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Rapid Inversion versus Stable Chiral Center Formation. Different Behavior of Coordinated Nitrogens in Four- and Five-Coordinate Platinum(II) Complexes with N,N′-Disubstituted Ethylenediamines

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The four- and five-coordinate complexes $[PtCl_2(N,N'\text{-}R_2en)]$ (**1**) and $[Pt(\eta^2\text{-}C_2H_4)Cl_2(N,N'\text{-}R_2en)]$ (**2**) (R = *i*-Pr (**a**), *t*-Bu (**b**), *R*-CHMePh (**c**), *R*,*S*-CHMePh (**d**); en = ethylenediamine) have been obtained in their stereomeric forms and the processes of proton exchange and racemization at the nitrogens investigated. At room temperature the four-coordinate species (**1a–d**) have stable chirality at the coordinated nitrogens and do not exchange the NH protons after several hours or even days in a chloroform solution saturated with D_2O. Under similar conditions the five-coordinate complexes (**2a–d**) undergo rapid inversion of configuration at the nitrogens and exchange the NH protons in a few seconds. In the latter case spectroscopic and structural data indicate that both processes take place by release of the platinum–nitrogen bond rather than by a preliminary NH bond dissociation. Lowering the temperature of compounds **2a–d** stabilizes their chirality at the nitrogen atoms, which assume the same configuration (either *R* or *S*); this allows a trans conformation of the ligand with both *N*-alkyl substituents in equatorial positions. When the *N*-alkyl substituents of the diamine are chiral groups of a given configuration (e.g. *R*-CHMePh), the corresponding complex (**2c**) can have adjacent C and N atoms with either equal or different configurations. Of the two diastereomers that would be obtained therefrom, only one is found either in solution or in the solid state. This is characterized by having equal absolute configuration on adjacent C and N atoms, which allows the CHMePh group to direct the less bulky proton toward the apical Cl atoms of the trigonal bipyramid and the immediately bigger Me group toward the equatorial olefin. The energy of activation for ethylene rotation and nitrogen inversion in complex **2d** has been determined by variable-temperature ^1H and ^{13}C NMR. The crystal structures of the following complexes were determined by single-crystal diffraction and the different conformations of the diamine ligands compared: **1a**-*trans* [space group $P2_1/n$, $a = 17.048$ (7) Å, $b = 9.487$ (5) Å, $c = 7.857$ (5) Å, $\beta = 92.60$ (3)°], **1b**-*cis* [space group $P2_1/n$, $a = 14.188$ (6) Å, $b = 8.776$ (5) Å, $c = 12.144$ (6) Å, $\beta = 112.72$ (3)°], **1d**-*cis2* [space group $P2_1/c$, $a = 11.712$ (3) Å, $b = 15.880$ (4) Å, $c = 10.874$ (3) Å, $\beta = 108.71$ (2)°], **2c**-*trans1* [space group $C2$, $a = 10.730$ (3) Å, $b = 8.374$ (3) Å, $c = 12.777$ (3) Å, $\beta = 109.81$ (2)°], and **2d**-*trans* [space group $P2_1/c$, $a = 11.455$ (2) Å, $b = 21.376$ (5) Å, $c = 8.872$ (3) Å, $\beta = 99.86$ (3)°].

Introduction

It is well-known that amine complexes of several transition elements have fairly stable configurations at the coordinated nitrogens that allow secondary amines to be resolved into their optical antimers and the rates for the proton exchange and racemization at the asymmetric centers to be measured.[1-3] It is generally understood that a base-catalyzed proton exchange leads to a deprotonated intermediate that can undergo inversion before reprotonation. A substantial difference between rates of exchange and racemization has been observed. In the case of platinum complexes the retention ratios (k_{ex}/k_{rac}) for four-coordinate Pt^{II} and six-coordinate Pt^{IV} complexes are 10^2 and 10^4, respectively.[4]

