ENANTIOSELECTIVE COORDINATION OF STYRENE IN TWO TYPES OF

PLATINUM(II) COMPLEXES CONTAINING A BIDENTATE L-ALANINATO LIGAND,

AND SOME ASPECTS ON THE MOLECULAR ORBITAL CHARACTERISTICS OF THE

CORRESPONDING DIASTEREOMERS

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Summary

Enantioselective π-coordination of styrene has been investigated
by using PMR and CD spectroscopy for two types of Pt(II) complexes,
which contain L-alanine as a chiral bidentate ligand in <u>trans</u> or
<u>cis</u>(N,olefin)-form. By virtue of the chemical-shift difference
appearing in the methyl protons of the L-alaninato ligand, the
diastereomeric composition was determined directly for both cases.
The equilibrated nature of the isolated diastereomeric mixtures was
ascertained by their spectral behavior on extra addition of free
styrene. Factors for the enantioselection are discussed in terms of
quantum-chemical properties for some models of the corresponding
diastereomers.

Introduction

Enantioselective coordination of prochiral olefins in the pre-equilibrium step often forms a key process for asymmetric syntheses when chiral metal-complex catalysts are used [1]. Although the optical activity in olefin complexes has been extensively investigated and reviewed [2], factors that control the enantioselection involved seem still ambiguous.

We report here the direct determination of the diastereomeric composition by PMR [3-6] for π-coordination of styrene in two types of Pt(II) complexes, which contain L-alanine as a chiral bidentate ligand in trans or cis(N,olefin)-form. The equilibrated nature of the isolated diastereomeric mixtures was ensured on the basis of the behavior of their PMR and CD spectra toward the extra addition of free styrene.

In an attempt to interpret the observed chirality phenomena in a quantitative manner, quantum-chemical calculations were made for some models of each diastereomeric pair to analyze from both steric and stereo-electronic [7,8] viewpoints.

Results and Discussion

1. PMR and CD spectra of the π-complex diastereomers

The two types of styrene complexes of Pt(II) which contain chlorine and L-alanine were obtained by applying the procedures for ethylene-Pt(II) analogues [9-12]. PMR-spectral characteristics of the vinyl protons of the coordinated styrene (Table 1) show reasonable order in magnitude in view of the trans-influence of N- or O-ligands compared to the Cl ligand [13,14].

Table 1. PMR-spectral parameters for the vinyl protons of [PtCl($\underline{\underline{L}}$-ala)(styrene)] complexes[a]

type of chelation	ligand atom			gem		cis		trans	
	trans	cis	cis	δ_H(ppm)	$^2\underline{J}_{PtH}$(Hz)	δ_H(ppm)	$^2\underline{J}_{PtH}$(Hz)	δ_H(ppm)	$^2\underline{J}_{PtH}$(Hz)
$\underline{trans}$(N,olefin)	N	O	Cl	6.46	60.3	5.20	57.2	4.67	63.3
$\underline{cis}$(N,olefin)	O	N	Cl	6.15	73.8	4.84	66.0	4.36	73.0
(Zeise's type salt)	Cl	Cl	Cl	6.31	73.5	4.92	60.0	4.29	70.8

a) PMR spectra (60 MHz) were recorded in the CD_3OD solution at 35 °C with reference to internal TMS standard.

The PMR spectrum of the diastereomeric mixture of trans(N,olefin)-chloro-L-alaninato-styreneplatinum(II) (1) is given in Fig. 1a. The conspicuous pattern of this spectrum is the presence of two sets of doublet peaks, both of which are assigned to the methyl protons of the L-alaninato ligand (centered at 1.33 and 1.39 ppm, the peak rati of 1.14). By adding a trace amount of free styrene, these peaks coalesced into one doublet peak centered at the averaged position (Fig.
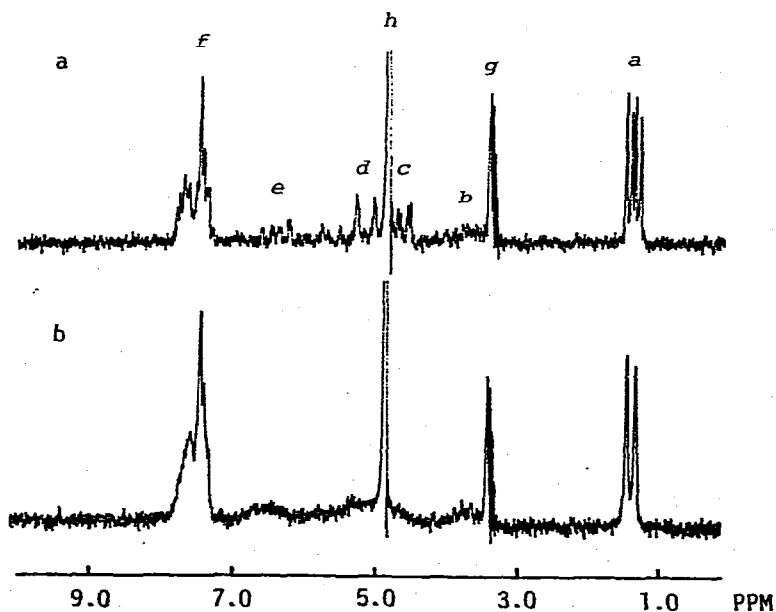

