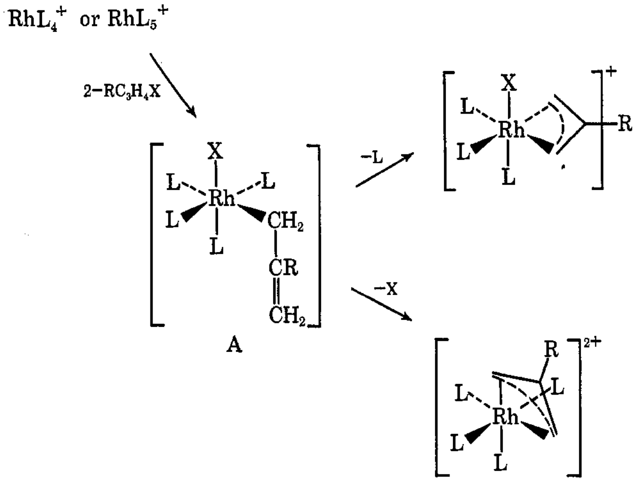
groups in the nmr spectra of these derivatives are very complex and are thus not further discussed. However, the ligand methyl resonances in the spectra of the derivatives $\{Rh(2\text{-}RC_3H_4)[P(OC_2H_5)_3]_4\}[anion]_2$ occur as two triplets of equal intensity, which is consistent with structure IV.

The reactions of the cations $Rh[P(OR)_3]_5^+$ ($R = CH_3, C_2H_5$) and RhL_4^+ $\{L = P(OR)_3$ [$R = CH_3, C_2H_5$, $i\text{-}C_3H_7$], $P(CH_3)_2C_6H_5\}$ with allyl halides, $2\text{-}R'C_3H_4X$, can be rationalized in terms of a general mechanism involving a σ-allyl species, A, as intermediate, *viz.*



The unbonded olefinic group in the intermediate A effects either displacement of the halide group to give a dipositive cation $Rh(\pi\text{-}2\text{-}R'C_3H_4)L_4^{2+}$ or replacement of a neutral ligand to form the unipositive cation $RhX(\pi\text{-}2\text{-}R'C_3H_4)L_3^+$. Attempts were made to isolate the proposed σ-allyl intermediates but these were unsuccessful; this is attributed to the high intramolecular reactivity of these species. However, the preferential formation of the dipositive cations $Rh(\pi\text{-}2\text{-}R'C_3H_4)[P(OR)_3]_4^{2+}$ ($R' = H, CH_3$; $R = CH_3, C_2H_5$) in methanol is consistent with the proposed mechanism; methanol being a powerful ionizing solvent promotes the displacement of a halide group in preference to a neutral ligand from the intermediate A. It is interesting that, of the cations RhL_4^+ and RhL_5^+ treated with allyl halides, only those containing the ligands $P(OCH_3)_3$ and $P(OC_2H_5)_3$ gave dipositive cations of the type $Rh(\pi\text{-}2\text{-}RC_3H_4)L_4^{2+}$. The reaction of allyl chloride with the cations RhL_4^+ [$L = P(O\text{-}i\text{-}C_3H_7)_3$, $P(CH_3)_2C_6H_5$] using methanol as solvent gave the chloro species $RhCl(\pi\text{-}C_3H_5)L_3^+$ as the sole products.

Halogen displacement, similar to that proposed above, has been reported for a series of iridium–σ-allyl complexes.[16] Thus $IrCl_2(\sigma\text{-}C_3H_5)(CO)[P(CH_3)_2C_6H_5]_2$ has been found to be converted to the cationic complex $\{IrCl(\pi\text{-}C_3H_5)(CO)[P(CH_3)_2C_6H_5]_2\}B(C_6H_5)_4$ in methanol in the presence of sodium tetraphenylboron. The conversion of σ- to π-allyl complexes as a result of ligand replacement by the olefinic group of the σ-allyl group is well established. For instance $Mn(CO)_5(\sigma\text{-}C_3H_5)$ readily loses carbon monoxide on heating to give the π-allyl derivative $Mn(CO)_4(\pi\text{-}C_3H_5)$.[17] However, few examples are known in which the olefinic group of a σ-allyl group effects either ligand replacement or halogen displacement in the same molecule. A pertinent example is the reaction of the cobalt(I) complex $Co(\pi\text{-}C_5H_5)(CO)_2$ with allyl iodide in tetrahydrofuran to give the two products $[Co(\pi\text{-}C_3H_5)(\pi\text{-}C_5H_5)(CO)]I$ and $CoI(\pi\text{-}C_3H_5)(\pi\text{-}C_5H_5)$.[18]