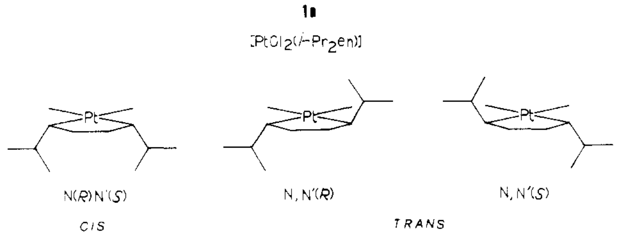
More recently several five-coordinate platinum(II) complexes of formula $[Pt(\eta^2\text{-olefin})(N\text{-}N)X_2]$ (N–N = dinitrogen donor ligand, X = halogen atom) have been synthesized and their behavior in solution has been investigated.[5-10] In aprotic solvents both stable configuration and rapid inversion of configuration at the coordinated nitrogens have been proposed. With stable configuration at the coordinated nitrogens a symmetrically substituted diamine would give two isomeric species with cis and trans conformations of the ligand.[11] Although some preference for one of the two possibilities could be anticipated, the occurrence of both forms was reported. Moreover, the configuration of the nitrogen atoms was reported to be completely determined by that of an adjacent chiral substituent directly bound to them.[9a] In the case of fast inversion of configuration at nitrogens N–H bond dissociation was suggested as a route to the inversion of configuration.[10a]

This paper is concerned with the behavior of five- and four-coordinate platinum(II) complexes with symmetrically substituted ethylenediamines in relation to the questions raised above.

Materials and Methods

Starting Materials. Commercial reagent grade chemicals were used without further purification.

Chart I. Schematic Drawings of the Different Stereoisomers of $[PtCl_2(i\text{-}Pr_2en)]$ (**1a**)



The ligands *R*,*R*-mben [**c**, mben = *N*,*N*′-bis(α-methylbenzyl)-ethylenediamine] was prepared by the method of Terent'ev et al. from

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(R)-α-methylbenzylamine (Aldrich) and 1,2-dibromoethane.[12]

The ligand R,S-mben (**d**) was prepared by heating to reflux an equimolar mixture of racemic α-methylbenzylamine and 1,2-dibromoethane until a yellow crystalline precipitate of the hydrobromide separated. This was filtered, washed with ether, and dried. The solid was dissolved in water, the solution was treated with an excess of potassium hydroxide, and the amine, which separated out as a brown oily liquid, was separated from the aqueous layer and treated with the stoichiometric amount of hydrochloric acid to form a yellowish crystalline precipitate. The mixture of R,R-, S,S-, and R,S-mben·2HCl was then treated with methanol. The $R,R/S,S$ racemic mixture, being more soluble in this solvent, dissolved, leaving as a solid residue almost pure R,S-mben·2HCl. This was separated by filtration of the mother liquor, washed three times with methanol and then with ether, and dried. Anal. Calcd for $C_{18}H_{26}Cl_2N_2$: C, 63.3; H, 7.7; Cl, 20.8; N, 8.2. Found: C, 63.1; H, 7.8; Cl, 21.2; N, 8.2.

Zeise's salt, $K_2[Pt(\eta^2\text{-}C_2H_4)Cl_3]$, was prepared according to the method of Cramer et al. from potassium tetrachloroplatinate(II) and ethylene gas.[13]

$[PtCl_2(DMSO)_2]$ was prepared by the method of Kukushkin et al.[14] and used as starting material for the preparation of the ionic species $[PtCl(DMSO)(N,N'\text{-}R_2en)]Cl$ according to the method of Romeo et al.[15]

Preparation of Complexes. The five-coordinate complexes $[Pt(\eta^2\text{-}C_2H_4)Cl_2(N,N'\text{-}R_2en)]$ (**2a–d**) were prepared by the general procedure reported in ref 5. Anal. Calcd for $C_{10}H_{24}Cl_2N_2Pt$: C, 27.4; H, 5.5; Cl, 16.2; N, 6.4. Found for **2a**: C, 27.1; H, 5.2; Cl, 16.4; N, 6.2. Calcd for $C_{12}H_{28}Cl_2N_2Pt$: C, 30.9; H, 6.0; Cl, 15.2; N, 6.0. Found for **2b**: C, 31.1; H, 6.2; Cl, 15.3; N, 6.1. Calcd for $C_{20}H_{28}Cl_2N_2Pt$: C, 42.7; H, 5.0; Cl, 12.6; N, 5.0. Found for **2c**: C, 42.1; H, 5.2; Cl, 12.7; N, 4.8. Found for **2d**: C, 41.9; H, 5.2; Cl, 12.8; N, 4.9.

