

Kinetics of Substitution Reactions of Olefins in *trans*-Dichloro(η^2 -2-methyl-2-butene)platinum(II) Complexes Containing Pyridine or Aniline Derivatives

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Kinetics of substitution of *cis*-1,2-dichloroethylene (dce), 2,3-dimethyl-2-butene (dmb), and 2-methyl-2-butene (mbn) for the coordinated mbn in the new optically active complexes of the type *trans*-[PtCl₂(*S*-mbn)L] (L = 4-substituted pyridine and aniline) were studied in benzene and dichloromethane by measuring the decrease in CD strength at ca. 24 000 cm⁻¹. The observed first-order rate constant k_o in the presence of a large excess of free olefin increased with increase in the olefin concentration. ($k_o = k_2[\text{olefin}]$; k_2 represents k_{py} and k_{ani} for the complexes containing pyridine and aniline derivatives, respectively.) The k_{ani} decreased on addition of free L but reached constant value (k_{ani}') in more than 0.005 M L solution, which can be reckoned as the rate of direct bimolecular substitution. The k_{py} , which reflects the rate of direct bimolecular substitution, increased in the sequence of the incoming olefin dmb < dce < mbn, and this order is interpreted by considering both the electronic and steric effect of the substituents on the ethylene moiety. The k_{py} and k_{ani}' values for the reaction with dce decreased with increase in +I effect of the 4-substituents on the aromatic rings of L. The σ character of the Pt-N bond seems to play an important role in the kinetic trans effect.

Introduction

Square-planar platinum(II) complexes exhibit catalytic actions on a variety of reactions, especially those involving olefin as substrate.² For elucidating the mechanism of catalytic activity, it is essential to understand the progress of individual reactions and the ruling factor for each process. Coordination and liberation of olefins on and from the planar complex should be important elementary processes for many reactions such as oligomerization, polymerization, and isomerization of olefins.

It has been long known that the trans effect^{3,4} is one of the dominating factors in substitution reactions of square-planar complexes but is interpreted only qualitatively at the present stage. We found significant stereoselectivity, both thermodynamic and kinetic, in the substitution of *trans*-2-butene (tbn) for ethylene in *trans*(N,olefin)-[PtCl(L-am)(C₂H₄)] in acetone (L-am⁻ stands for L-aminocarboxylate anion).⁵ The thermodynamic and kinetic optical yields were governed by the asymmetric nitrogen of L-am⁻, which is trans to the ethylene to be replaced. Such an observation stimulated us to study the trans effect of amino nitrogens upon the substitution of olefins^{6,7} in platinum(II) complexes.

Since olefin exchange in these complexes gives little change in UV absorption spectra, the rate cannot be measured by the UV absorption method. A substitution reaction involving the change in CD strength, however, should be useful. Whenever an asymmetrically coordinated prochiral olefin is replaced by a nonprochiral olefin, the progress of olefin exchange should be reflected in the change of CD pattern. We prepared new optically active complexes of the type *trans*-[PtCl₂(*S*-mbn)L], where mbn is 2-methyl-2-butene and L is 4-substituted pyridine and aniline. The CD strength of this complex decreased and finally disappeared on addition of a large excess of nonprochiral *cis*-1,2-dichloroethylene (dce). The rate was measured by observing the change in CD strength with time. The 4-substituted pyridine and aniline derivatives are useful for giving various electronic trans effect, while the stereochemical

Table I. Analytical Data of the New Complexes, *trans*-[PtCl₂(*S*-mbn)(L)]

L	C, %		H, %		N, %	
	calcd	found	calcd	found	calcd	found
4-CN-py	30.01	30.14	3.21	3.23	6.36	6.41
4-Cl-py	26.71	26.61	3.14	3.08	3.12	2.83
py	28.92	28.69	3.64	3.46	3.37	3.33
4-CH ₃ -py	30.78	30.58	3.99	3.99	3.26	3.30
4-NH ₂ -py	27.91	27.83	3.76	3.73	6.51	6.62
4-Cl-ani	28.49	28.33	3.48	3.47	3.02	3.04
ani	30.78	30.71	3.99	3.93	3.26	3.23
4-CH ₃ -ani	32.51	32.39	4.32	4.30	3.16	3.41

effect remains unchanged. The substitution of other olefins including mbn and 2,3-dimethyl-2-butene (dmb) for the coordinated mbn was also examined.

