starting materials *trans*-L$_2$Pt(C$\equiv$CH)$_2$[19] and *trans*-L$_2$PtMeCl[27] were prepared by literature methods. The reagent [*trans*-PtL$_2$(Me)(acetone)]PF$_6$ (**23**) was prepared by a procedure similar that reported for preparing the analogous PMe$_2$Ph derivative.[28]

A 0.1-mmol portion of **23** was added to an acetone suspension of 0.053 g (0.11 mmol) of **14** at 25 °C as an acetone solution. Within 15 min the acetylide reactant complex dissolved, and the reaction solution changed color from nearly colorless to pale yellow. After the solution was stirred for 6 h, the solution color had changed to orange-red. After 24 h of reaction, the solvent was removed under reduced pressure. The reaction residue was washed with three portions of hexane/ether (1:4) solution. The product was precipitated from THF/pentane solution as a dark red oil that formed a dry red solid when dried under vacuum (0.035 g, 30%): decomp pt 85–90 °C; IR (CH$_2$Cl$_2$) ν(C$\equiv$C) 2080 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.90–1.20 (m, 36, PCH$_2$*CH*$_3$), 1.80–2.20 (m, 28, P*CH*$_2$CH$_3$ + C$\equiv$CMe + CH), 5.68, 6.29 (m, 1 C=CH, 2 somers). Anal. Calcd for C$_{29}$H$_{65}$F$_6$P$_5$Pt$_2$: C, 32.48; H, 6.06; P, 14.44. Found: C, 32.42; H, 5.82; P, 14.21.

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Registry No. **2**, 51716-77-9; **3a**, 106357-35-1; **3b**, 106357-37-3; **5**, 106297-59-0; **6**, 106297-61-4; **7**, 106297-65-8; **8**, 106297-69-2; **9**, 106297-67-0; **10**, 106319-58-8; **11**, 106297-63-6; **12**, 106297-71-6; **13**, 106297-57-8; **14**, 34230-58-5; **15**, 34230-61-0; **16**, 12308-30-4; **17**, 97086-92-5; **18**, 87960-48-3; **19**, 69140-93-8; **20**, 18533-63-6; **21**, 31386-97-7; **23**, 106297-72-7; Pt, 7440-06-4; Fe, 7439-89-6; Au, 7440-57-5; W, 7440-33-7; Ni, 7440-02-0; Pd, 7440-05-3.

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Stereochemistry of Diastereoisomeric Complexes *cis*-Dichloro[(*S*)-α-methylbenzylamine][(*S*,*S*)- or (*R*,*R*)-2-vinyltetrahydropyran]platinum(II)

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The stereochemistry in solution of the diastereoisomeric complexes *cis*-dichloro[(*S*)-α-methylbenzylamine][(*S*)-2-vinyl-(*S*)-tetrahydropyran]platinum(II) and *cis*-dichloro[(*S*)-α-methylbenzylamine][(*R*)-2-vinyl-(*R*)-tetrahydropyran]platinum(II) was established by circular dichroism, ^{1}H NMR, and ^{195}Pt NMR investigations. In both diastereoisomers an intramolecular hydrogen bond, N–H$\cdots$O, between the amine group and the oxygen atom of the 2-vinyltetrahydropyran determines the stereochemistry of the complexes in solution.

Introduction

A number of studies have been made on chiral dichloro(amine)(olefin)platinum(II) complexes undertaken to elucidate the stereochemistry of coordinated ligands in solution.[1-5]

Repulsive steric interactions were claimed as responsible for the enantioface differentiation in the coordination of the olefin to the metal.[1,2] The presence of an oxygen atom in the case of unsaturated ethers can introduce a nonbonding electron repulsive interaction with chlorine atoms or/and an attractive interaction via the intramolecular hydrogen bond with a cis amine group,[6-8] making the stereochemistry of coordinated ligands very different.

Recently two diastereoisomeric complexes containing a chiral amine and a chiral allyl ether as organic ligands, namely, *cis*-dichloro[(*S*)-α-methylbenzylamine][(*S*)-2-vinyltetrahydropyran]platinum(II) (**1**) and *cis*-dichloro[(*S*)-α-methylbenzylamine][(*R*)-2-vinyltetrahydropyran]platinum(II) (**2**), have been prepared,[9] and the molecular structure of **1** in the solid state has been studied by X-ray analysis.[10]

We found it extremely interesting to compare the stereochemistry of the two diastereoisomeric complexes **1** and **2** arising from the two enantiomers of a vinyl derivative in the frame of the investigations on the origin of the stereospecificity observed in some important catalytic organic reactions such as hydroformylation, hydrogenation, and stereospecific polymerization. Indeed the aforementioned Pt(II) complexes can be taken as models of the coordination step of the enantiomer pair to the same asymmetric catalytic center in order to get information on the reactive intermediates that are of value for the stereochemical pathway of the reaction.

