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Review

Preparation, circular dichroism and substitution reactions of platinum(II) complexes with asymmetric olefin ligands*

Kazuo Saito

Coordination Chemistry Laboratories, Institute for Molecular Science, Okazaki 444 (Japan)

and Kazuo Kashiwabara

Department of Chemistry, Faculty of Science, Nagoya University, Nagoya 464 (Japan)

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Abstract

A review is presented of separation of optically active platinum(II) complexes with prochiral olefin ligands by use of the diastereoisomers formed with optically active aminocarboxylates, and of their CD spectra. The CD pattern shown is to be determined not only by the absolute configuration of olefin ligands but also by the asymmetric nitrogen formed upon coordination of the amino moiety. The change in CD on olefin substitution is useful for kinetic studies. The *trans* effect, stereoselectivity, and asymmetric induction which accompanies the substitution are discussed in terms of steric hindrance and mutual ligand interaction.

Since Cope and his co-workers first synthesized an optically active platinum(II) complex containing an asymmetrically coordinated olefin, namely [$PtCl_2$(α-methylbenzylamine)(*trans*-cyclooctene)] [1], a variety of such compounds have been made. They are of great importance not only for their structural interest, but also as precursors for catalytic reactions involving olefins [2]. We have found a facile procedure for separating the optical isomers involving use of mixed ligand complexes with aminocarboxylates. The CD spectra have been examined with reference to the contribution of the absolute configuration of the olefin ligand and that of the asymmetric nitrogen of the coordinated amino group (e.g. L-prolinate, *N*-substituted alaninate and valinate). Observation of change in the CD strength with time provides a useful procedure for kinetic studies of olefin substitution, which is an

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important elementary reaction in complex catalysis and can otherwise be studied only with difficulty. This article reviews such studies, mostly carried out in our laboratories.

Preparation and separation of optical isomers

Since the structure of Zeise's salt was elucidated, a large variety of mixed ligand platinum(II) olefin complexes have been prepared, but resolution of enantiomers has been extremely difficult. Olefins capable of giving enantiomeric pairs, as shown in Fig. 1, are called prochiral olefins. Propene, (*E*)-2-butene (*trans*-2-butene, subsequently denoted by tbn) and 2-methyl-2-butene (mbn) are prochiral, but ethylene, (*Z*)-2-butene (*cis*-2-butene) and 2,3-dimethyl-2-butene (dmb) are not. Separation of optical isomers of platinum(II) complexes containing prochiral olefins is possible only by use of diastereoisomers with another optically active ligand. The complex $[PtCl_2(L)(L')]$ has geometrical, *cis* and *trans* isomers, and these can be separately synthesized by utilizing the *trans* effect.

$$K[PtCl_3(C_2H_4)] + L \rightarrow \text{trans-}[PtCl_2(C_2H_4)(L)] \xrightarrow{\text{olefin}} \textit{trans}\text{-}[PtCl_2(\text{olefin})(L)] \quad (1)$$

$$K[PtCl_3(L)] + C_2H_4 \rightarrow \textit{cis}\text{-}[PtCl_2(C_2H_4)(L)] \xrightarrow{\text{olefin}} \textit{cis}\text{-}[PtCl_2(\text{olefin})(L)] \quad (2)$$

Reaction 1 depends on the stronger *trans*-effect of ethylene than of chloride, and examples involve (+)-α-methylbenzylamine [1] and (−)- and (+)-1-phenylethylamine [3]. Reaction 2 utilizes the stronger *trans*-effect of chloride than of L-(amines), and complexes with (−)-(*S*)-1-phenylethylamine [4] and (*R*)-*p*-tolylmethylsulphoxide [5] were prepared.

Geometrical isomers of platinum(II) complexes containing optically active bidentate aminocarboxylates can be synthesized in a similar manner [6,7] (Scheme 1).

When the olefin is prochiral, the products are diastereoisomeric pairs, and can be separated by taking advantage of their different solubilities in organic solvents or by fractional crystallization. The separated products have two asymmetric centers, one in the aminocarboxylate and the other in the prochiral olefin moiety. Enantiomers of the type $[PtCl_3(\text{olefin})]^-$ can be obtained by treating the diastereoisomeric compound with hydrochloric acid, the aminocarboxylate or amine being liberated and chloride ions taking up the coordination sites [3,8,9]. Recently enantiomers of