[16] A. J. Deeming and B. L. Shaw, *J. Chem. Soc. A*, 1562 (1969).

[17] H. D. Kaesz, R. B. King, and F. G. A. Stone, *Z. Naturforsch. B*, **15**, 682 (1960).

[18] R. F. Heck, *J. Org. Chem.*, **28**, 604 (1963).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, TOHOKU UNIVERSITY, SENDAI, JAPAN, AND THE TODD WEHR CHEMISTRY BUILDING, MARQUETTE UNIVERSITY, MILWAUKEE, WISCONSIN 53233

Platinum(II)–Olefin Complexes Containing Amino Acids. II. Preparation and Structure of Chloro(L-prolinato)(olefin)platinum(II) Complexes[1]

BY KAZUO KONYA, JUNNOSUKE FUJITA, AND KAZUO NAKAMOTO*

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Seven complexes of the type PtCl(L-prolinato)(olefin) have been synthesized, and their diastereoisomers isolated by crystallization from suitable solvents. The absolute configurations of these isomers have been elucidated from their CD spectra. The rate of racemization of diastereoisomers has been related to the relative strength of the metal–olefin bond.

An enantiomeric pair is produced when an olefin such as propylene or *trans*-2-butene coordinates to a metal through a π bond. In 1964, Paiaro and Panunzi[2] examined such an isomerism by resolving diastereoisomers of the type *trans*-$PtCl_2$((*R*)- or (*S*)-α-phenethylamine)(olefin).[3] However, the diastereoisomers of this type often give an oily product and are difficult to isolate in a crystalline form. In the previous paper,[4] we have reported the preparation and structure of several platinum(II)–ethylene complexes containing various amino acids. These olefin complexes containing amino acids can be prepared and their diastereoisomers can be iso-

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* To whom correspondence should be addressed at Marquette University.

[1] This work was supported by American Chemical Society–Petroleum Research Fund unrestricted research grant (3318–C3,5).

[2] G. Paiaro and A. Panunzi, *J. Amer. Chem. Soc.*, **86**, 5148 (1964); A. Panunzi and G. Paiaro, *ibid.*, **88**, 4843 (1966).

[3] The definition of the *R* or *S* configuration is given by R. S. Cahn, C. Ingold, and V. Prelog, *Angew. Chem., Int. Ed. Engl.*, **5**, 385(1966).

[4] K. Konya, J. Fujita, and K. Nakamoto, *Inorg. Chem.*, **9**, 2794 (1970).

lated relatively easily. This is particularly true for those containing L-proline. Different from simple amino acids such as glycine and alanine, proline has a bulky pyrrolidine ring which exerts steric repulsion against the olefin in the complex. The magnitude of such steric repulsion will be markedly different between diastereoisomers. This, in turn, suggests that the solubilities of diastereoisomers of the L-proline complex may be quite different and these isomers may be separated relatively easily. We have, therefore, attempted to prepare and isolate the diastereoisomers of the type *N-trans*-PtCl(L-prol)(olefin)[5] in this investigation.

Experimental Section

Preparation of Compounds. ***N-trans*-PtCl(L-prol)(C_2H_4).**—This complex was synthesized according to the method reported previously[4] and used as the starting material for the preparation of other compounds.