In this paper we established the stereochemistry in solution of the diastereoisomeric complexes **1** and **2** by circular dichroism (CD) and NMR, pointing out the role played by intramolecular interactions on the conformational arrangement of the ligands and assigning the ab-

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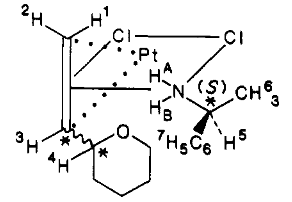
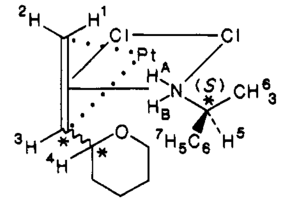
Table I. ^{1}H NMR and ^{195}Pt NMR Parameters for the Diastereoisomeric Complexes cis-Dichloro[(*S*)-α-methylbenzylamine][(*S*)-2-vinyl-(*S*)-tetrahydropyran]platinum(II) (1) and *cis*-Dichloro[(*S*)-α-methylbenzylamine)[(*R*)-2-vinyl-(*R*)-tetrahydropyran]platinum(II) (2) in CDCl$_3$ at 25 °C



		1 (*S*,*S*,*S*)		2 (*S*,*R*,*R*)	
		δ^a	J^b	δ^a	J^b
^{1}H	H^1	4.39 (d)	J_{1-3} = 13.7; J_{Pt} = 50	3.40 (d)	J_{1-3} = 13.7; J_{Pt} = 50
	H^2	4.51 (d)	J_{2-3} = 8.7; J_{Pt} = 60	3.96 (d)	J_{2-3} = 8.7; J_{Pt} = 60
	H^3	5.39 (dd)	J_{Pt} = 70	5.20 (dd)	J_{Pt} = 70
	H^4	4.48 (bd)	J_{ax-ax} = 11.4	4.56 (bd)	J_{ax-ax} = 11.4
	H^5	4.44 (m)		4.40–4.50^c	
	H^6	1.74 (d)	J_{6-5} = 7.5	1.67 (d)	J_{6-5} = 7.0
	H^7	7.22–7.44 (m)		7.40–7.50 (m)	
	H^A	4.11 (bd)	J_{A-B} = 8.0; J_{A-5} = 1	4.40–4.50^c	
	H^B	5.86 (bt)	J_{B-A} = 8.0; J_{B-5} = 8.0	5.85 (bt)	J_{B-A} = 8.0; J_{B-5} = 8.0
^{195}Pt		–2725		–2701	

^{a} δ (^{1}H) in parts per million from Me$_4$Si. Multiplicities given in parentheses: d, doublet; bd, broad doublet; dd, double doublet; bt, broad triplet; m, multiplet. δ(^{135}Pt) in parts per million from Na$_2$PtCl$_6$. ^{b} Coupling constants *J* in Hz. ^{c} The resonances of the protons H^A and H^5 are superimposed.

Table II. NOE Data for Some Protons of 1 and 2



		NOE, %	
irradiate	observe	1	2
H^1	H^7		16
H^6	H^1	8	

solute configuration to chiral centers of the vinyl derivative.

Experimental Section

General Considerations. Complexes 1 and 2 were prepared as previously described.[9] NMR spectra were measured in CDCl$_3$ on a Bruker WM-250 spectrometer at 250 MHz for ^{1}H and at 53.6 MHz for ^{195}Pt. NOE experiments were performed on a Varian VXR-300 spectrometer on a carefully degassed solution containing 10% (w/v) of 1 and 2 in CDCl$_3$. Circular dichroism spectra of 1 and 2 were recorded in the 300–500 nm region on a Jobin Yvon III dichrograph at 25 °C (CHCl$_3$ solution; *c* 1–5 g/L; 1-cm cell).

Circular dichroism (CD) and NMR analysis of complexes 1 and 2 were performed both immediately after dissolution of the samples and at successive intervals thereafter. Significant changes in the spectral parameters were observed only after several hours, showing that epimerization was very slow.