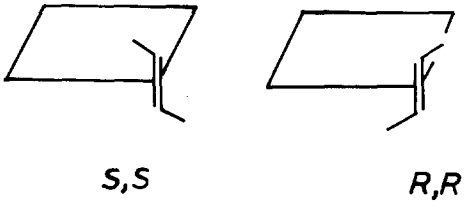
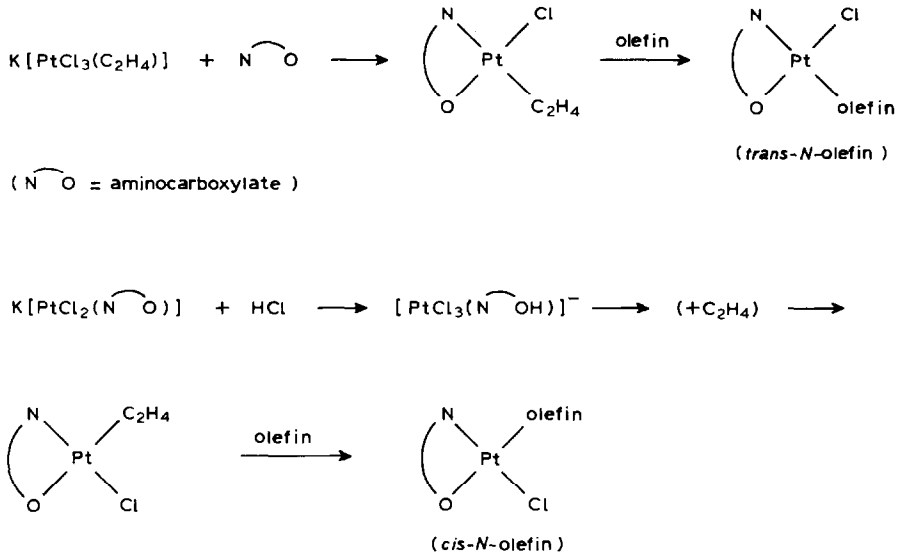


Fig. 1. Asymmetric coordination of (*E*)-2-butene.



SCHEME 1.

$[PtCl_3(olefin)]^-$ (olefin = propene, 1-butene, and tbn) were resolved by use of the *S*-trimethyl(α-methylbenzyl)ammonium salt $[S\text{-}(CH_3)_3NCH(CH_3)(C_6H_5)]^+$ [10].

Known optical isomers of platinum(II) complexes with asymmetric olefin were for a long time limited to anions or uncharged species with coordination number 4. The first examples involving cationic species and one with coordination number 5 were provided by $(+)^{CD}_{335}$-[PtCl(*o*-benzenediamine)(*S*-2-methyl-2-butene)]$B(C_6H_5)_4$ [11], and (+)-[$PtCl_2$((*E*)-2-butene)(2,3-butanedionebis(*N*,*N*-dimethylhydrazone))] [12], respectively.

Circular dichroism spectra

The circular dichroism (CD) spectra of optically active platinum(II)-olefin complexes were first studied by Corradini et al., who used them to measure the ratio of diastereoisomers formed in solution [13]. The studies have subsequently been extended to various compounds, mostly with the objectives of: (a) estimating the absolute configuration of the asymmetrically coordinated olefin; (b) studying the kinetics and stereoselectivity of reactions involving displacement of the coordinated olefin by another olefin; and (c) estimating the optical yields of reactions involving asymmetric induction.

Relationship with the absolute configuration

Scott and his collaborators were the first to discuss the relationship between the absolute configuration of asymmetrically coordinated olefin and the form of the CD spectra of the complex $[PtCl_2(amine)(olefin)]$ [14]. They suggested that the CD pattern in the *d–d* transition region is mainly governed by the absolute configuration of olefins, and is fairly independent of the absolute configuration of the amine or the geometrical isomerism of the complex.