The four-coordinate complexes $[PtCl_2(N,N'\text{-}R_2en)]$ (**1a-d**) were prepared by three different methods: (i) decomposition of the cationic species $[PtCl(DMSO)(N,N'\text{-}R_2en)]Cl$, (ii) reaction of $K_2[PtCl_4]$ with the diamine in alcohol–water mixtures, and (iii) decomposition of the corresponding five-coordinate species.

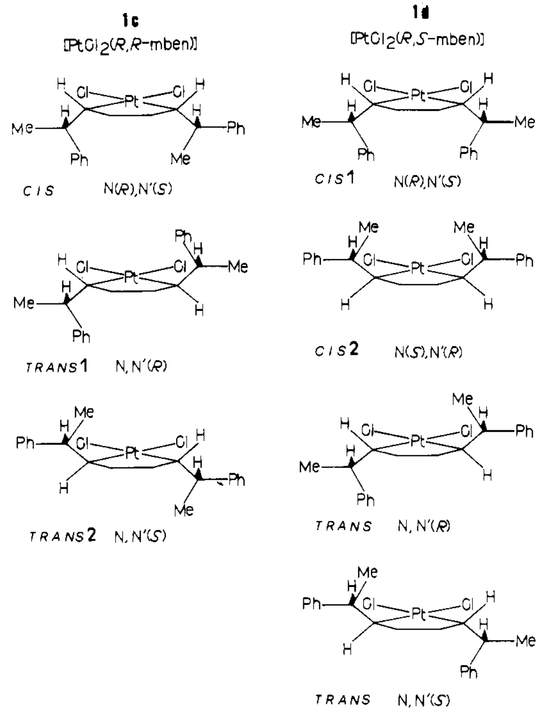
[PtCl$_2$(*i*-Pr$_2$en)] (1a-*cis*, Chart I).[11] $[PtCl(DMSO)(i\text{-}Pr_2en)]Cl$ (1 g) suspended in 10 cm^3 of CH_2Cl_2 in a closed flask was stirred at room temperature for 10 days until the suspension became greenish. The solid (0.6 g) was separated, then washed with methanol and diethyl ether, and dried in the air; yield 70%. Anal. Calcd for $C_8H_{20}Cl_2N_2Pt$: C, 23.4; H, 4.9; Cl, 17.3; N, 6.8. Found: C, 22.8; H, 4.8; Cl, 16.9; N, 6.5.

[PtCl$_2$(*i*-Pr$_2$en)] (1a-*trans*, Chart I).[11] $[PtCl(DMSO)(i\text{-}Pr_2en)]Cl$ (1 g) suspended in 7 cm^3 of DMF (dimethylformamide) was stirred at room temperature for 4 days until the suspension became pale yellow. The solid (0.7 g) was separated, washed with 2 cm^3 of DMF and then with methanol and diethyl ether, and dried in the air; yield 80%. Anal. Found: C, 23.3; H, 5.1; Cl, 17.0; N, 6.7.

Slow decomposition of $[PtCl(DMSO)(i\text{-}Pr_2en)]Cl$ in DMF solution gave crystals of **1a**-*trans* suitable for X-ray diffraction analysis.

[PtCl$_2$(*t*-Bu$_2$en)] (1b-*cis*). The decomposition of the ionic intermediate $[PtCl(DMSO)(t\text{-}Bu_2en)]Cl$ always gave a large excess of the cis isomer, which, depending upon the solvent used, could be obtained in two crystalline forms.

Chart II. Schematic Drawings of the Different Stereoisomers of $[PtCl_2(R,R\text{-mben})]$ (**1c**) and $[PtCl_2(R,S\text{-mben})]$ (**1d**)[a]



[a] The less bulky protons of CHMePh are directed toward the cis chlorine atoms.

One form was obtained by slow addition of a solution of *t*-Bu$_2$en (0.17 g) in methanol (10 cm^3) to a solution of $[PtCl_2(DMSO)_2]$ (0.42 g) in the same solvent (40 cm^3). After 65 h of stirring at room temperature, the resulting yellow solution was concentrated to a small volume (5 cm^3) under reduced pressure, filtered and cooled to 0 °C. Yellow crystals of **1b**-*cis* slowly separated out; these were filtered off, washed twice with methanol, and dried; yield 80%. Anal. Calcd for $C_{10}H_{24}Cl_2N_2Pt$: C, 27.4; H, 5.5; Cl, 16.2; N, 6.4. Found: C, 27.5; H, 5.6; Cl, 16.4;, N, 6.3.