Experimental Section

Materials. Tetraphenylphosphonium Trichloro[(*S*)-2-methyl-2-butene]platinate(II). Tetraphenylphosphonium chloride (6.0 × 10⁻⁴ mol) in water (5-6 cm³) was dripped with stirring into optically active *trans*(N,mbn)-[PtCl(L-pro)(*S*-mbn)]⁸ (L-pro⁻ stands for L-proline anion) (5.0 × 10⁻⁴ mol) in concentrated hydrochloric acid (5 cm³). Precipitated P(C₆H₅)₄[PtCl₃(*S*-mbn)] was filtered off, washed with water (10 cm³), and dried in vacuo. Anal. Calcd for C₂₉H₃₀PtCl₃P: C, 48.99; H, 4.25. Found: C, 49.30; H, 4.40.

trans-[PtCl₂(*S*-mbn)(4-X-py)]. The para-substituted pyridine (3.0 × 10⁻⁴ mol) was added with stirring to the phosphonium salt (3.0 × 10⁻⁴ mol) in acetone (20 cm³). The mixture was treated with water (30 cm³) and ice cooled to give insoluble *trans*-[PtCl₂(*S*-mbn)(4-X-py)] (X = CN, Cl, H, CH₃, and NH₂), which was filtered off, washed with water (10 cm³) and dried in vacuo. *trans*-[PtCl₂(*S*-mbn)(4-X-aniline)] (X = Cl, H, and CH₃) was similarly prepared by use of 4-X-aniline in place of 4-X-pyridine in ethanol. The results of chemical analysis of C, H, and N are listed in Table I.

2-Methyl-2-butene (mbn), 2,3-dimethyl-2-butene (dmb), and *cis*-1,2-dichloroethylene (dce) were of guaranteed grade (Tokyo Kasei Co.) and used without further purification. Commercial benzene and dichloromethane of guaranteed grade were used as solvent without further purification.

Kinetic Runs. The UV absorption of all the complexes gives several shoulders in the region from 20 000 to 40 000 cm⁻¹. There are a few CD peaks in this region, but those at 24 100 and 23 530 cm⁻¹ are common for the complexes containing the pyridine and the aniline derivatives, respectively, and useful for the kinetic measurements. The complex was dissolved in benzene or dichloromethane to give a 3.0 × 10⁻³ M solution (1 cm³), cooled, and mixed with a given amount of cooled olefin solution (0.05-0.5 M) (1-6 cm³) and the amine solution (whenever necessary) in the same solvent. The solution (7 cm³) was

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Table II. Second-Order Rate Constants (k_{py}) for the Substitution Reactions of Various Olefins in *trans*-[PtCl₂(*S*-mbn)(4-X-py)]

X	$10^2 k_{py(dce), a}$ M ⁻¹ s ⁻¹	$10^2 k_{py(dce), b}$ M ⁻¹ s ⁻¹			$10^2 k_{py(mbn), b}$ M ⁻¹ s ⁻¹			$10^2 k_{py(dmb), b}$ M ⁻¹ s ⁻¹	σ^c
	17.0 °C	8.0 °C	17.0 °C	25.0 °C	8.0 °C	17.0 °C	25.0 °C	17.0 °C	
CN	20.0	8.82	20.0		72.6	173	602	0.917	0.660
Cl						30.3		0.386	0.227
H	3.19	1.71	3.78	7.39	6.85	18.6	58.9	0.213	0.0
CH ₃	1.77	0.651	1.44	2.89	1.22	2.98	8.68	0.100	-0.170
NH ₂						0.677			-0.660

^a In benzene. ^b In dichloromethane. ^c Hammett substituent constant.¹³

placed in a thermostated cell box of a spectrometer (8.0, 17.0, and 25.0 °C), and the CD strength was recorded at 23 530 or 24 100 cm⁻¹. Since the reaction was caused to proceed in a large excess of olefin, the decrease in CD strength was treated by the pseudo-first-order kinetic formula to give the observed rate constant k_o

$$k_o = -\ln [x_t/x_0]/t \quad (1)$$

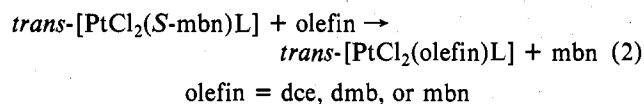
where x_t and x_0 denote the CD strengths at time t and 0, respectively.