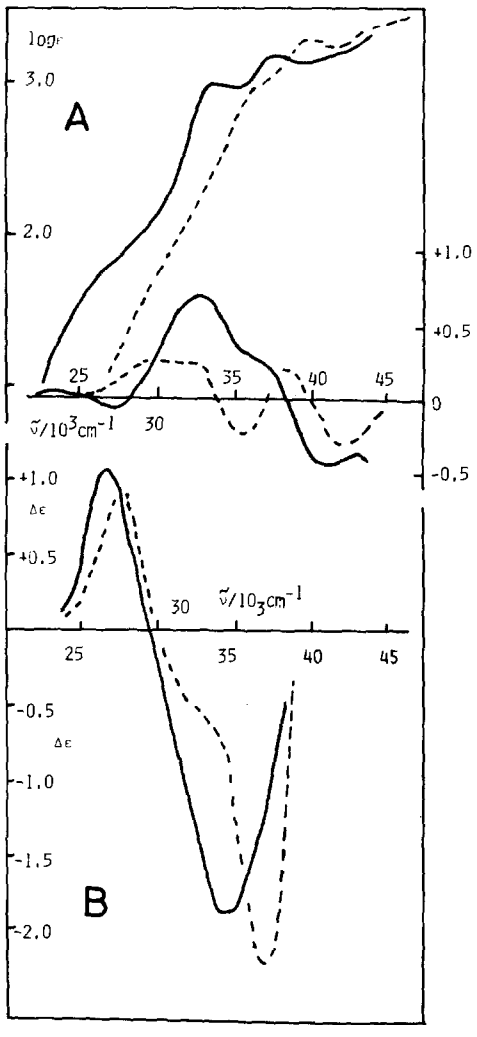


Fig. 2. Absorption and CD spectra of *trans* (———) and *cis* (- - - - - -) (*N*-olefin)[PtCl(L-prolinate)(olefin)] in ethanol; A: olefin = C_2H_4; B, *S,S*-tbn.

We have considered whether such a relationship also applies for aminocarboxylate (am) complexes of the type *trans*- and *cis*-(*N*-olefin)[PtCl(L-am)(olefin)]. Figure 2A shows that the CD patterns of the *cis*- and *trans*-isomer of [PtCl(L-prolinate)(C_2H_4)] are significantly different from one another. The CD peak arises from the contribution of the L-prolinate ligand, and the CD strength at the peak corresponds with a 3/7 *cis/trans* ratio. However, the CD patterns of the geometrical isomers of [PtCl(L-prolinate)(*S,S*-(*E*)-2-butene)] (Fig. 2B) are similar to one another, and the CD strength is much larger, indicating that the contribution of *S,S*-(*E*)-2-butene is far greater than that of L-prolinate. The sign of the CD is (+) in the region of the *d–d* transition, and (−) at higher wave numbers.

The contribution of the olefin is more accurately estimated by deducing the contribution of the aminocarboxylate; e.g. $\Delta\varepsilon$(*trans*-(*N*-tbn)-[PtCl(L-prol)(*S,S*-tbn)])

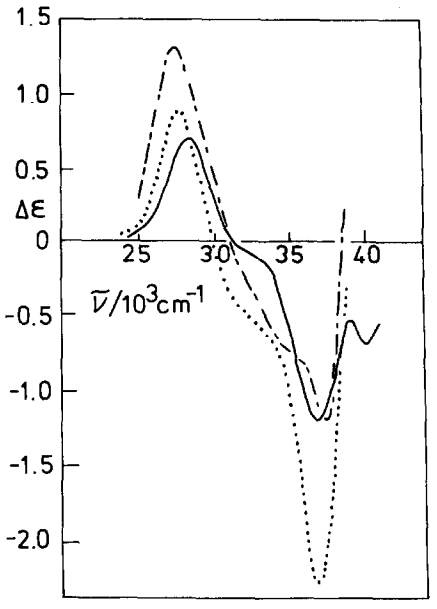


Fig. 3. CD Spectra of *cis*-(*N*-olefin) complexes; ——— [PtCl(*o*-benzenediamine)(*S*-mbn)]$^+$ in ethanol, ------ difference between [PtCl(L-prolinate)(C_2H_4)] and [PtCl(L-prolinate)(*S*,*S*-tbn)] in CH_3CN, and -·-· difference between [$PtCl_2$(*S*-α-methylbenzylamine)(C_2H_4)] and [$PtCl_2$(*S*-α-methylbenzylamine)(*S*,*S*-tbn)] in acetone.

and Δε(*trans*-(*N*-C_2H_4)-[PtCl(L-prol)(C_2H_4)]) (tbn = (*E*)-2-butene). Figure 3 shows the CD pattern of complexes containing *cis*-(*N*-olefin) geometrical isomerism. All of them exhibit (+) and (−) peaks in the 28000 and 36000 cm^{-1} region, respectively, and the patterns are not only similar to one another but also to that of [$PtCl_3$(*S*,*S*-tbn)]$^-$. Hence the absolute configuration of asymmetric olefin in the complexes of the type [PtCl(L-am)(olefin)] can be estimated from the sign of the CD in the *d*–*d* transition region (~ 28000 cm^{-1}) regardless of the type of aminocarboxylate. Thus it is clear that the empirical rule proposed by Scott et al. is also applicable to aminocarboxylate complexes [15].