Fig. 1   PMR spectrum (60 MHz) of the diastereomeric mixture of
         trans(N,olefin)-chloro-L-alaninato-styreneplatinum(II),
         [PtCl(CH$_3$(a)CH(b)(NH$_2$)(COO))(CH$_2$(c,d)=CH(e)C$_6$H$_5$(f)], in
         CD$_3$OD at 35 °C (a), and its change by the addition of a
         trace amount of free styrene (b). The absorptions of
         g (CD$_2$H) and h (OH, appeared partly due to exchange with
         amino-protons) are isotopic impurities of the solvent.

1b). This observed peak coalescence, together with both the low-field shift and the line broadening of the vinyl-proton signals (Fig. 1b compared with Fig. 1a), indicates that two different coordinating modes of styrene become indistinguishable on a PMR time scale. This is in accord with the high rate of the exchange reaction in solution between coordinated and dissolved olefins for Zeise's type salts [2,15,16].

Since the coordinated olefin rotates freely about the platinum-olefin bond axis at room temperature [17,18], the observed splitting of the methyl doublet should be ascribed to the diastereomers formed by the coordination of styrene. This was confirmed by the CD absorption peak observed near 400 nm (Fig. 2), which is characteristic of the chirality of coordinated olefins in Pt(II) complexes [19]. The $\Delta\epsilon$ value for the absorption was determined as 0.025 with a correction made for the contribution of the L-alaninato moiety by using the CD spectrum of the corresponding ethylene complex [12]. The value of $|\Delta\epsilon|$ for the single diastereomer (0.38), calculated by taking the corrected value (0.025) and the excess % in the mixture (6.6 %), is reasonable in comparison with those for similar optically active compounds [6,12, 20,21].

It is noticeable that the observed CD spectrum was not at all changed by the addition of free styrene. Since, as shown by PMR, the diastereomers readily come to equilibrium in the presence of a trace amount of free styrene, this fact demonstrates the equilibrated nature of the diastereomeric mixture isolated.

With respect to cis(N,olefin)-chloro-L-alaninato-styreneplatinum(II) (2), a larger chemical-shift difference was observed for the methyl protons of the L-alaninato ligand (two doublets centered at 1.13 and 1.49; Fig. 3). This may be explained by the magnetic
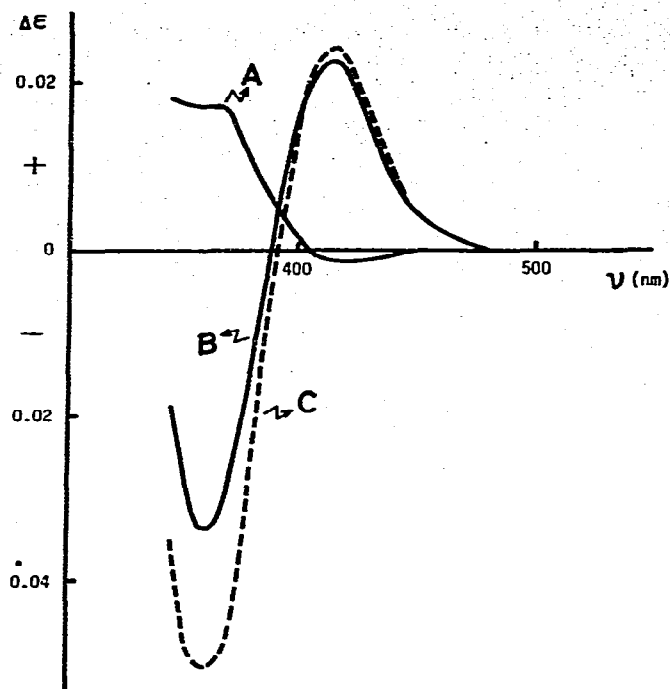
Fig. 2   CD spectra of the π-complexes of ethylene (A) and styrene (B)
of the type, trans(N,olefin)-[PtCl(L-ala)(olefin)], in CH$_3$OH.
The curve C represents the estimated net CD absorption (B - A)
for the enantioselective coordination of styrene.