Measurements. The CD was recorded with a JASCO J-40 spectrometer and a special cell jacket for keeping the temperature constant. The UV absorption was recorded with a Hitachi 323 spectrometer.

Results

Synthesis. Optically active *trans*(*N*,mbn)-[PtCl(L-pro)(*S*-mbn)], which exhibited a plus CD peak with $\Delta\epsilon$ 1.0 at 23 800 cm⁻¹, was used as the starting material. The P(C₆H₅)₄-[PtCl₃(mbn)] has a plus CD peak with $\Delta\epsilon$ 0.5 at 22 990 cm⁻¹, and the absolute configuration of the mbn was determined to be *S* in accordance with the empirical rule.⁸ All the complexes of *trans*-[PtCl₂(mbn)L] exhibited plus CD peaks with $\Delta\epsilon$ ca. 0.4 in the 23 530–24 100-cm⁻¹ region and the mbn was also assigned to *S* configuration. All the reactions proceeded with retention of *S* configuration of coordinated mbn. The products racemized spontaneously in various solvents at different rates. The half-lives of the complexes containing the pyridine and the aniline derivatives were 1 h in acetone and several hours in ethanol, respectively, under the present synthetic conditions. The synthesis was completed within a few minutes and the decrease in CD strength was very small during the synthesis. The CD of all the complexes was strong enough for accurate kinetic studies.

Kinetic Data. In the absence of free olefin the first-order rate constants of the spontaneous racemization of the pyridine and the aniline complex were less than 1×10^{-6} and 1×10^{-5} s⁻¹, respectively, at 17 °C in benzene. Such a CD decrease can be ignored as compared with the big CD change in the presence of free olefin. Spontaneous racemization should accompany the displacement of the coordinated olefin by a solvent molecule. The above facts suggest that such a substitution is negligibly small. When dce or dmb was added to the optically active complex in benzene or dichloromethane, the UV absorption spectrum changed very slightly and neither a new peak nor a shoulder appeared. When mbn was added to the complex in dichloromethane, the UV absorption did not change. These facts indicate that the k_o values reflect the rate of the following olefin exchange alone.



Pyridine System. The k_o value obtained from X at 24 100 cm⁻¹ was independent of the concentration of the complex (1×10^{-3} – 6.0×10^{-3} M) but increased linearly with increase in concentration of added dce in benzene as shown in Figure 1. The intercepts, which correspond to the rate of spontaneous racemization, were less than 1×10^{-6} s⁻¹ and can be ignored under the present condition. Hence eq 3 holds. Addition of

$$\text{rate} = k_{py(dce)}[\text{complex}][\text{olefin}] \quad (3)$$

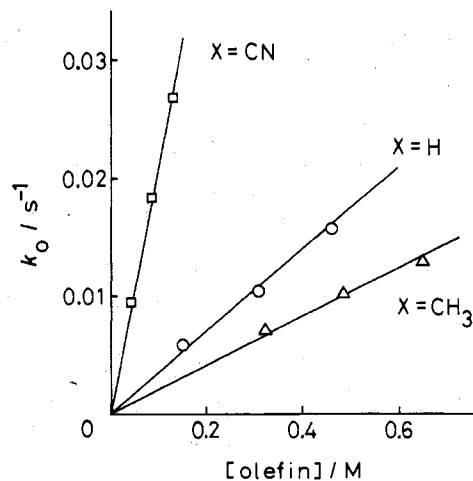


Figure 1. Relationship between k_o and the concentration of added dce in benzene at 17.0 °C (*trans*-[PtCl₂(*S*-mbn)(4-X-py)], 3.00×10^{-3} M).