***N-trans*-PtCl(L-prol)(olefin).**—The following six olefins were used: propylene, *trans*-2-butene, *cis*-2-butene, isobutene, 2-methyl-2-butene, and styrene. All complexes were prepared by the following method. *N-trans*-PtCl(L-prol)(C_2H_4) was dissolved in acetone and treated with an olefin for 3 hr at 30–40° by refluxing the mixture in a one-neck flask equipped with a condenser which is cooled by Dry Ice–acetone. The solution was filtered and condensed under reduced pressure. The crude (often oily) product was obtained by evaporating the solvent. It was recrystallized from acetone or chloroform by adding *n*-hexane.

K[$PtCl_2$(L-prol)].—This complex was prepared by a method similar to that used for the preparation of K[$PtCl_2$(L-ala)].[6] Table I shows the results of microanalysis.

TABLE I

RESULTS OF MICROANALYSIS

	% C		% H		% N	
	Calcd	Found	Calcd	Found	Calcd	Found
PtCl(L-prol)(ethylene)	22.56	22.88	2.97	3.30	3.67	3.67
PtCl(L-prol)(propylene)	24.85	25.14	3.36	3.65	3.62	3.65
PtCl(L-prol)(*trans*-2-butene)	26.97	27.44	3.77	4.02	3.50	3.47
PtCl(L-prol)(*cis*-2-butene)	26.97	27.76	3.77	3.96	3.50	3.47
PtCl(L-prol)(isobutene)	26.97	27.18	3.77	4.05	3.50	3.49
PtCl(L-prol)(2-methyl-2-butene	28.96	29.55	4.13	4.51	3.38	3.31
PtCl(L-prol)(styrene)	34.79	35.11	3.37	3.69	3.12	3.03
K[$PtCl_2$(L-prol)]	14.43	14.13	1.70	1.41	3.37	3.48

Spectral Measurements.—As was demonstrated by Paiaro and Panunzi,[2] the diastereoisomeric pairs can be separated into their optical isomers by recrystallization from suitable solvents. Table II gives the signs of the CD bands of the diastereoisomers thus obtained. In the case of the propylene complex, both solvents used gave only the (+) isomer. Table III lists the rates of racemization (half-life) measured in the two solvents. These values were determined by measuring the intensity of a CD band as a function of time at the specific wavelength indicated.

TABLE II

CD SIGNS OF COMPLEXES RESOLVED BY USING DIFFERENT SOLVENTS[a]

Solvent used	Acetone–*n*-hexane	Chloroform–*n*-hexane
PtCl(L-prol)(propylene)	(+)	(+)
PtCl(L-prol)(*trans*-2-butene)	(+)	(−)
PtCl(L-prol)(2-methyl-2-butene)	(+)	(−)
PtCl(L-prol)(styrene)	(+)	(−)

[a] (+) and (−) represent the sign of $\Delta\epsilon$ ($= \epsilon_l - \epsilon_r$) at 380 m$\mu$ (26,300 cm^{-1}) in ethanol. In this case, (+) and (−) signs correspond to the *S* and *R* configurations of the olefin, respectively.

TABLE III

HALF-LIFE OF RACEMIZATION (18°)

	In C_2H_5OH[a]	In concd HCl[b]
PtCl(L-prol)(styrene)	100 sec (dark)	. . .[c]
PtCl(L-prol)(propylene)	6 min (dark)	. . .[c]
PtCl[(L-prol)(*trans*-2-butene)	Almost no racemization	6 hr(dark) 100 min (light)
PtCl(L-prol)(2-methyl-2-butene)	Almost no racemization	16 hr (light)

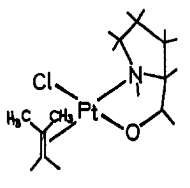
[a] Measured at 380 mμ (26,300 cm^{-1}). [b] Measured at 420 mμ (23,800 cm^{-1}). [c] Too rapid to be measured.

Ultraviolet and visible (uv) absorption spectra were obtained with a Hitachi 124 recording spectrophotometer. The CD curves were recorded on a JASCO Model ORD/UV-5 spectrophotometer equipped with a CD attachment. All the measurements were carried out at room temperature.