anisotropic effect of the phenyl group [22], which is closer to the
methyl protons in 2 than in 1. The peak coalescence of these methyl
doublets was found to occur under more severe conditions (excess
amount of free styrene at slightly elevated temperature), probably
reflecting the smaller trans-effect of O-ligands than that of N-ligands
[23,24].

According to the quadrant rule proposed for the relationship
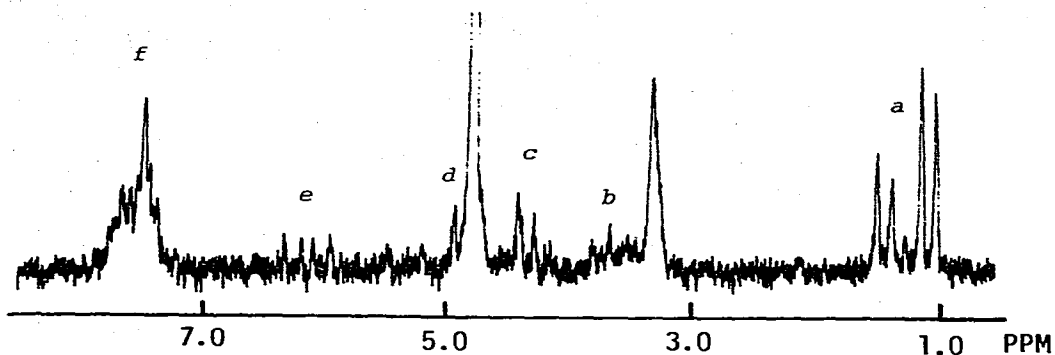between the absolute configuration and the CD sign of the chiral

Fig. 3   PMR spectrum (60 MHz) of the diastereomeric mixture of

cis(N,olefin)-chloro-L-alaninato-styreneplatinum(II),

[PtCl(CH$_3$(a)CH(b)(NH$_2$)(COO))(CH$_2$(c,d)=CH(e)C$_6$H$_5$(f)], in

CD$_3$OD at 35 °C.

olefin-Pt(II) complexes [19], the negative CD absorption with the

peak maximum at 378 nm (Fig. 4) suggests the prevailing configuration

of R for the coordinated styrene in 2 (on the same basis, S in 1).

The results are summarized in Table 2.

In the case of the platinum(II) π-complex of unsymmetrical

olefins with different neighboring cis-ligands, the van der Waal's

radius of the ligand atom is a measure of the relative stability of

the possible two types of rotational isomers [17,18,25]. The more

stable isomers, judged by this criterion (O, N < Cl), are depicted

in Figs. 5 and 6 for each of the diastereomers of 1 and 2, respectively.

It is of interest in these figures that both of the configurations

with the longer Ph-Me distance (S for 1 and R for 2) agree with the

prevailing configurations observed. Quantitative estimation of the

steric interaction between the substituents of asymmetric carbons is

described in the following section.

Table 2. Enantioface differentiation in [PtCl($\underline{\underline{L}}$-ala)(styrene)] complexes

type of chelation	diastereomeric ratio[a] (% excess)	CD[b] $\Delta\epsilon$	ν_{max} (nm)	prevailing configuration of coordinated styrene
$\underline{trans}$(N,olefin)	1.14 ± 0.03 (6.6 %)	0.025	414	$\underline{S}$
$\underline{cis}$(N,olefin)	1.27 ± 0.06 (11.9 %)	-0.062	378	$\underline{R}$

a) Averaged values for two runs, with the standard deviations determined by ten PMR measurements.