Contribution of asymmetric nitrogen

Figure 4 shows the CD spectra of the complexes differing only in the aminocarboxylate ligand. When a methyl or benzyl group is present on the NH moiety of L-prolinate, the CD peak around 34000 cm^{-1} changes, but there is only weak CD in the *d*–*d* transition region at lower wave numbers. The former peak must be due to the contribution of the asymmetric nitrogen of the pyrrolidine ring. The L-alaninato complex, which contains no asymmetric nitrogen, shows only very weak CD over the whole wavelength range, indicating a very small contribution by the asymmetric carbon. Such a relationship can be more clearly seen by examining the CD spectra in Fig. 5, which shows the difference in CD between two complexes of the type *trans*-(*N*-olefin)-[PtCl(L-am)(C_2H_4)] in acetonitrile. The valinato complex has no asymmetric nitrogen, but an asymmetric nitrogen is created by introduction of a benzyl group on the nitrogen. The CD pattern changes markedly, as shown in Fig.

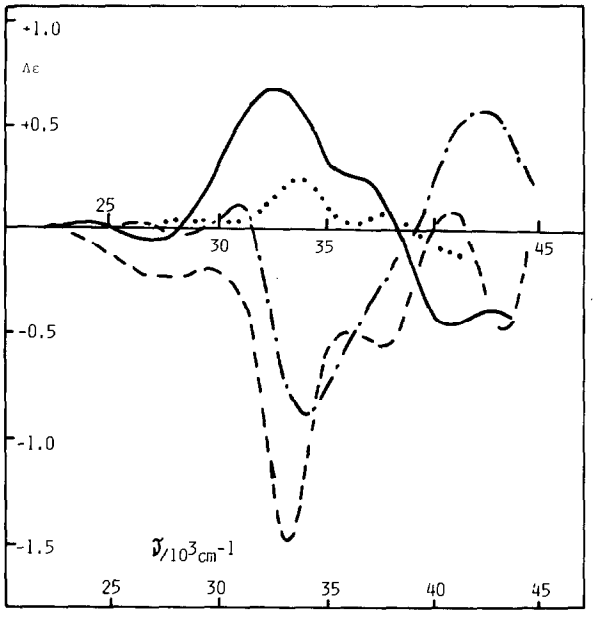


Fig. 4. CS Spectra of *trans*-(N-C_2H_4)[PtCl(L-am)(C_2H_4)] in CH_3CN. (L-am = ——— prolinate, · – · – · N-methyl-L-pro, - - - - - - N = benzyl-L-pro, · · · · · · alaninate).

5A and 5B [16]. The broken line in Fig. 6A relates to the contribution of the asymmetric nitrogen produced by the presence of the benzyl group. The solid line of Fig. 6A also shows a similar contribution resulting from the attachment of a benzyl group to the nitrogen of the prolinate ligand. The two lines almost coincide showing that the effect of attaching the benzyl group to nitrogen is the same for L-valinate and L-prolinate. The effect of introducing a methyl group to produce an asymmetric nitrogen is also the same for L-prolinate and on L-hydroxyprolinate, as can be seen from Fig. 6B. The CD strength of those complexes containing ethylene or (E)-2-butene, [PtCl(L-am)(olefin)] is much greater than that of those not containing an olefin ligand, e.g. $[PtCl_2(L\text{-am})]^-$ [16,17].

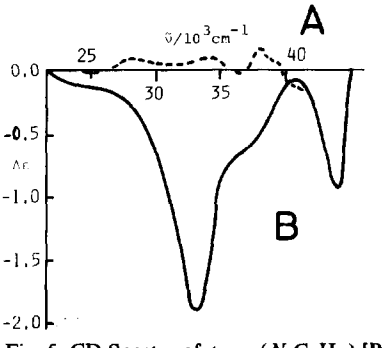


Fig. 5. CD Spectra of *trans*-(N-C_2H_4)-[PtCl(L-am)(C_2H_4)] in CH_3CN; A, L-am = L-valinate; B, N-benzyl-L-valinate.

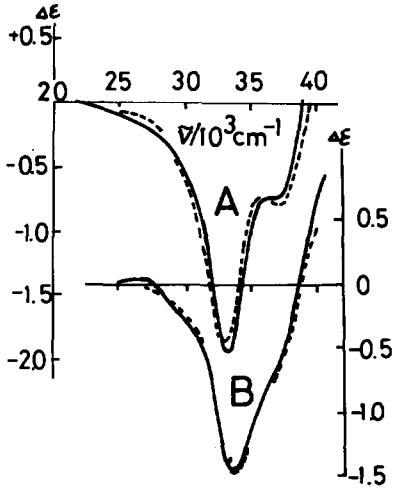


Fig. 6. Difference in CD spectra between *trans*-(N-C_2H_4)[PtCl(L-am)(C_2H_4)] in CH_3CN. A, ——— between L-prolinate and N-benzyl-L-pro, - - - - - - L-valinate and N-benzyl-L-val; B, ——— L-pro and N-methyl-L-pro, - - - - - - L-hydroxyprolinate and N-methyl-L-hydroxyprolinate.