The above compound dissolves in CH_2Cl_2 or $CHCl_3$ to give a clear solution from which were obtained by slow evaporation yellow crystals of a compound having different IR spectra but similar NMR spectra in $CDCl_3$, CD_2Cl_2, CD_3OD, and DMF-d_7. The X-ray analysis showed the two compounds to have the same molecular structure but different crystal packing.

[PtCl$_2$(*t*-Bu$_2$en)] (1b-*trans*). This isomer could be obtained by decomposition of the corresponding five-coordinate species. A solution of 0.20 g of **2b** in 5 cm^3 of $CHCl_3$, in a screw-lid-closed flask, was allowed to decompose at 50 °C in a water bath (at lower temperature the decomposition is very slow). After 20 days yellow-orange crystals of **1b**-*trans* had separated from the solution; these were collected by filtration of the mother liquor, washed with $CHCl_3$, and dried; yield 40%. Anal. Found: C, 27.9; H, 5.6; Cl, 15.6; N, 6.3.

[PtCl$_2$(*R*,*R*-mben)] (1c-*cis*) and [PtCl$_2$(*R*,*S*-mben)] (1d-*cis2*) (in the latter case two cis diastereomers are allowed; see Chart II) were obtained in nearly quantitative yields by decomposition of the corresponding ionic intermediates [PtCl(DMSO)(mben)]Cl. The salt (1 mmol) was dissolved in methanol (10 cm^3), and by warming (40 °C, 2 h, **c**; 80 °C, 60 h, **d**) and stirring of the solutions, yellow precipitates of the desired compounds separated. In all cases the yields were above 80%. Anal. Calcd for $C_{18}H_{24}Cl_2N_2Pt$: C, 40.4; H, 4.5; Cl, 13.3; N, 5.2. Found for **1c**-*cis*: C, 39.9; H, 4.7; Cl, 14.0; N, 5.1. Found for **1d**-*cis2*: C, 40.1; H, 4.6; Cl, 13.8; N, 5.1.

Crystals of **1d**-*cis2* suitable for X-ray diffraction analysis were obtained by slow decomposition (15 days at 0 °C) of $[PtCl(DMSO)(R,S\text{-mben})]Cl$ dissolved in chloroform.

[PtCl$_2$(*R*,*R*-mben)] (1c-*trans1* and 1c-*trans2*) and [PtCl$_2$(*R*,*S*-mben)] (1d-*cis1* and 1d-*trans*) (see Chart II) were obtained by reaction of $K_2[PtCl_4]$ with the appropriate ligand. In a typical experiment 1 mmol of ligand dissolved in 20 cm^3 of methanol was added to a stoichiometric amount of $K_2[PtCl_4]$ dissolved in 20 cm^3 of water. The resulting solution was left at 5 °C and stirred for 7 days. The yellow precipitate that separated was collected by filtration of the mother liquor, washed twice with aqueous methanol (1:1 v/v), dried, and treated with 10 cm^3 of CH_2Cl_2, which dissolves the more soluble isomers **1c**-*cis* and **1d**-*cis1*,

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(11) In this case and throughout the text cis and trans do not refer to the relative positions of the coordinated nitrogens, which are always cis, but to the relative positions of the nitrogen substituents with respect to the chelate ring. Note that cis and trans conformations correspond to different and equal absolute configurations at the coordinated nitrogens.