b) Contribution from the $\underline{\underline{L}}$-alaninato ligand was corrected by using the corresponding ethylene complexes.
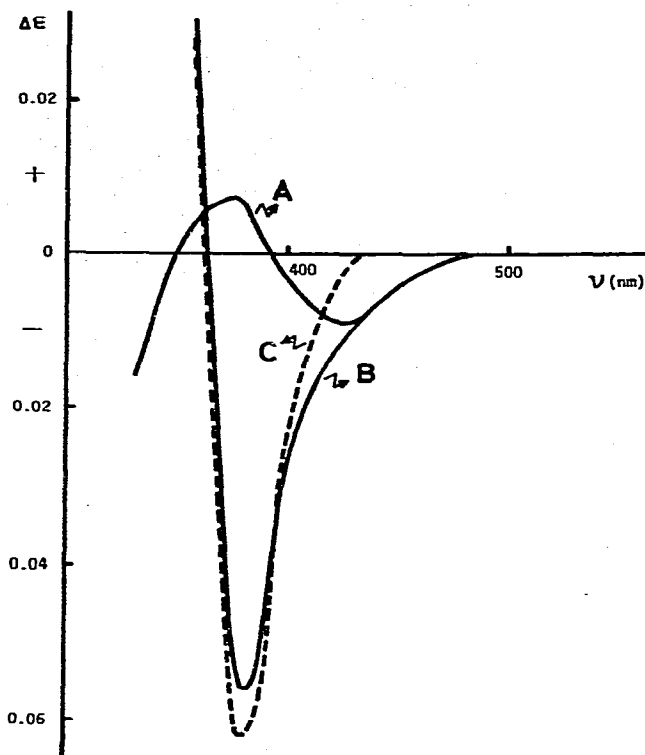
Fig. 4 CD spectra of the π-complexes of ethylene (A) and styrene (B) of the type, cis(N,olefin)-[PtCl(L-ala)(olefin)], in CH_3OH. The curve C represents the estimated net CD absorption (B - A) for the enantioselective coordination of styrene.

 With regard to the marked difference in enantioselectivity between the trans and cis(N,olefin)-forms, it is to be noted that the coordinated styrene undergoes a larger electronic influence in the latter form as revealed in their PMR properties (i.e., $^2J_{PtH}$ for the vinyl protons and the chemical-shift difference (from the free
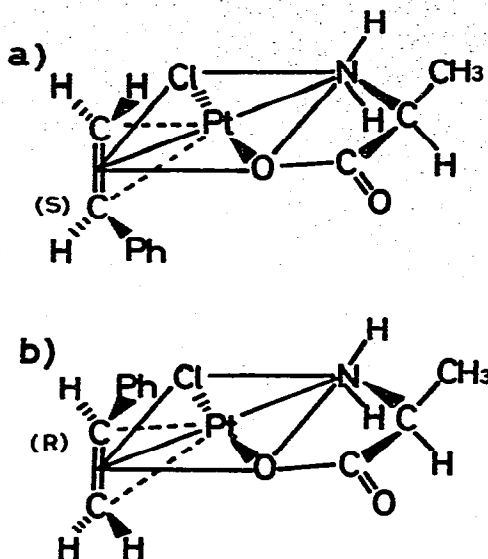
Fig. 5 Diastereomers of _trans_(N,olefin)-chloro-_L_-alaninato-
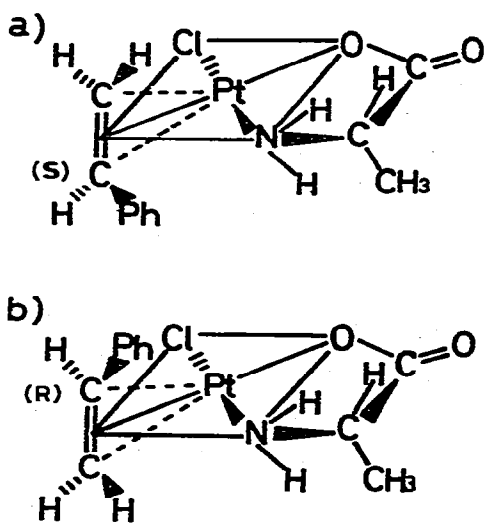styreneplatinum(II) with the structure of phenyl group
directed to the _cis_ O-ligand.