^{1}H NMR and ^{195}Pt NMR parameters are reported in Table I and II.

Circular Dichroism. CD spectra of 1 and 2 before epimerization are presented in Figure 1. Complex 1 shows a positive CD band with a maximum at 345 nm (Δε = +0.43); the intensity of the band decreases slowly and reaches a constant value of –0.07 after 2 days. Complex 2 shows a negative CD band with $\Delta\epsilon_{max}$ –0.64 at 345 nm; after epimerization, the intensity of the band reaches a value of –0.26 at the same wavelength.

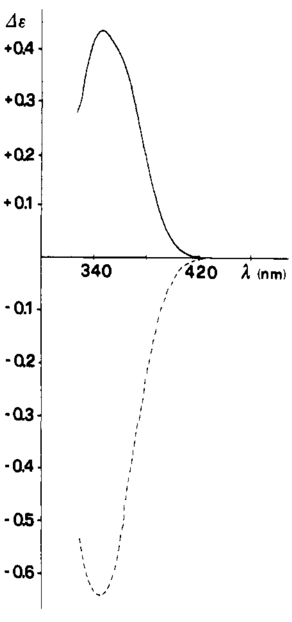


Figure 1. Circular dichroism spectra of complexes 1 (—) and 2 (---) before epimerization in CHCl$_3$ at 25 °C.

Discussion and Conclusions

Configurational Assignment. In order to establish the stereochemistry of the diastereoisomeric complexes 1 and 2, the absolute configuration of the asymmetric carbon atom bonded to platinum has to be determined for each diastereoisomer, being the absolute configuration of the amine ligands *S* in both the cases and that of the asymmetric carbon atom of the tetrahydropyran rings *S* in 1[10] and *R* in 2, respectively.

X-ray structural analysis of the complex 1 showed that the absolute configuration of the chiral center bonded to the metal is *S*.[10] Owing to the absence of a fast epimerization, complex 1 can be defined as the *S*,*S*,*S* diastereoisomer after dissolution.

Previous studies on platinum(II) complexes containing simple chiral or prochiral olefins showed that the absolute configuration of the asymmetric carbon atom bonded to the metal is reflected in the sign of the lowest energy CD band.[4,5,11,12] Therefore the positive sign of the CD band at 345 nm shown by 1 is correlated to the *S* absolute configuration of the asymmetric center bonded to the metal. Accordingly, the *R* absolute configuration must be assigned to the same chiral center in the case of the diastereoisomer 2, which shows a negative sign for 345-nm CD band, and hence 2 is quoted as *S*,*R*,*R*.

Conformational Analysis. Since, in principle, the coordinated vinyl group of 1 and 2 can rotate about the metal–olefin bond, two ground-state isomers are possible (Chart I). Steric repulsive interactions could favor rotamers **1b** and **2b**, in which the group attached to the double bond of the unsaturated ether is directed toward the Cl atom, i.e., the less bulky cis ligand. On the contrary repulsive nonbonding electron interactions with chlorine or/and attractive interactions between the oxygen atom

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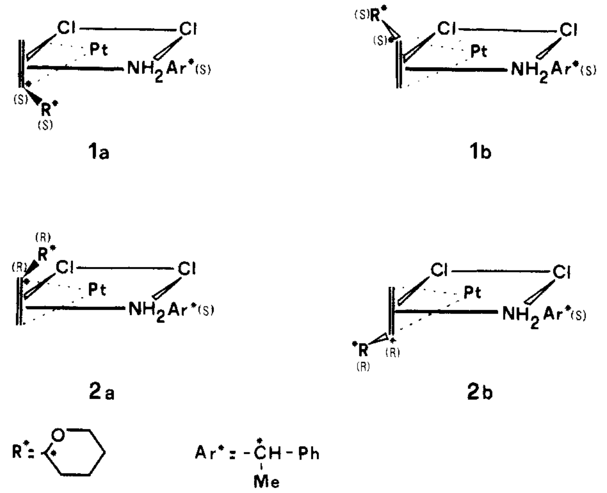
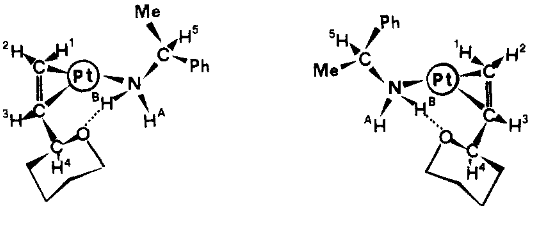
Chart I. Rotational Isomers (a and b) of Diastereomeric Complexes 1 and 2



1a 1b 2a 2b

Chart II. Conformation of the Organic Ligands in 1 and 2



1 2

of the ether and the amine group could predominate over steric requirements and hence favor rotamers **1a** and **2a**.