Scott and Wrixon interpreted the relationship between the sign of the CD and absolute configuration of the asymmetrically coordinated olefin on the basis of quadrant rule [18]. We have appplied this rule to the contribution of asymmetric nitrogen. Figure 7 shows a projection of *trans*-(N-ethylene)[PtCl(N-alkyl-L-pro)(S,S-tbn)]; the square plane of the complex is represented by the horizontal line, the Pt–N bond is perpendicular to the plane of the paper, and the asymmetric nitrogen is underneath the platinum(II) and is shown by a large dotted circle. When the quadrant rule is applied on the basis of this projection, the contribution of the minus quadrant at the lower left-hand side behind the paper depends on the size of the moiety shown by a triangle. The larger the size of the group (benzyl, methyl and hydrogen), the greater should be the contribution of minus sign. Figure 7B shows the projection of S,S-(E)-2-butene in which the C–C moiety is across the square plane of the complex behind the paper. The contribution of the same minus region predominates as it does for the complex with asymmetric nitrogen.

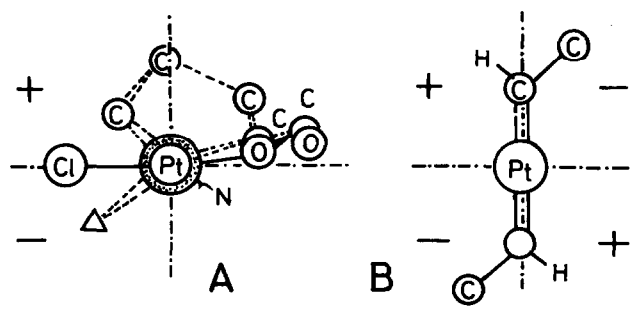


Fig. 7. Projection of *trans*-(N-tbn)[PtCl(N-substituted-L-pro)(S,S-tbn)]. Pt–N bond across the paper; A, N underneath Pt; B, tbn underneath Pt.

These observations suggest that there must be a mutual interaction between the asymmetric nitrogen and the coordinated olefin molecule through the platinum(II) ion. Venanzi et al. assigned the absorption bands of Zeise's salt in 31000 to 45000 cm^{-1} region to d-π^*(ethylene) transition [19]. $(C_6H_5)_4P[PtCl_3(S,S\text{-2-butene})]$ gives CD peaks with $\Delta\varepsilon$'s -1.3 and $+3.3$ at ca. 35000 and 39500 cm^{-1} in acetonitrile [8]. The former CD must correspond to the same transition to which the main CD of Fig. 6 is related. It thus appears that the d-π^*(ethylene) transition is perturbed by the asymmetric nitrogen *trans* to ethylene so that a marked CD appears in this region.

Value for kinetic studies of olefin substitution

Replacement of coordinated olefin by another olefin molecule is one of the important elementary reactions in catalysis by complexes. The kinetics can, however, be studied by the usual spectrophotometric method only with difficulty because a change in the olefin ligand brings about an insignificant change in the visible and ultraviolet spectrum. NMR spectroscopy is sometimes useful for studying the kinetics of olefin substitution [20], but available to only limited variety of reaction systems under special conditions. The CD spectroscopy is a useful tool whenever diamagnetic complexes of asymmetrically coordinated olefins are involved.

Trans-effect on olefin substitution

We have studied the *trans*-effect involved in the following substitution reactions in which an asymmetrically coordinated olefin is replaced by a non-prochiral olefin [9]:

$$\textit{trans}\text{-}[PtCl_2(L)(S\text{-mbn})] + \text{dce (or dmb)} \rightarrow \textit{trans}\text{-}[PtCl_2(L)(\text{dce or dmb})] + \text{mbn} \qquad (3)$$

(mbn = 2-methyl-2-butene, dce = *cis*-1,2-dichloroethylene, dmb = 2,3-dimethyl-2-butene; L = 4-substituted pyridine or aniline)