Table III. Activation Parameters for the Data of Table II at 8.0, 17.0, and 25.0 °C in Dichloromethane

X	dce ^a		mbn ^a	
	ΔH^\ddagger , kJ mol ⁻¹	ΔS^\ddagger , J mol ⁻¹ K ⁻¹	ΔH^\ddagger , kJ mol ⁻¹	ΔS^\ddagger , J mol ⁻¹ K ⁻¹
CN	(56)	(-63)	86 ± 13	57 ± 44
H	57 ± 1	-75 ± 4	85 ± 1	37 ± 23
CH ₃	56 ± 3	-79 ± 17	78 ± 9	-5 ± 30

^a Added olefin.

free L to the reaction mixture did not change the second-order rate constant $k_{py(dce)}$, which reflects the rate of direct bimolecular substitution. The $k_{py(dce)}$ was similarly measured in dichloromethane to give the same value as in benzene. The rate constants and activation parameters are given in Table II and Table III, respectively. The $k_{py(dce)}$ decreases in the order X = CN, H, and CH₃, and the plot of log $k_{py(dce)}$ vs. Hammett's constant of pyridine derivative gave a straight line.

The replacement of coordinated *S*-mbn by mbn and dmb was also examined in dichloromethane. The rate constants ($k_{py(mbn)}$ and $k_{py(dmb)}$) and the activation parameters are summarized in Tables II and III, respectively. The plot of log $k_{py(mbn)}$ or log $k_{py(dmb)}$ vs. Hammett's constant of pyridine derivative gave a straight line.

Aniline System. The k_o value obtained from X at 23 530 cm⁻¹ was independent of the complex concentration (1.0×10^{-3} – 9.0×10^{-3} M) but linearly dependent on the dce concentration in benzene, as shown in Figure 2. The intercepts which correspond to the rate of spontaneous racemization were less than 1×10^{-5} s⁻¹ and can be ignored under the given experimental conditions. Hence the rate is expressed by eq 4. The relationship between the concentration of added 4-

$$\text{rate} = k_{ani(dce)}[\text{complex}][\text{olefin}] \quad (4)$$

chloroaniline and $k_{ani(dce)}$ is shown in Figure 3. The $k_{ani(dce)}$ decreases on addition of free 4-chloroaniline and reaches a

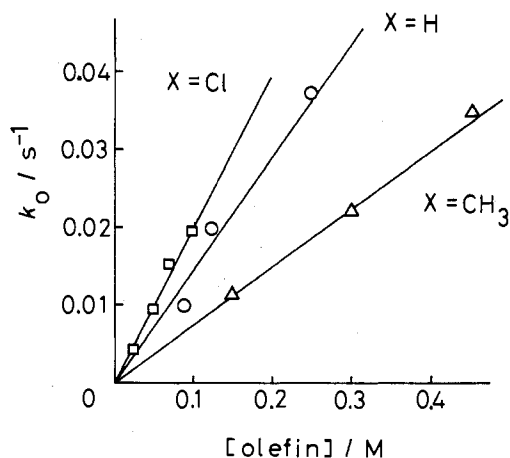


Figure 2. Relationship between k_0 and the concentration of added dce in benzene at 17.0 °C (*trans*-[PtCl₂(*S*-mbn)(4-*X*-ani)], 3.00×10^{-3} M).

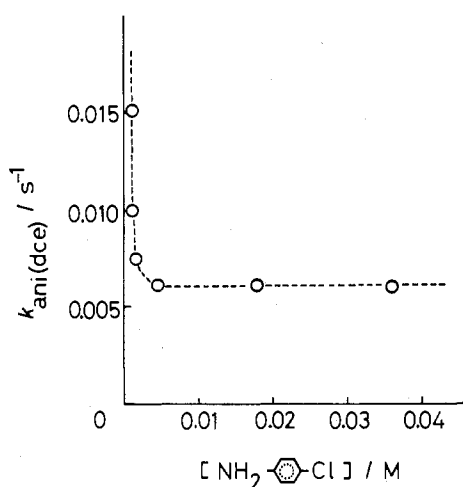


Figure 3. Relationship between $k_{\text{ani(dce)}}$ and the concentration of added 4-chloroaniline in benzene at 17.0 °C (*trans*-[PtCl₂(*S*-mbn)(4-Cl-ani)], 3.00×10^{-3} M; [dce], 6.97×10^{-2} M).