Fig. 6 Diastereomers of _cis_(N,olefin)-chloro-_L_-alaninato-
styreneplatinum(II) with the structure of phenyl group
directed to the _cis_ NH_2-ligand.

state) among them; Table 1) [26]. Some factors inherent in the chemical-bonding nature of the complexes may be responsible for the enantioselection independently or coupled with steric ones.

2. Quantum-chemical calculations on some models of the diastereomers

A. Calculation and geometry

Quantum-chemical calculations were made on some models of the studied diastereomers by using the Extended Hückel molecular orbital (EHMO) method [27], which was applied to the MO calculations of Zeise's type salts in previous work [13]. With respect to the parameters of Slater exponents [28,29] and valence state ionization potentials [29,30], the same values as reported were used.

The coordination structures for styrene and the L-alaninato ligand were evaluated according to the X-ray structural analyses of di-μ-chloro-dichlorobis(styrene)dipalladium(II) [31] and bis(L-prolinato) palladium(II) [32], respectively, on the basis of the identical value (1.31 Å) of ionic radius for Pt(II) and Pd(II) ions [33]. It was assumed that the five-membered chelating ring was coplanar to the square-planar coordination plane of platinum, and that the olefin moiety was planar and intersected perpendicularly by the plane at the center of the vinyl carbons.

B. Molecular orbital characteristics of the diastereomers

Figure 7 presents the MO energy levels of the diastereomers with various stereo-isomeric structures concerning both the coordinated styrene and the L-alaninato chelate ligand. The MO characteristics of the respective diastereomer sets approximately correspond with each other in the order of MO numbers.
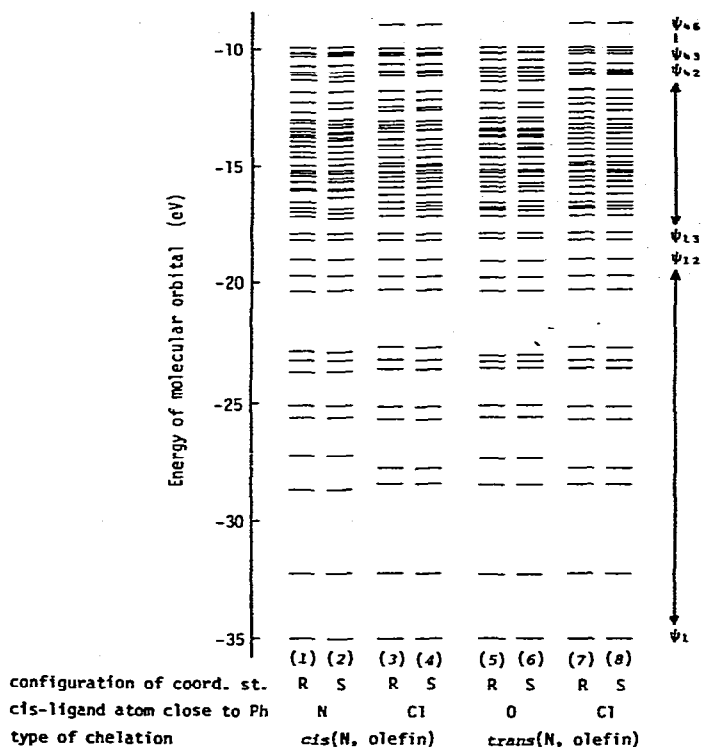
Fig. 7 Mclecular-orbital energy levels for the diastereomers of the
[PtCl(L-ala)(styrene)] complex with the eight kinds of
stereo-isomeric structures, concerning (i) the absolute
configuration of coordinated styrene, (ii) the rotation about
the platinum-styrene bond axis, and (iii) the type of chelati
for the L-alaninato ligand. Their total EHMO energies were
calculated as -1551.137 eV (1), -1551.057 eV (2), -1549.010
eV (3), -1549.007 eV (4), -1553.407 eV (5), -1553.400 eV (6),
-1549.050 eV (7), and -1549.052 eV (8), respectively.