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Table I. Experimental Data for the X-ray Diffraction Study

	1a-*trans*	**1b**-*cis*	**1d**-*cis2*	**2d**-*trans*	**2c**-*trans1*
mol formula	$C_8H_{20}Cl_2N_2Pt$	$C_{10}H_{24}Cl_2N_2Pt$	$C_{18}H_{24}Cl_2N_2Pt$	$C_{20}H_{28}Cl_2N_2Pt$	$C_{20}H_{28}Cl_2N_2Pt$
mol wt	410.25	438.31	524.40	562.45	562.45
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P2_1/c$	$C2$
data collecn temp	room temp				
radiation	Nb-filtered Mo Kα (λ = 0.71069 Å)				
a, Å	17.048 (7)	14.188 (6)	11.712 (3)	11.455 (2)	10.730 (3)
b, Å	9.487 (5)	8.776 (5)	15.880 (4)	21.376 (5)	8.374 (3)
c, Å	7.857 (5)	12.144 (6)	10.874 (3)	8.872 (3)	12.777 (3)
β, deg	92.60 (3)	112.72 (3)	108.71 (2)	99.86 (3)	109.81 (2)
V, Å^3	1269 (1)	1395 (1)	1915.5 (9)	2140 (1)	1080.1 (6)
Z	4	4	4	4	2
D_{calcd}, g cm^{-3}	2.147	2.087	1.853	1.745	1.729
F(000)	776	840	1032	1096	548
cryst dimens, mm	0.08 × 0.12 × 0.37	0.28 × 0.55 × 0.72	0.32 × 0.48 × 0.52	0.15 × 0.40 × 0.44	0.25 × 0.30 × 0.35
linear abs coeff, cm^{-1}	115.59	105.28	76.83	68.81	68.17
max–min transmissn factor	1.175–0.811	1.551–0.595	1.248–0.800	1.546–0.646	1.225–0.725
diffractometer	Siemens AED				
scan type	$\theta/2\theta$				
scan speed (in θ), deg min^{-1}	3–12				
scan width, deg	$(\theta - 0.55) - (\theta + 0.55 + 0.346 \tan\theta)$				
2 θ range, deg	6–54	6–56	6–52	6–50	6–54
no. of rflns measd	$\pm h,k,l$	$h,k,\pm l$	$\pm h,k,l$	$\pm h,k,l$	$h,k,\pm l$
std refln	one measd after every 50 rflns				
no. of unique data	2777	3344	3721	3763	2288
no. of unique obsd data [$I > 2\sigma(I)$]	1264	2621	2715	2586	2174
R	0.0459	0.0452	0.0294	0.0893	0.0517
R_w	0.0500	0.0613	0.0419	0.0941	0.0636
K	0.974	1.087	0.8478	1.3971	0.7701
g	0.001	0.003	0.005	0.005	0.004

respectively. The pale yellow residue was dried again; yield 40%.

In the case of *R*,*R*-mben the compound so obtained is a 1:1 mixture of the two possible diastereomers having a trans conformation of the ligand. All attempts to separate the two by fractional crystallization were unsuccessful. Finally, they were separated by HPLC on a LiChrosorb CN column with dichloromethane as eluent. Anal. Found for **1c**-*trans1*: C, 39.9; H, 4.7; Cl, 13.0; N, 5.1. Found for **1c**-*trans2*: C, 39.7; H, 4.7; Cl, 13.2; N, 5.0.

In the case of *R*,*S*-mben treatment with CH_2Cl_2 only removes **1d**-*cis1* while **1d**-*cis2* is left in the solid residue together with **1d**-*trans*. To obtain the pure trans isomer, the raw material was treated with 10 cm^3 of DMF, which dissolves the trans species, leaving the contaminant as a fine powder. The mixture is then filtered and water added to the filtrate. The trans racemate, **1d**-*trans*, precipitates as a pale yellow powder. This was separated, washed with water, acetone, and diethyl ether, and dried; yield 40%. Anal. Found: C, 39.9; H, 4.5; Cl, 13.0; N, 5.4.

The **1d**-*cis1* isomer was obtained from the CH_2Cl_2 solution above, which was concentrated to small volume and chromatographed on a open column of silica gel (eluant 8/2 v/v CH_2Cl_2/acetone). Evaporation of the solvent and recrystallization from CH_2Cl_2/diethyl ether gave a 20% yield of pure product. Anal. Found: C, 40.6; H, 4.9; Cl, 12.7; N, 5.2.