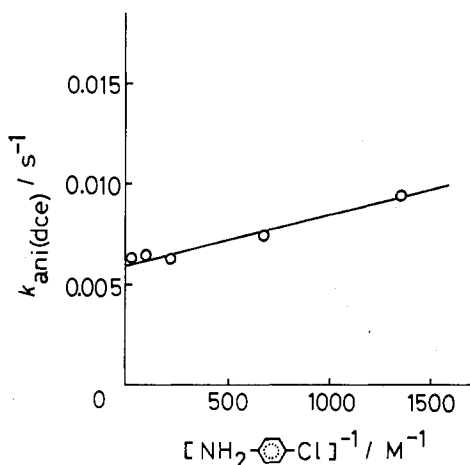


Figure 4. Relationship between $k_{\text{ani(dce)}}$ and $1/[4\text{-Cl-aniline}]$ in benzene at 17.0 °C (*trans*-[PtCl₂(*S*-mbn)(4-Cl-ani)], 3.00×10^{-3} M; [dce], 6.97×10^{-2} M).

constant value. The plot of $k_{\text{ani(dce)}}$ vs. the reciprocal of the 4-chloroaniline concentration ($[L]$) gave a straight line as shown in Figure 4. Hence eq 5 holds in the given concentration range. The substitution seems to proceed through two

$$k_{\text{ani(dce)}} = A + B/[L] \quad (5)$$

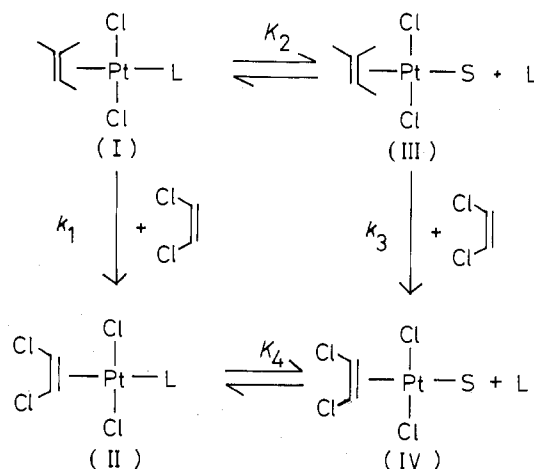


Figure 5. Reaction paths of the aniline system (S; solvent molecule; L, amine ligand). k_1 corresponds to $k_{\text{py(dce)}}$ and is written as $k'_{\text{ani(dce)}}$ in Figure 6.

Table IV. Second-Order Rate Constants (k_1^a) for the Substitution Reaction of Olefin in *trans*-[PtCl₂(*S*-mbn)(4-*X*-ani)] in Benzene at 17.0 °C

X	$10^2 k_1, ^a \text{ M}^{-1} \text{ s}^{-1}$	σ^b
Cl	8.87	0.227
H	8.13	0.0
CH ₃	6.44	-0.170

^a k_1 corresponds to $k_{\text{py(dce)}}$ and is written as $k'_{\text{ani(dce)}}$ in Figure 6. ^b Hammett substituent constant.^{1,3}

routes as seen in Figure 5. The one with the rate constant k_1 is the direct bimolecular substitution of dce for *S*-mbn. The K_2 value in the other route should be the equilibrium constant for the displacement of the amine ligand (L) by a solvent molecule, and the k_3 is the rate constant of the succeeding bimolecular substitution of dce for *S*-mbn. Since the UV absorption spectrum of the freshly prepared complex solution remained unchanged for several hours, the complex solution used in the kinetic runs must have reached the preequilibrium at least under the experimental conditions. Then the rate equation is given by eq 6. The UV absorption spectrum of

$$-\frac{d[\text{complex}]}{dt} = \frac{[\text{complex}][\text{dce}](k_1[L] + k_3K_2)}{[L] + K_2} \quad (6)$$

the complex solution containing a large excess of L did not change at least for several hours, and the solvolysis should be negligible in such a solution. If a considerable amount of III (Figure 5) containing benzene as ligand were formed, a significant change in the UV absorption pattern would be expected because of the difference in coordinating atoms. However, when the contribution of free L is deduced from the observed spectrum of the complex solution containing a large excess of L, the remaining pattern coincided with the freshly prepared complex solution. Hence the K_2 value should be very small, and eq 6 is reduced to eq 7. The A and B of eq 5 should