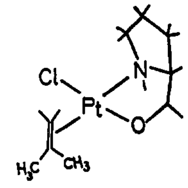
Results and Discussion

The complex PtCl(L-prol)(olefin) may take the N-trans or O-trans structure which can be distinguished by uv and ir spectroscopy.[4] In the present case, all six complexes prepared were found to be N-trans since their uv spectra in ethanol are very similar to that of *N-trans*-PtCl(L-ala)(C_2H_4).[4] Several attempts to prepare the O-trans isomers of these complexes by the reported method[4] were unsuccessful. This may be due to steric repulsion between the olefin and pyrrolidine ring of the L-prolinato group.

Except the *trans*-2-butene complex, the N-trans isomer may take configurations a and b if rotation about the Pt–olefin bond does not occur. It has been shown, however, theat such a rotation occurs relatively easily at room temperature.[7] In fact, the pmr spectrum of *N-trans*-PtCl(L-prol)(isobutene) gives only one methyl signal at 1.90 ppm (in $CDCl_3$, TMS as the internal standard). Therefore, the presence of such rotational isomers was ignored in the present work.



(a)



(b)

Figure 1 compares the uv and CD spectra of K[$PtCl_2$(L-prol)] in water and *N-trans*-PtCl(L-prol)(C_2H_4) in ethanol. The uv spectrum of the former compound exhibits three bands at *ca.* 24,000 (singlet–triplet), 30,000 (singlet–singlet), and 35,000 cm^{-1} (singlet–singlet) which were assigned to the d–d transitions with spin multiplicities indicated in parentheses.[8] In the latter compound, the presence of these d–d transitions is obscured by the appearance of a strong charge-transfer (metal–olefin) band at *ca.* 35,000 cm^{-1}.[9] Nevertheless, the CD spectra of both compounds are surprisingly similar to each other, although the peaks of the ethylene complex are located at higher frequencies than those of the dichloro complex. This result indicates that a CD band associated with the charge-transfer transition does not appear in the region of d–d transitions. Upon coordination, *cis*-2-butene forms

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[5] "*N-trans*" indicates the structure in which the nitrogen atom of the chelated L-prolinato anion (L-prol) is coordinated to the Pt atom in the trans position to the olefin (see ref 4).

[6] H. Ley and K. Fichen, *Ber.*, **45**, 377 (1912).

[7] C. E. Holloway, G. Hulley, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc. A*, 53 (1969); 1653 (1970).

[8] H. Ito, to be submitted for publication.

[9] R. G. Denning, F. R. Hartley, and L. M. Venanzi, *J. Chem. Soc. A*, 1322 (1967)

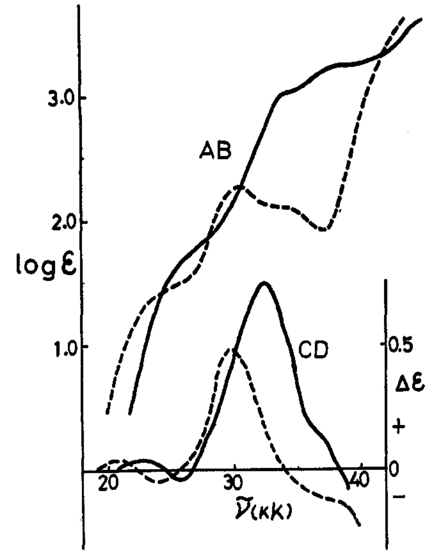

Figure 1.—Absorption (AB) and CD spectra of *N-trans*-PtCl(L-prol)(C_2H_4) in C_2H_5OH (——) and K[$PtCl_2$(L-prol)] in water (- - - - - -).