The mbn complex was resolved by the fractional precipitation of *trans*-(*N*-mbn)[PtCl(L-prol)(mbn)], converted into $(C_6H_5)_4P[PtCl_3(S\text{-mbn})]$ with hydrochloric acid, and then into *trans*-$[PtCl_2(L)(S\text{-mbn})]$ by treatment of the tetraphenylphosphonium salt with L in acetone or ethanol. The rate of the reaction was determined by monitoring the decrease with time of the CD strength at 23500 or 24100 cm^{-1} in benzene or acetone solution containing the complex ($\sim 10^{-3}$ M), dce (or dmb) (0.05 to 0.5 M) and also, where necessary, L. The observed (pseudo) first order rate constant k_1 was found to be proportional to the concentration of dce or dmb.

$$\text{rate} = k_2[\text{complex}][\text{olefin}]$$

The activation enthalpies and entropies are within the usual range for substitution reactions of square planar platinum(II) complexes, and hence the substitution must have an S_N2 mechanism. Figure 8 shows a plot of k_2 against the values of the pk_a for L. It is seen that the greater the pK_a the smaller the log k_2 values. The gradients are 0.94 ± 0.44 and 1.11 ± 0.28, respectively, for substitution by dce and dmb, and are considered to be equal within the experimental error.

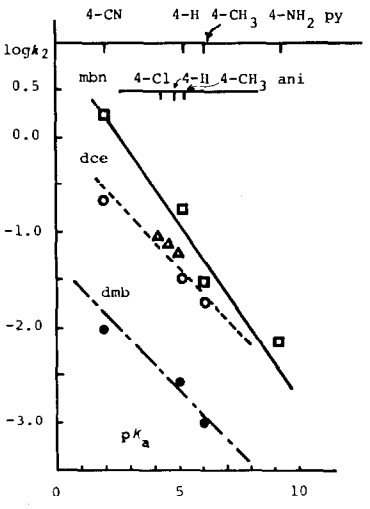


Fig. 8. Relationship between the k_2 of the substitution of non-prochiral olefin for mbn in *trans*-[$PtCl_2$(*N*-base)(*S*-mbn)] in CH_2Cl_2 and pK_a of the base.

Larger k_2 values for substitution by dce than by dmb can be understood in terms of steric effects on the formation of the transition state. Free dmb has a higher Lewis basicity and so is expected to be more nucleophilic than dce, but its displacement of coordinated *S*-mbn is slower than that by dce by one order of magnitude. The approach of the bulkier olefin dmb to the platinum(II) ion in the complex would involve much greater steric hindrance and so lower the substitution rate [9].

The decrease of k_2 with the pK_a of the nitrogen base can be accounted for as follows. If the σ-donating effect of the nitrogen base *trans* to the coordinated olefin predominates, the stronger is the base the more it will increase the electron density on platnum(II) and so retard the nucleophilic attack of the incoming olefin to form a σ Pt–olefin bond.

Figure 9 shows the variation with temperature of the ethylene proton NMR signal of *trans*-(*N*-olefin)[PtBrCl(C_2H_4)(L)] in deuterated nitromethane. The pres-

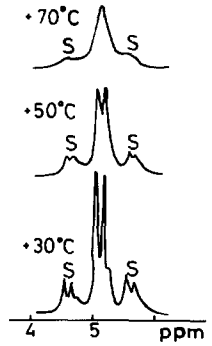


Fig. 9. Change in PMR signal of ethylene ptoton of *trans*-(*N*-C_2H_4)[PtBrCl(4-X-pyridine)(C_2H_4)] in CD_3NO_2 at 30–70 °C. (S, satellite due to ^{195}Pt; vs. tetramethylsilane).

Table 1

Thermodynamic data for the olefin rotation in *trans*-(N-C_2H_4)[PtBrCl(4-X-pyridine)(C_2H_4)]

X	solvent	T(K) [a]	$\Delta G^{\ddagger}$ (kJ mol^{-1})
CH_3	CD_3NO_2	323±3	66±2
H	CD_3NO_2	328±3	67±2
Cl	$(CD_3)_2CO$	295±3	60±2
CN	$(CD_3)_2CO$	298±3	61±2
CN	CD_3NO_2	300±3	61±2

[a] Coalescence temperature.

ence of satellite peaks due to ^{195}Pt indicates that the coalescence is an intramolecular phenomenon. The coalescence temperature and the $\Delta G^{\ddagger}$ values in Table 1 show that the differences between the complexes are very modest. The coalescence arises from the rotation of the ethylene molecule about the Pt–olefin axis accompanied by breaking of the Pt–olefin π-bond, and the data indicate that a change in the substituent at the 4-position of pyridine does not much change the strength of that bond [21]. Hence we think that our suggestion that the results in Fig. 8 can be accounted for in terms of the contribution of the olefin to Pt σ-bonding is verified.