X-ray Crystallography. Crystals of the compounds **1a**-*trans*, **1b**-*cis*, **1d**-*cis2*, **2c**-*trans1*, and **2d**-*trans* were selected for the X-ray analyses. The crystals of **2d**-*trans* were of poor quality. Crystallographic data for the five compounds are collected in Table I. Unit cell parameters were obtained by least-squares refinement of the values (in the range 9–16°) of 30 carefully centered reflections chosen from different regions of the reciprocal space. Data were collected at room temperature, the individual profiles having been analyzed by the method of Lehmann and Larsen.[16] The structure amplitudes were obtained after the usual Lorentz and polarization reduction.[17] A correction for absorption effects was applied.[18] Only the observed reflections were used in the structure solution and refinement.

All structures were solved by using conventional Patterson and Fourier techniques and refined by full-matrix least squares. In the last cycles of refinement anisotropic thermal parameters were used for all the non-hydrogen atoms. For the compound **2c**-*trans1* the configuration of the carbon atoms could be confirmed, because of the acentric space group, by using the coordinates $-x$, $-y$, $-z$ for the non-hydrogen atoms in independent cycles of refinement. A large difference in the *R* value was obtained for the structure with the expected configuration, 0.0517 against 0.0576, together with much better values of bond distances. The hydrogen atoms of the compound **1d**-*cis2* and the ethylene hydrogens of **2c**-*trans1* were clearly located in the final difference Fourier maps but not refined; those of the other compounds (except the ethylene hydrogens of **2d**-*trans*) were placed at their geometrically calculated positions and included in the final structure calculations with isotropic thermal parameters. The function minimized during the refinement was $\sum w|\Delta F|^2$. The weighting scheme $w = K[\sigma^2(F_o) + gF_o^2]^{-1}$ was used in the last cycles of refinement for all five compounds. The scattering factors were taken from ref 19 with the exceptions of those of the hydrogen atoms, which were taken from ref 20. Corrections for the real and immaginary components of the anomalous dispersion were made for the Pt and Cl atoms. Final atomic coordinates for the five compounds are listed in Tables SI–SIII, SV, SVII, SIX, and SXI; thermal parameters are given in Tables SIV, SVI, SVIII, SX, and SXII (supplementary material). Selected bond distances and angles are reported in Tables II and III.

Physical Measurements. IR spectra in the range 4000–400 cm^{-1} were recorded as KBr pellets; spectra in the range 400–200 cm^{-1} were recorded as Polythene pellets on a Perkin-Elmer 283 spectrophotometer. ^{1}H NMR spectra were obtained with Varian XL 200 and Bruker AM 250 spectrometers; the values are given in Table IV. ^{1}H-decoupled ^{195}Pt NMR spectra were recorded on the Bruker AM 250 instrument operating at 53.529 MHz and using a sweep width of 38.5 KHz, a pulse width of 10 μs, and an acquisition time of 0.213 s; the chemical shift values, referred to $Na_2[PtCl_6]$ used as external standard and uncorrected for the solvent, were −2220 ppm for **1c**-*cis* (deuterioacetone) and −2189 and −2107 ppm for **1c**-*trans1* and **1c**-*trans2* ($CDCl_3$). HPLC separations were performed with a Waters instrument.

Calculation of the ΔG^*'s. Values of the free energy of activation, for the olefin rotation and nitrogen inversion, were calculated by using the expression $\Delta G^*_{T_c} = -RT \ln [\pi(\Delta\nu)h/2^{1/2}kT]$, where $\Delta\nu$ represents the chemical shift difference ($\Delta\delta$ in Hz) of the coalescing peaks in the absence of exchange, *T* represents the coalescence temperature, and *R*, *k*, and *h* have their normal thermodynamic significances.[21]

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Table II. Selected Bond Distances (Å) and Angles (deg) in the Four-Coordinate Compounds