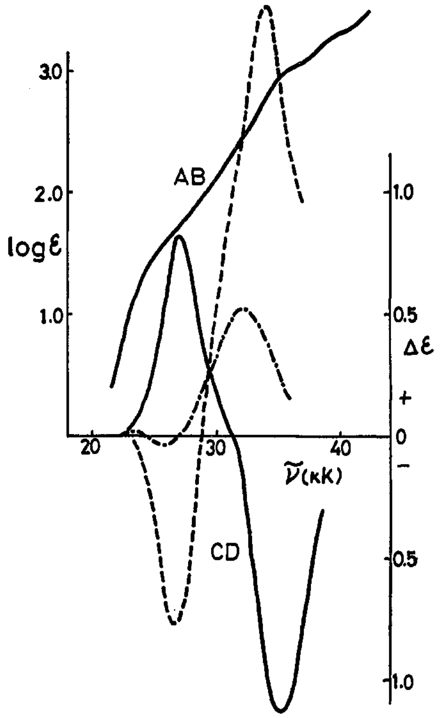

Figure 2.—Absorption (AB) and CD spectra of the (+)$^{\Delta\epsilon}_{380}$ (——) and (−)$^{\Delta\epsilon}_{380}$ (- - - - - -) isomers of PtCl(L-prol)(*trans*-2-butene) in C_2H_5OH and the estimated vicinal effect curve of L-proline [= ((+) + (—))/2] (-·-·).

two asymmetric carbon atoms which have opposite configurations, yielding a meso compound. Isobutene forms no asymmetric carbon atoms. Thus, the CD spectra of these olefin complexes are very much similar to that of the ethylene complex.

In concentrated HCl solution, the PtCl(L-prol)(olefin) type complexes dissociate rapidly into the L-prolinato and $PtCl_3$(olefin)$^-$ ions.[4] Both (+)$^{\Delta\epsilon}_{380}$ and (−)$^{\Delta\epsilon}_{380}$ isomers[10] of *N-trans*-PtCl(L-prol)(*trans*-2-butene) in concentrated HCl solution show an enantiomeric CD curve with each other, indicating that the complexes were dissociated into the L-prolinato and $PtCl_3$(*trans*-2-butene)$^-$ ions and the optical resolution of the latter ion has been carried out almost completely. If the olefin is styrene or propylene, the complex is racemized very fast in concentrated HCl solution and no CD is observed. The $PtCl_3$(olefin)$^-$ ion thus obtained is relatively stable in concentrated HCl solution and its uv spectrum is almost the same as that of Zeise's salt.

Figure 2 shows the uv and CD spectra of both isomers of *N-trans*-PtCl(L-prol)(*trans*-2-butene) in ethanol. Their CD curves are not enantiomeric because the vicinal effect of the L-prolinato group contributes equally to these CD curves. The vicinal effect curve of the L-prolinato group can be obtained by adding these two CD curves and dividing the resultant CD values by 2 at each wavelength (see Figure 2). The curve thus obtained is very similar to that of the ethylene complex shown in Figure 1. This result suggests that the vicinal effects of the L-prolinato and olefin groups contribute additively to the CD curve probably because there is no appreciable interaction between these two groups.

Figure 3 compares the CD spectra of (+)$^{\Delta\epsilon}_{380}$-PtCl(L-prol)(*trans*-2-butene) in ethanol and concentrated HCl with that of Pt_2Cl_4((*S*,*S*)-*trans*-cyclooctene)$_2$,[11] in which the absolute configuration of the olefin ligand has been determined by chemical methods.[12] The CD curve of (+)$^{\Delta\epsilon}_{380}$-PtCl(L-prol)(*trans*-2-butene) in concentrated HCl solution shows a strong positive band at 23,800 cm^{-1}, and the whole pattern of the CD curve is very similar to that of the cyclooctene complex. Thus, the configuration of *trans*-2-butene in the above complex may be assigned to *S*,*S*. The same isomer shows a strong positive band at 27,000 cm^{-1} in ethanol solution. As is shown in Figure 2, the L-prolinato group con-