$$-\frac{d[\text{complex}]}{dt} = [\text{complex}][\text{dce}]\{k_1 + (k_3K_2/[L])\} \quad (7)$$

correspond to the k_1 and the product k_3K_2 , respectively. The k_1 values are evaluated from the intercepts of the plots in Figure 4. The $k_{\text{ani(dce)}}$ values for the other two complexes (X = H and CH₃) changed similarly and were treated similarly to calculate k_1 values. All the results are summarized in Table IV. They reflect the rate of direct bimolecular substitution, and decrease in the order of X = Cl, H, and CH₃. The plot of $\log k_1$ vs. Hammett's constant of aniline derivative gave a straight line.

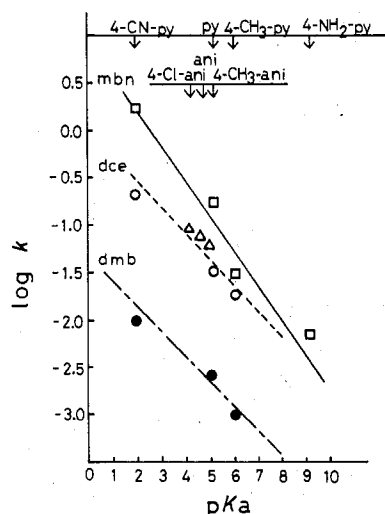


Figure 6. Relationship between the logarithms of the second-order rate constants and pK_a in benzene or dichloromethane at 17.0 °C ($[complex], 3.00 \times 10^{-3} M$): $\log k'_{ani(dce)}$ (Δ); $\log k_{py(mbn)}$ (\square); $\log k_{py(dce)}$ (\circ); $\log k_{py(dmb)}$ (\bullet).

Discussion

Olefin-Olefin Substitution. On the reaction of various olefins with *trans*-[PtCl₂(*S*-mbn)L] in benzene or dichloromethane, the unique product was *trans*-[PtCl₂(olefin)L]. Such an ease of substitution of an olefin molecule for the coordinated olefin was demonstrated by the substitution reactions of *trans*-[PtCl₂(olefin)(ligand)]^{6,9} (ligand = pyridine *N*-oxide or aniline) and also by our previous work dealing with complexes of the types [PtCl₃(tbn)]⁻¹⁰ and *trans*- and *cis*-(*N*,olefin)-[PtCl(L-am)(olefin)].^{7,11} Despite the marked *trans* effect of olefins, the olefin molecule itself, not the *trans* ligand to it, is replaced by an olefin. This fact may be related to the difficulty with which platinum(II) complexes with two olefin ligands at *trans* sites are prepared. The bivalent platinum ion does not seem to accommodate highly back-donating ligands in *trans* positions in stable complexes.

Difference in Reaction Paths. When dce was added to the optically active complex solution in benzene, different reaction paths were observed for the two systems involving pyridine and aniline derivatives as amino ligand. The complexes with pyridine derivatives give only the $k_{py(dce)}$ route, which is the direct bimolecular substitution of olefin. The complexes with aniline derivatives have two routes. The k_1 path is the direct substitution, which can be compared to the $k_{py(dce)}$ path, and henceforth written by $k'_{ani(dce)}$. The k_3 path is via an intermediate having the solvent molecule as ligand. No experimental evidence was obtained for the presence of the intermediate, but the formation of, e.g., *trans*-[PtCl₂(C₆H₆)(*S*-mbn)] does not seem very unlikely, because benzene is capable of coordinating to Pt(II) by use of the π electrons. Neither individual value of k_3 nor K_2 was obtained.

The reason the k_3 route is obtained in the aniline system alone may be related to the strength of Pt-N bonds. However, the σ -bond strength cannot account for the difference, because the pK_a value of 4-cyanopyridine, which fails to give the k_3 route, is smaller than that of the aniline derivatives. The Pt-N bond between pyridine derivatives and Pt(II) may be reinforced by π -bonding,¹² so that its cleavage is minimized. Such an

effect is not expected for the Pt-aniline bond, because of the absence of π -accepting orbitals.