1a-*trans*		**1b**-*cis*		**1d**-*cis2*	
Pt–Cl(1)	2.295 (6)	Pt–Cl(1)	2.281 (3)	Pt–Cl(1)	2.301 (2)
Pt–Cl(2)	2.301(6)	Pt–Cl(2)	2.299 (3)	Pt–Cl(2)	2.296 (3)
Pt–N(1)	2.05 (2)	Pt–N(1)	2.078 (8)	Pt–N(1)	2.028 (7)
Pt–N(2)	2.08 (2)	Pt–N(2)	2.097 (9)	Pt–N(2)	2.061 (6)
N(1)–C(1)	1.48 (3)	N(1)–C(1)	1.48 (1)	N(1)–C(1)	1.48 (1)
N(1)–C(3)	1.54 (3)	N(1)–C(3)	1.53 (2)	N(1)–C(3)	1.53 (1)
N(2)–C(2)	1.52 (3)	N(2)–C(2)	1.49 (1)	N(2)–C(2)	1.50 (1)
N(2)–C(6)	1.49 (3)	N(2)–C(7)	1.51 (1)	N(2)–C(5)	1.53 (1)
C(1)–C(2)	1.49 (4)	C(1)–C(2)	1.49 (1)	C(1)–C(2)	1.54 (1)
C(3)–C(4)	1.53 (4)	C(3)–C(4)	1.50 (2)	C(3)–C(4)	1.54 (1)
C(3)–C(5)	1.53 (4)	C(3)–C(5)	1.50 (2)	C(3)–C(7)	1.52 (1)
C(6)–C(7)	1.52 (4)	C(3)–C(6)	1.50 (2)	C(5)–C(6)	1.54 (1)
C(6)–C(8)	1.52 (4)	C(7)–C(8)	1.52 (2)	C(5)–C(13)	1.52 (1)
		C(7)–C(9)	1.50 (2)		
		C(7)–C(10)	1.51 (2)		
Cl(1)–Pt–Cl(2)	89.3 (2)	Cl(1)–Pt–Cl(2)	86.3 (1)	Cl(1)–Pt–Cl(2)	91.2 (1)
Cl(1)–Pt–N(1)	94.6 (5)	Cl(1)–Pt–N(1)	91.4 (3)	Cl(1)–Pt–N(1)	93.5 (2)
Cl(2)–Pt–N(2)	93.2 (5)	Cl(2)–Pt–N(2)	96.6 (3)	Cl(2)–Pt–N(2)	90.2 (2)
N(1)–Pt–N(2)	83.0 (6)	N(1)–Pt–N(2)	85.0 (4)	N(1)–Pt–N(2)	85.0 (3)
Pt–N(1)–C(1)	110 (2)	Pt–N(1)–C(1)	101.8 (6)	Pt–N(1)–C(1)	108.9 (5)
Pt–N(1)–C(3)	118 (1)	Pt–N(1)–C(3)	122.4 (6)	Pt–N(1)–C(3)	119.4 (5)
C(1)–N(1)–C(3)	112 (2)	C(1)–N(1)–C(3)	117.7 (8)	C(1)–N(1)–C(3)	110.3 (6)
Pt–N(2)–C(2)	106 (2)	Pt–N(2)–C(2)	106.7 (7)	Pt–N(2)–C(2)	107.6 (5)
Pt–N(2)–C(6)	119 (1)	Pt–N(2)–C(7)	125.6 (7)	Pt–N(2)–C(5)	115.7 (5)
C(2)–N(2)–C(6)	113 (2)	C(2)–N(2)–C(7)	111.4 (8)	C(2)–N(2)–C(5)	116.5 (6)
N(1)–C(1)–C(2)	105 (2)	N(1)–C(1)–C(2)	109.7 (8)	N(1)–C(1)–C(2)	106.6 (6)
N(2)–C(2)–C(1)	108 (2)	N(2)–C(2)–C(1)	109.6 (8)	N(2)–C(2)–C(1)	109.8 (7)
N(1)–C(3)–C(4)	109 (2)	N(1)–C(3)–C(4)	110.9 (10)	N(1)–C(3)–C(4)	110.7 (7)
N(1)–C(3)–C(5)	110 (2)	N(1)–C(3)–C(5)	108.1 (10)	N(1)–C(3)–C(7)	109.2 (6)
C(4)–C(3)–C(5)	112 (2)	N(1)–C(3)–C(6)	111.0 (9)	C(4)–C(3)–C(7)	116.2 (7)
N(2)–C(6)–C(7)	111 (2)	C(4)–C(3)–C(5)	108.7 (12)	N(2)–C(5)–C(6)	112.8 (7)
N(2)–C(6)–C(8)	108 (2)	C(4)–C(3)–C(6)	110.0 (11)	N(2)–C(5)–C(13)	108.8 (7)
C(7)–C(6)–C(8)	114 (2)	C(5)–C(3)–C(6)	108.1 (12)	C(6)–C(5)–C(13)	113.6 (7)
		N(2)–C(7)–C(8)	107.1 (10)		
		N(2)–C(7)–C(9)	110.9 (9)		
		N(2)–C(7)–C(10)	110.0 (9)		
		C(8)–C(7)–C(9)	107.0 (9)		
		C(8)–C(7)–C(10)	115.3 (10)		
		C(9)–C(7)–C(10)	106.6 (10)		