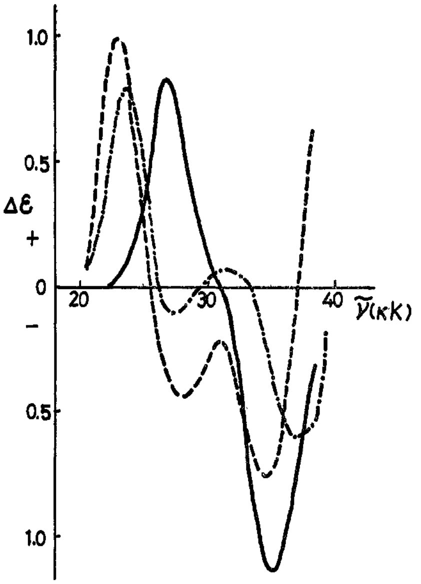

Figure 3.—CD spectra of (+)$^{\Delta\epsilon}_{380}$-PtCl(L-prol)(*trans*-2-butene) in C_2H_5OH (——) and in concentrated HCl (—·—) and of Pt_2Cl_4((*S*,*S*)-*trans*-cyclooctene)$_2$ (- - - - - -).[11]

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(10) (+)$^{\Delta\epsilon}_{380}$ indicates a diastereoisomer which gives a positive sign of $\Delta\epsilon$ ($= \epsilon_l - \epsilon_r$) at 380 mμ (26,300 cm^{-1}).

(11) A. D. Wrixon, E. Premuzic, and A. L. Scott, *Chem. Commun.*, 639 (1968).

(12) A. C. Cope and A. S. Mehta, *J. Amer. Chem. Soc.*, **86**, 5626 (1964).

tributes very little to the CD curve in this region. Thus, the band at 27,000 cm^{-1} is attributed largely to the olefin group. The configuration of *trans*-2-butene in the $(+)^{\Delta\epsilon}_{380}$ isomer should be the same in the two solvents. Therefore, the positive band at 27,000 cm^{-1} in ethanol may correspond to the positive band at 23,800 cm^{-1} in concentrated HCl solution. As stated before, the L-prolinato group of the olefin complex is replaced by the chloride ion in concentrated HCl solution. Thus, the observed red shift of the 27,000-cm^{-1} band in going from ethanol to concentrated HCl solution may be attributed to the weaker ligand field of the chloride ion relative to that of the L-prolinato group. The above conclusions are in good agreement with the observation that *cis*-$PtCl_2$((*R*,*R*)-*trans*-2-butene)((*S*)-α-methylbenzylamine), whose absolute configuration has been determined by X-ray analysis, gives a negative band at 26,700 cm^{-1}.[13] Therefore, the absolute configuration of the olefin in a Pt(II) complex can be assigned empirically based on the sign of the CD band in the 23,000–28,000-cm^{-1} region (d–d transitions).[13,14] For example, $(+)^{\Delta\epsilon}_{380}$-PtCl(L-prol)(2-methyl-2-butene) exhibits a positive band at 23,800 cm^{-1} in concentrated HCl solution and at 26,300 cm^{-1} in ethanol. Thus, the configuration of the olefin in this complex must be *S*.

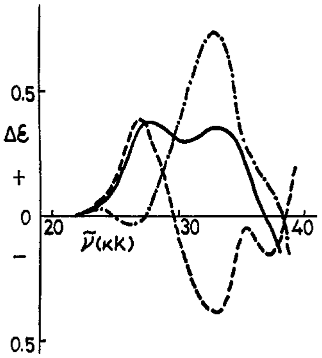

Figure 4.—CD spectra of $(+)^{\Delta\epsilon}_{380}$-PtCl(L-prol)(propylene) in C_2H_5OH: (a) ——, fresh solution; (b) –·–·, solution racemized completely (diastereoisomeric pair); (c) - - - - - -, estimated vicinal effect curve of propylene (= (a − b)).