The slope of the plot in Fig. 8 for the introduction of mbn in place of coordinated S-mbn is different from that for the other two. Since mbn is a prochiral olefin, the rate found by the present method represents rate of substitution with inversion of configuration only. The stereoselectivity of the olefin substitution (vide infra) must involve many factors, and so a different slope is observed. The total rate of substitution involving both retention and inversion of configuration would be much greater than that shown in Fig. 8.

Stereoselective olefin exchange

Use of complexes as catalysts in hydrogenation of olefins results in stereoselective reactions. In order to establish the origin of the selectivity we examined the stereoselectivity of the substitution of prochiral olefin for asymmetrically-coordinated olefin.

$$[PtCl_3(S,S\text{-tbn})]^- + \text{tbn}^{\star} \rightarrow [PtCl_3(S,S\text{- or } R,R\text{-tbn}^{\star})]^- + \text{tbn} \qquad (4)$$

The rate of this olefin exchange can be determined by two methods, viz. isotopic labelling with (E)-2-butene[^3H] and measurement of the CD. The former gives the

Table 2

Second order rate constants and activation parameters for the substitution of tbn for [$PtCl_3$(S,S-tbn[^3H])]$^-$ in acetone

t (°C)	k_{ret} [a]	k_{inv}	k_{ret}/k_{inv}
8.0	62.0	8.7	7.2
−5.0	31.7	3.4	9.3
−20.0	10.1	1.3	7.8
$\Delta H^{\ddagger}$	36.3	37.6	kJ mol^{-1}
$\Delta S^{\ddagger}$	−138	−149	J mol^{-1} K^{-1}

[a] k's in 10^{-3} M^{-1} s^{-1}.

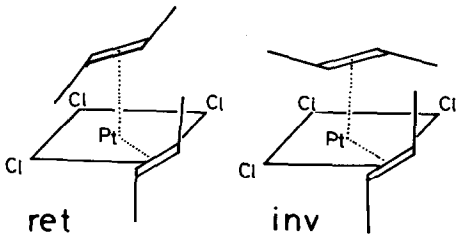


Fig. 10. Transition state on the nucleophilic attack of tbn upon $[PtCl_3(S,S\text{-tbn})]^-$.

total rate for reactions involving retention and inversion of configuration, whereas the latter gives twice the rate of reaction involving inversion of configuration. Hence we can obtain k_{ret} and k_{inv} values by using both types of rate measurement. (Use of non-prochiral *cis*-2-butene as nucleophile gave identical rates by the two methods, indicating the absence of any local exchange of protons.)

Table 2 shows that there is a marked stereoselectivity towards retention of configuration. The selectivity is presumably governed by the steric effect depicted in Fig. 10. The activation parameters show that the entropy term is responsible for the selectivity [8]. When complexes containing L-aminocarboxylate, *trans*-(*N*-tbn)-[PtCl(L-am)(*S*,*S*-tbn)] are used, the selectivity is more marked [22].

Asymmetric induction on olefin exchange

When *trans*-(*N*-ethylene)-[PtCl(L-prol)(C_2H_4)] ($\sim 10^{-3}$ *M*) was treated with an excess of tbn ($\sim 10^{-1}$ *M*) in acetone at $-25\,^\circ C$ the CD spectrum changed in the way shown in Fig. 11. The strength at 26300 cm^{-1} first increases to a maximum then decreases to reach a constant value. There was no appreciable change in the absorption spectrum [23]. A similar change in the CD strength was also observed when related ethylene complexes containing other L-aminocarboxylates were used. The change in CD in the initial stage must be related to the substitution of prochiral

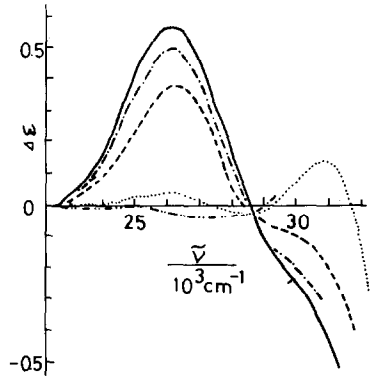


Fig. 11. Change of CD spectrum with time on the reaction of *trans*-(*N*-C_2H_4)[PtCl(*N*-methyl-L-prolinate)(C_2H_4)] with tbn in acetone at $-28\,^\circ C$. ····· original - - - - - - 1 min; ·–·–· 2 min; ——— 4 min; ···–·–·– infinite time.