From the viewpoint of constituent AO's, the MO's are roughly classified into three groups: (i) $\psi_1 \sim \psi_{12}$ (s orbitals of C, N, O and Cl), (ii) $\psi_{13} \sim \psi_{42}$ (p orbitals of C, N, O and Cl), and (iii) $\psi_{43} \sim \psi_{46}$ (5d orbitals of Pt), where hydrogen 1s orbitals are dispersed in various levels of MO's. The MO's of the first group are mainly localized to an atom or a group (ψ_1, ψ_2 to COO, ψ_3 to N, ψ_5, ψ_6 to Cl, ψ_7 to CH$_3$, ψ_{10} to C*(-CH$_3$), and ψ_4, ψ_8, ψ_9, ψ_{11}, ψ_{12} to styrene), constituting skeletal orbitals for the structure of the complex, and hence energy differences between the diastereomeric pairs are all negligibly small in these orbitals. Energetical correspondence also holds for the MO's of the third group, although the ligand AO's are included to some extent in conformity with the requirement of the symmetry of platinum 5d orbitals. The circular dichroism of the d-d transition of these Pt(II) complexes to reflect the chirality of either the coordinated styrene or the L-alaninato ligand may be reconciled with this MO character [34]. It is unique in the second region that a noticeable difference in the MO-energy pattern is brought about by the adequately-delocalized mode of the involved MO's for the intramolecular chiral discrimination [35]. From the standpoint of the efficiency of MO delocalization, it is conceivable that the bonding properties of the diastereomers such as the strength of the carbon-platinum bond [13,36] would contribute to the enantioselection.

As far as the total EHMO energy is concerned, the largest difference was observed between the cis(N,olefin)-type diastereomers with the structures shown in Fig. 6; the (R,S)-diastereomer is more stable (0.080 eV) in qualitative agreement with the experimental result. Since the energy difference is far smaller (less than one order of magnitude) for the other three sets, further analyses were focussed on the corresponding cis(N,olefin)-diastereomers.

C. Steric and stereo-electronic effects in the diastereomers

In order to elucidate in detail the diastereomeric nature of the molecule, the total EHMO energy was decomposed into the atomic and interatomic energies (eq. 1) in terms of Mulliken [38] net atomic orbital and overlap populations, respectively [39].

$$\underline{E} = \sum_{\underline{j}}^{AO's} \underline{q}_{\underline{j}}\underline{H}_{\underline{jj}} + \frac{K}{2} \sum_{\underline{j}<\underline{k}} \underline{p}_{\underline{jk}}(\underline{H}_{\underline{jj}} + \underline{H}_{\underline{kk}}) \qquad (1)$$

where $\underline{q}_{\underline{j}}$ and $\underline{p}_{\underline{jk}}$ are the total Mulliken net AO population and the total Mulliken overlap population, respectively, and $\underline{H}_{\underline{jj}}$ the valence state ionization potential of the AO, $\underline{x}_{\underline{j}}$. For the value of the free parameter, $\underline{K}$, 1.75 [27] was adopted.

The analyses from this viewpoint showed that substantial interactions exist between the substituents of the asymmetric carbons (Table for all the other structures, the corresponding interaction energies were negligibly small). The order of the anti-bonding interaction between the phenyl and the methyl groups in the $(\underline{S},\underline{S})$-configuration is comparable to the steric repulsion for the vicinal hydrogens of eclipsed ethane [39]. However, this repulsive energy was partially compensated by other contributions associated with the methyl group (the C-H bond energy (0.062 eV), the atomic energy of its carbon (0.044 eV), etc.) in the present case.

Table 3. Interaction energies between the substituents of the two asymmetric carbons of styrene- and $\underline{\underline{L}}$-alaninato-ligands[a]

configuration of coordinated styrene	C_6H_5-CH_3	C_6H_5-H	CH_2-CH_3	CH_2-H	H-CH_3	H-H
$\underline{S}$	0.312	0.010	0.001	-0.001	0.000	0.000
$\underline{R}$	0.020	-0.039	-0.002	0.001	0.000	0.000

a) Energies are given in eV.

In the second place, a unique mode was suggested for the diastereotopic amino-hydrogens of the complexes, although the role of the diastereotopic atoms (or substituents) in chirality phenomena [40] has been less noticed so far. As shown in Table 4, the values of net charge on the amino-hydrogens are dependent mainly on the relative position to the phenyl group rather than the fixed configuration of the asymmetric carbon at the geminal position (cf. Fig. 6). Since a "normal" value (as calculated for the trans(N,olefin)-diastereomers or another rotamer with the cis(N,olefin)-form) lies near to 0.20, it is concluded that the phenyl group at the coordinating position repels the electron of the amino-hydrogen which is located closer to it. This may be caused by a large repulsive interaction (2.392, 2.346 eV; Table 4) between the phenyl group and the amino-hydrogen concerned.