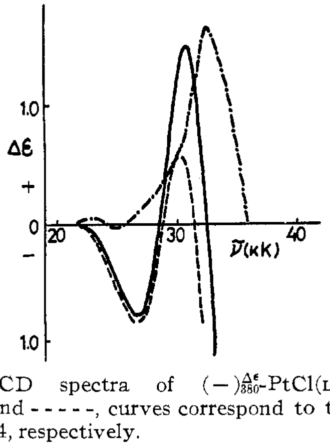

Figure 5.—CD spectra of $(-)^{\Delta\epsilon}_{380}$-PtCl(L-prol)(styrene): ——, —·—·, and - - - - -, curves correspond to the curves a, b, and c of Figure 4, respectively.

Figures 4 and 5 show the CD curves of $(+)^{\Delta\epsilon}_{380}$ PtCl(L-prol)(propylene) and of $(-)^{\Delta\epsilon}_{380}$-PtCl(L-prol)(styrene) in ethanol. These complexes racemize rapidly in concentrated HCl solution and fairly rapidly even in ethanol. The vicinal effect curve of the olefin indicated by the broken line was obtained by subtracting the CD value of a completely racemized sample from that of a fresh solution at each wavelength. The signs of these CD curves at *ca.* 26,000 cm^{-1} indicate that the configurations of propylene and styrene in these complexes are *S* and *R*, respectively.

Rate of Racemization.—The half-life of racemization listed in Table III was obtained by measuring the intensity of the CD band at 380 mμ (26,300 cm^{-1}). The *trans*-2-butene and 2-methyl-2-butene complexes do not racemize in ethanol at 18° but do so upon addition of free olefin. The styrene and propylene complexes racemize relatively fast even in ethanol solution.

Figure 6 gives the CD curve of the $(+)^{\Delta\epsilon}_{380}$ isomer of the *trans*-2-butene complex in concentrated HCl and of the propylene complex in ethanol as a function of time. In the former, the rate of racemization of the $PtCl_3(\textit{trans}\text{-2-butene})^-$ ion was measured whereas that of the olefin part of PtCl(L-prol)(propylene) was measured in the latter. The presence of the isosbestic points at least indicates that these complexes do not decompose during the racemization. It was also noted that the racemization reaction is photosensitive; the rate of racemization of the *trans*-2-butene complex is 4 times faster in light than in dark.

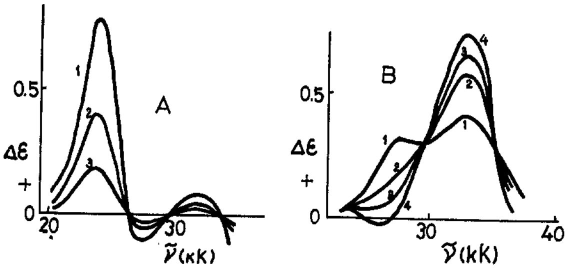

Figure 6.—CD variation with time. (A) $(+)^{\Delta\epsilon}_{380}$-PtCl(L-prol)(*trans*-2-butene) in concentrated HCl: (1) fresh sample; (2) after 100 min; (3) after 200 min. (B) $(+)^{\Delta\epsilon}_{380}$-PtCl(L-prol)(propylene) in C_2H_5OH: (1) fresh sample; (2) after 6 min; (3) after 12 min; (4) after 1 day.

The racemization may occur through the dissociation of the olefin or the rotation of the olefin molecule about the C=C axis. The latter involves transient rupture of the σ as well as the π bond between the metal and the olefin. The rotation about the Pt–olefin bond does not cause racemization. The rate of racemization decreases in the following order of olefin: styrene > propylene > *trans*-2-butene > 2-methyl-2-butene. This order may be regarded as an increasing order of the strength of the Pt–olefin bond, since, in general, the introduction of the methyl group strengthens the Pt–olefin bond whereas that of the phenyl group weakens it. Detailed kinetic studies on racemization of these olefin complexes are now in progress and will be reported later.

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[13] P. Corrandini, G. Paiaro, A. Panunzi, S. F. Mason, and G. H. Searle, *J. Amer. Chem. Soc.*, **88**, 2864 (1966).

[14] E. Benedetti, P. Corrandini, and C. Pedone, *J. Organometal. Chem.*, **18**, 203 (1969).