Table 3

Kinetic and thermodynamic optical yield of *trans*-(*N*-olefin)[PtCl(L-am)(olefin)] of the reaction of ethylene complexes with prochiral olefins

L-am [a]	t (°C)	solvent	p_{max} (%)	p_{eq} (%)	Olefin
L-pro	8.0	acetone	35	−12 (*SS*)	tbn
	−27.5	acetone	34		tbn
	8.0	acetone	7	+6 (*S*)	mbn
N-me-L-pro	8.0	acetine	53	−6 (*RR*)	tbn
	8.0	acetone	7	−1 (*R*)	mbn
N-bz-L-pro	8.0	acetone	24	−1 (*RR*)	tbn
	8.0	CH_2Cl_2	28		tbn
N-bz-L-val	8.0	acetone	40	−10 (*RR*)	tbn
	8.0	CH_3CN	39	−9 (*RR*)	tbn
	8.0	L-ma [a]	35		tbn
L-val	−30.0	acetone	0	0	tbn
L-ala	−30.0	acetone	0	0	tbn
L-hyp	8.0	acetone	37	+8 (*SS*)	tbn
	8.0	acetone	6	+3 (*S*)	mbn
N-me-L-hyp	8.0	acetone	32	−7 (*RR*)	tbn
	8.0	acetone	3	0	mbn
L-*allo*-hyp	8.0	acetone	37	+6 (*SS*)	tbn
	8.0	acetone	19	+7 (*S*)	mbn
cis-(*N*-//)-L-pro	8.0	acetone	33		tbn
	−13.0	acetone	34	−27 (*RR*)	tbn

[a] pro, prolinate; me, methyl; bz, benzyl; val, valinate; ala, alaninate; hyp, hydroxyprolinate; L-ma, L-menthylacetate; tbn, (*E*)-2-butene; mbn, 2-methyl-2-butene.

tbn for the ethylene, and that at the later stages to the epimerization of the product (eq. 5).

$$\textit{trans}\text{-}(N\text{-ethylene})\text{-}[\mathrm{PtCl}(\text{L-am})(\mathrm{C_2H_4})] + \text{tbn} \rightarrow \textit{trans}(N\text{-tbn})\text{-}[\mathrm{PtCl}(\text{L-am})(S,S\text{- or } R,R\text{-tbn})] + \mathrm{C_2H_4} \quad (5)$$

Both stages can be kinetically analyzed, and the optical yields in the first and the second stage calculated by use of the following equations,

$$P_{max} = (\Delta\varepsilon_{max} - \Delta\varepsilon_{vic})/(\Delta\varepsilon_{resolv} - \Delta\varepsilon_{vic}) \quad (6)$$

$$P_{eq} = (\Delta\varepsilon_{eq} - \Delta\varepsilon_{vic})/(\Delta\varepsilon_{resolv} - \Delta\varepsilon_{vic}) \quad (7)$$

where the various $\Delta\varepsilon$'s represemt the CD strength at 26300 cm^{-1} at the maximum, that at the equilibrium state, that of the initial ethylene complex, and that of the resolved tbn complex. The results are tabulated in Table 3. The plus and minus signs correspond respectively to predominant formation of the *S,S*- and *R,R*-tbn complex.

It can be seen that the L-alaninato and L-valinato complexes not containing asymmetric nitrogen do not give asymmetrically coordinated tbn. The first stage must be governed by steric effects, and the *S,S*-configuration is always favored. The magnitude of the p_{max} value seems to be related to the nature of the substituent on the asymmetric nitrogen, but not on the location of the OH substituent on the pyrrolidine ring. The incoming tbn must approach the complex from the opposite side to that occupied by pyrrolidine. Molecular model studies indicate that the

approach of tbn to Pt involves less steric hindrance in the *S,S*-configuration rather than in the *R,R*-configuration. *trans*-2-Butene gives larger p values than 2-methyl-2-butene, presumably because of the presence of two asymmetric centers. There is no appreciable solvent effect on p_{max} values even when optically active solvents are used. However, it is difficult to interpret the variation of the p_{max} values with the structures of the complexes.

The p_{eq} values do not parallel the p_{max} values, and even the signs are different. Since the CD strength of the solution remains unchanged after the equilibrium state is reached, they must be governed by a thermodynamic effect. When the CD sign of a given complex at the equilibrium state is examined in relation to Fig. 6, there is a distinct relationship. Positive and negative signs at 35000 cm^{-1} correspond with preferential formation of *S,S*- and *R,R*-tbn, respectively. We considered this result in terms of an interaction between the asymmetric nitrogen and the olefin *trans* to it through the platinum(II) ion. The induction of asymmetry governed by the different stabilities of *S,S*- and *R,R*-tbn *trans* to asymmetric nitrogen may provide a novel example of a case in which the selectivity is related to the electronic effect rather than steric effect.

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