ease of formation of the *S,S*- and *R,R*-tbn complexes should reflect the stability of the transition state. Two possible structures are considered for the five coordinated transition state.[12] Whenever a trigonal bipyramidal structure is formed as intermediate or transition state, the ligand to be replaced is reckoned to be located at the basal position. In the present complex either amino nitrogen or carboxyl oxygen occupies the basal position depending on the trans or cis isomerism of the original complex, respectively. The mutual location between the incoming tbn, which always occupies one of the basal positions, and the asymmetric nitrogen, which should play the most important role in determining the selectivity, should differ depending on the geometrical isomerism. In the square pyramidal structure, on the other hand, the mutual locations between nucleophilic tbn and asymmetric nitrogen do not differ much for both geometrical isomers. From our experimental results, however, the p_{max} values are almost equal for the formation of *trans* and *cis*(*N*, olefin) [PtCl(L-pro)(*S,S*-tbn)], indicating that the transition state would be more appropriately apporoximated by the square pyramidal structure. This interpretation is in line with the suggestion made for the isotopic exchange between [$PtCl_3$(tbn[^3H])] and tbn.[3]

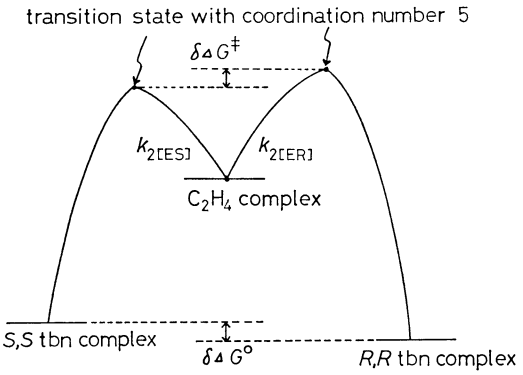

Fig. 3. Schematic diagram of the change in Gibbs free energy on the reaction of *trans*(*N*,ethylene)[PtCl(L-am)(C_2H_4)] with prochiral olefins.

Detailed structure of the transition state cannot be discussed at the present stage, but the side from which the incoming olefin approaches platinum(II) plane might be as follows. The substituent on the amino nitrogen in the complex extends to the opposite side of the square plane to that where the pyrrolidine ring of L-prolinate does. The p_{max} values depend on the variety of the *N*-substituent, but the location of hydroxyl group on the 4-position of the pyrrolidine ring (L-hyp and L-ahyp) affects neither the p_{max} nor the rate constant. Thus the incoming tbn will approach platinum(II) from the opposite side to that occupied by the pyrrolidine. The bulkiness of the substituent on amino nitrogen of the aminocarboxylate affects the p_{max} in different ways depending on the kind of aminocarboxylate; *e.g.* introduction of benzyl group on L-valinate increases whereas that on L-prolinate decreases the p_{max}. Studies with molecular models suggest that the approach of tbn to the platinum(II) bound to *N*-substituted aminocarboxylate would be easier in *S,S*-configuration than in *R,R*-configuration. More than one factor should affect the p_{max} and $k_{2,d}$ values.

Asymmetric Induction on the Reaction with mbn. The p_{max} values for the formation of *S*-mbn complexes are

smaller than those of tbn complexes (Table 1). The transition state for the reactions with mbn should be similar to those with tbn. Free mbn has two methyl groups on one side of C=C double bond axis, and one methyl group and methine hydrogen on the other side. When the former side is directed to the coordinated L-amino nitrogen in the transition state, no difference is expected in the steric interactions, regardless of the orientation of the methine hydrogen. Such an attack does not result in a stereoselective substitution. When the other side faces the asymmetric nitrogen, a stereoselective formation can be expected to give p_{max} values similar to those on the attack of tbn. Participation of these two different transition states should be responsible for the smaller values of p_{max} on the substitution of mbn than those on reaction with tbn.

Comparison of Overall Rate Constants and the Contribution by the Substituents of the Coordinated L-Aminocarboxylates. Table 2 indicates that the individual rate constants, $k_{2[ES]}$, $k_{2[ER]}$, $k_{2[SE]}$, and $k_{2[RE]}$ are largely dependent on the variety of L-aminocarboxylate. However, an overall trend is obvious; *i.e.* the second order rate constants decrease in the following sequence, which is equal to that for the exchange of tbn in *trans*(*N*, olefin) [PtCl(L-am)(*S*,*S*-tbn)].[4]

L-hyp>L-pro>L-ahyp>*N*-me-L-hyp>*N*-bz-L-val>

N-me-L-pro>*cis*(*N*, olefin) L-pro>*N*-bz-L-pro

Introduction of trans OH (L-hyp) on 4-position of pyrrolidine ring increases whereas that of cis OH(L-ahyp) decreases the k_2 values both for L-pro and *N*-me-L-pro complexes. However, this effect is smaller than that of the introduction of *N*-substituents on the L-aminocarboxylates. Thus, the reaction rates of individual courses of olefin exchange is largely controlled by the moiety around amino nitrogen, and to a less extent by the substituents on the 4-position of the pyrrolidine ring. Such a trend seems to be interpreted by the stereochemistry of the transition state mentioned above.

References

1) P. Corradini, G. Paiaro, and A. Pununzi, *J. Am. Chem. Soc.*, **88**, 2863 (1966); A. Pununzi and G. Paiaro, *J. Am. Chem. Soc.*, **88**, 4843 (1966).
2) Y. Terai, H. Kido, J. Fujita, and K. Saito, *Bull. Chem. Soc. Jpn.*, **48**, 1233 (1975).
3) Y. Terai and K. Saito, *Bull. Chem. Soc. Jpn.*, **51**, 503 (1978).
4) Y. Terai, H. Kido, K. Kashiwabara, J. Fujita, and K. Saito *Bull. Chem. Soc. Jpn.*, **50**, 150 (1977).
5) J. Fujita, K. Konya, and K. Nakamoto, *Inorg. Chem.*, **9**, 2794 (1970).
6) A. A. Patchett and B. Witokop, *J. Am. Chem. Soc.*, **79**, 185 (1957).
7) F. Irreverre, K. Morita, A. V. Robertson, and B. Witokop, *J. Am. Chem. Soc.*, **85**, 2824 (1963).
8) P. Quitt, J. Hellerbach, and K. Vogler, *Helv. Chim. Acta*, **46**, 327 (1963).
9) A. B. Mauger and B. Witokop, *Chem. Rev.*, **66**, 48 (1966).
10) ($\Delta\varepsilon_{resolv} - \Delta\varepsilon_{vic}$) values of the tbn complexes are *ca.* 1—1.1 for various coordinated L-aminocarboxylates, whereas those of the mbn complexes are 0.7.
11) Y. Terai, H. Kido, and K. Saito, *Bull. Chem. Soc. Jpn.*, **50**, 3265 (1977).
12) L. Cattalini, *Prog. Inorg. Chem.*, **13**, 263 (1970).