Knowledge of the absolute stereochemistry of 1 and 2 and results of nuclear magnetic resonance analysis clearly demonstrate that only rotamers **1a** and **2a** are present in solution. The formation of an intramolecular hydrogen bond between the oxygen atom of the ether and a hydrogen of the amine group accounts for this preference. The presence of an intramolecular hydrogen bond in 1 and 2 was established on the basis of the unequivalence of the amine protons H^A and H^B in the proton NMR spectra: these protons give separate resonances and show geminal coupling in addition to coupling with ^{195}Pt (Table I). According to our recent studies on analogous platinum(II) complexes containing an achiral primary amine cis to a prochiral unsaturated ether,[7,8] the proton that shows the resonance at lower field, i.e. H^B, is the one involved in the intramolecular hydrogen bond. In addition in both diastereoisomers the proton H^B is coupled with vicinal proton H^5 (J H^B,H^5 = 8.0 Hz), while H^A shows no detectable coupling with the same proton H^5. Therefore, H^A is in a cisoid position and H^B in a transoid position relative to H^5 in both diastereoisomers (Chart II).

The relative positions of the methyl and phenyl groups of the amine with respect to the platinum moiety in complexes 1 and 2 are well reflected in the NOE data (Table II). Indeed in complex 1 saturation of the methyl protons of the amine produces enhancement of the resonance of the vinyl proton H^1, while in complex 2 no enhancement of the H^1 resonance is observed upon saturation of the methyl protons. On the other hand, enhancement of the intensity of the phenyl proton resonances of the amine is observed on saturation of the H^1 resonance only in the case of complex 2. It is noteworthy that no enhancement of the methyl or phenyl resonances is observed on saturation of the vinyl proton H^3 in both complexes. Hence the asymmetric carbon atom of the amine and the CH_2= group of the vinylic moiety lie on the same side of the coordination plane in both diastereoisomers: in 1 the methyl group of the amine is bent toward the CH_2= group; in 2 the phenyl group points to the same group (Chart II). Accordingly, vinyl protons H^1 and H^2 are shielded by the phenyl group to a larger extent in 2 than they are in 1 by the methyl group, while the vinyl proton H^3 shows the same chemical shift in 1 and 2 (Table I).

It is noted that in the ^{195}Pt NMR spectra complex 2 shows a lower field resonance with respect to the one observed in complex 1 (Table I). This result seems to indicate that the phenyl group produces a larger deshielding effect on the electron density of the metal than the methyl group does. A similar trend of the ^{195}Pt chemical shifts was observed also in the diastereoisomeric complexes *trans*-dichloro[*N*-methyl-α-methylbenzylamine][ethylene]platinum(II)[13].

In both diastereoisomers the spatial arrangement of the unsaturated ligand is the most suitable for intramolecular interaction between the oxygen atom and the amine group. Indeed the coupling pattern of the proton bonded to the asymmetric carbon atom of the tetrahydropyran ring, i.e., H^4, indicates that this proton is axial and hence the vinyl group lies in an equatorial position (Scheme II). In addition, the proton H^4 is cis to the vinyl proton H^3 in both complexes, the value of the coupling constant $J(H^3,H^4)$ (2 Hz) being very low (Table I). It should be noted that in the analogous complexes containing 3-methyl-substituted α-olefins,[11] in which the conformation of the ligands is determined by steric requirements, the hydrogen atom bonded to the asymmetric carbon atom and the H^3 vinyl proton are always in the trans position.

The results discussed above allow us to conclude that the unsaturated ligand assumes the same conformation in 1 and 2, and, owing to the opposite configuration of this ligand, the two diastereoisomers differ in the relative position of the phenyl and methyl groups of the amine with respect to the metal (Chart II).

It is interesting to note that in complex 1 the arrangement of the ligands in solultion is very similar to that found by X-ray analysis in the solid state. Thus the formation of the intramolecular hydrogen bond O···H–N plays a key role in the solid state as well as in solution in determining the stereochemistry of the complexes.

Registry No. 1, 106356-29-0; 2, 106252-74-8; ^{195}Pt, 14191-88-9.

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