Table 4. Net charge on the diastereotopic amino-hydrogens and their interaction energies with some substituents of asymmetric carbons

amino-hydrogen[a]	net charge[b]		energy of interaction (eV)[b]					
			C_6H_5		CH_3		$H^{[c]}$	
	S	R	S	R	S	R	S	R
CH_3 side	0.285	0.207	2.392	1.780	0.830	0.888	-0.074	-0.085
H side	0.209	0.287	1.780	2.346	-0.093	-0.069	0.518	0.497

a) The two amino-hydrogens are located on either trans (H side) or cis (CH_3 side) position toward the methyl group of the L-alaninato ligand.

b) S and R are the configurations of the coordinated styrene.

c) The hydrogen of methine group in the L-alaninato ligand.

Because the amino-hydrogens are thus unequivalent, the coordinating nitrogen atom of the <u>L</u>-alaninato ligand is practically chiral It is noteworthy that the bond energy between the nitrogen and the adjacent asymmetric carbon stabilizes the (<u>R</u>,<u>S</u>)-diastereomer by 0.03 eV in comparison with the (<u>S</u>,<u>S</u>)-isomer, and in particular this energy difference is brought about almost entirely by the p_π-p_π orbital interaction (p_π being designated by taking the coordination plane as a nodal plane). This interaction appears to be derived from the diastereomeric nature of the molecule itself, as both couples of the diastereotopic amino-hydrogens and the substituents of the asymmetric carbon (H, CH_3) lie parallel to the p_π orbitals (Fig. 8), capable of exerting, in a sense, vectorial influence on them. This situation is also analogous to the result of the EHMO calculations
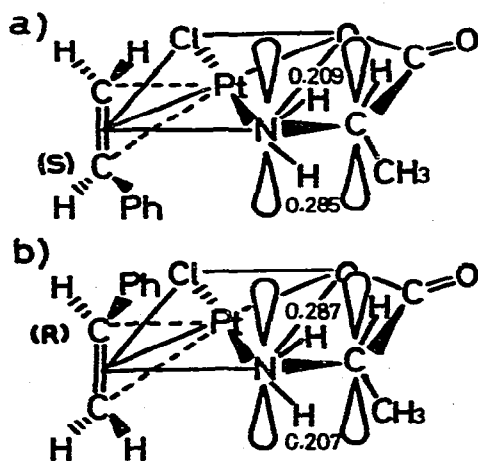

Fig. 8   The diastereomeric p_π(N)-p_π(C) orbital interaction due to the chirality of the nitrogen atom induced by the coordination of styrene. The figures correspond to the values of net charge on the amino-hydrogens.

on the ethane conformers [39] (p_π-type orbital interactions between carbon atoms significantly destabilize the eclipsed ethane, reflecting the spatial positions of methyl hydrogens).

According to this picture, the configuration of the L-alaninato ligand is transmitted through the electronic states of the diastereo-topic hydrogens to the chiral center of the coordinated styrene. It is likely that this kind of stereo-electronic factor becomes important, when the molecular orbitals are delocalized efficiently (promoted by proper metal-ligand bondings) in the π-type mode that will perceive the diastereomeric environment in the molecule.

Experimental

The PMR and CD spectra were recorded on a Hitachi R20-B and a JASCO J-20 spectrometers, respectively. Extended Hückel molecular orbital calculations were carried out by a FACOM 230-55 Computer at the University of Tokyo. The chemicals were obtained from standard commercial sources (G. R. grade), and were used without further purification.

Diastereomeric composition was determined by PMR (probe tem-perature, 35 °C) for such samples that were re-isolated in vacuo from a methanol solution after the sufficient equilibration with an excess amount of free styrene (at least 3 hrs) at 35 °C.

Acknowledgment

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36 Compared with the trans(N,olefin)-form, the cis-form gave greater values of Pt-C bond population (smaller values of C-C

(vinyl group) bond population) for all of the stereo-isomeric structures, reproducing the trans-influence order (N > O) for Zeise's type salts. In accord with the same order, the magnitude of mutual polarizability [37] calculated between platinum and vinyl protons (Π_{PtH}) also reproduced the observed tendency for the values of corresponding geminal Pt-H spin coupling constants.

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