Relationship to pK_a . Figure 6 illustrates the plot of $\log k_{py(dce)}$ and $\log k'_{ani(dce)}$ against pK_a of the amines. There seems to be a common linear relationship for both pyridine and aniline derivatives. It is apparent that the rate constants of direct olefin substitution are not affected by the presence of π bonding between Pt(II) and amino nitrogen. Hence the extent of *trans* effect in these systems can be interpreted on the basis of pK_a values, which reflect the σ -donating property of the amines. The nucleophilic attack of incoming dce upon Pt(II) seems to be retarded by the increase in electron density of the cation.

Substitution Reactions of Various Olefins. No solvent effect was observed on the $k_{py(dce)}$ of the complexes with 4-X-py in the two solvents benzene and dichloromethane (Table II). Thus the $k_{py(dce)}$ in benzene can be compared with the $k_{py(mbn)}$ and $k_{py(dmb)}$ in dichloromethane. The $k_{py(mbn)}$ and the $k_{py(dmb)}$ are also plotted as a function of pK_a in Figure 6. The rate constant k_{py} increases in the following sequence of incoming olefin: $dmb < dce < mbn$. Since dce and dmb are nonprochiral, the $k_{py(dce)}$ and $k_{py(dmb)}$ values represent the real rate of substitution. However, mbn is prochiral, and the $k_{py(mbn)}$ value reflects the rate of substitution with inversion of configuration only. Hence, the real substitution of mbn must proceed faster than is apparent in Figure 6. We discussed previously that the second-order rate constant of olefin exchange in the complex *trans*-(*N*,olefin)-[PtCl(L-am)(*S,S*-tbn)] increased with the decrease of the number of substituents on the ethylene moiety of the incoming olefin.^{7,11} The faster substitution with mbn than that with dmb is reasonably interpreted by such a steric effect. However, dce with two substituents on one side of the C=C bond axis gives smaller k_{py} than mbn does, indicating the contribution of another factor, the electronic effect. Since dce has two electronegative substituents, the electron density in the π orbital of the ethylene moiety must be smaller than that of mbn, so that the nucleophilic attack of dce upon Pt(II) will be less facilitated than that of mbn.

The two straight lines for $\log k_{py(dce)}$ and $\log k_{py(dmb)}$ in Figure 6 have gradients 0.94 ± 0.44 and 1.11 ± 0.28 , respectively, and can be reckoned equal to each other within experimental error. However, the gradient for $\log k_{py(mbn)}$ is 1.88 ± 0.33 and the difference seems significant. The $k_{py(mbn)}$ should be expressed by the product of the real substitution rate constant and the stereoselectivity factor. If the $k_{py(mbn)}$ values for the complexes with different X's were subject to dynamic selectivity to different extents, the difference in gradients could be accounted for.

Activation parameters for the $k_{py(dce)}$ (Table III) are the usual values for substitution reactions of square-planar platinum(II) complexes,^{2,3} but those for $k_{py(mbn)}$ (Table III) seem to be significantly different from them; i.e., the ΔS^\ddagger 's are positive and ΔH^\ddagger 's are much greater. However, satisfactory interpretation cannot be given at the present stage.

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Registry No. *trans*-[PtCl₂(*S*-mbn)(4-CN-py)], 71872-14-5; *trans*-[PtCl₂(*S*-mbn)(4-Cl-py)], 71872-13-4; *trans*-[PtCl₂(*S*-mbn)(py)], 71872-12-3; *trans*-[PtCl₂(*S*-mbn)(4-CH₃-py)], 71872-11-2; *trans*-[PtCl₂(*S*-mbn)(4-NH₂-py)], 71872-10-1; *trans*-[PtCl₂(*S*-mbn)(4-Cl-ani)], 71885-42-2; *trans*-[PtCl₂(*S*-mbn)(ani)], 71872-09-8; *trans*-[PtCl₂(*S*-mbn)(4-CH₃-ani)], 71872-08-7; dce, 540-59-0; mbn, 513-35-9; dmb, 563-79-1; *trans*-(*N*,mbn)-[PtCl(L-pro)(*S*-mbn)], 34802-65-8; P(C₆H₅)₄[PtCl₃(*S*-mbn)], 71885-41-1.

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