Results and Discussion

Four-Coordinate Complexes with Achiral Ligands. Chart I gives the structures of the isomers of [PtCl$_2$(*i*-Pr$_2$en)] (**1a**). The ^{1}H NMR spectrum of each isomer, in aprotic solvents and at 20 °C, showed one resonance for the CH and two resonances for the CH$_3$ protons of *i*-Pr. This indicates that the two methyl groups of *i*-Pr suffer a diastereotopic splitting due to the presence of a stable chiral center upon the nitrogens. One resonance was also observed for the NH protons with a ^{195}Pt coupling of 72 Hz. Addition of deuteriated water into the NMR tube did not cause a collapse of this signal, which remained unchanged 1 day after the addition. The en CH$_2$ protons gave two distinct absorptions in one case and a single broad signal in the other case; this allowed assignment of the former to the cis and the latter to the trans isomer. The assignment was confirmed by the X-ray structure determination of one of the two isomers, **1a**-*trans*.

The cis and trans forms of the analogous complex [PtCl$_2$(*t*-Bu$_2$en)] (**1b**) were also prepared. The decomposition of the ionic intermediate [PtCl(DMSO)(*t*-Bu$_2$en)]Cl only afforded the **1b**-*cis* species. Depending upon the solvent used, this isomer could be obtained in two crystalline forms having different IR spectra in the solid, but identical NMR spectra in solution. We excluded the possibility that the two species could be related to the cis and trans isomers since this would require a fast interconversion rate in solution. Other possibilities were a different puckering of the chelate ring and a different packing of the molecules in the crystal. An X-ray investigation showed that this last was the case.[22]

The isomer **1b**-*trans* could be prepared by decomposition, in chlorinated solvents, of the five-coordinate complex [Pt(η^2-C$_2$H$_4$)Cl$_2$(*t*-Bu$_2$en)] (**2b**). Being less soluble in this solvent, **1b**-*trans* precipitates preferentially, leaving in solution the other isomer.

The ^{1}H NMR spectra showed, for each isomer, equivalent NH and *t*-Bu protons. The en CH$_2$ protons gave a multiplet grouped in two and one resonance pattern for the cis and trans forms, respectively. There was no sign of isomerization of one form into the other after several hours in solution. Also in this case saturation of the chloroform solution with deuteriated water did not lead to a collapse of the NH signals, which remained unchanged after days in solution.

Five-Coordinate Complexes with Achiral Ligands. The five-coordinate platinum/olefin complexes [Pt(η^2-olefin)Cl$_2$(N-N)], in which N-N is a bidentate N-donor ligand, are synthesized in quantitative yield by reaction of K[Pt(η^2-olefin)Cl$_3$] with the N-N ligand. The solid-state structure of a representative of this class of compounds was first established in 1976;[5b] few other examples were reported thereafter.[7a,9,10a] These compounds have a general tendency to release the olefin and give the corresponding four-coordinate species; however, the complexes with *i*-Pr$_2$en and *t*-Bu$_2$en are by far the most stable among those with diamine ligands and persist in chloroform solution for several days compared with the few seconds of the analogous compound with Me$_4$en.[5c]

The complex [Pt(η^2-C$_2$H$_4$)Cl$_2$(*i*-Pr$_2$en)] (**2a**) is obtained, in the solid state, in only one out of the two possible cis and trans forms. It exhibits, in solution, a temperature-variable ^{1}H NMR spectrum. At 20 °C only one chemical shift is observed for the CH and CH$_3$ protons of *i*-Pr, and the absence of diastereotopic splitting for the two Me groups of *i*-Pr indicates that the nitrogens are not stable chiral centers but undergo rapid inversion of configuration. One sharp signal is also observed for the en CH$_2$ protons. The NH

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[22] The structure of the second type of crystals revealed no important differences in structural parameters of the complex and practically the same conformation of the ligand. Crystals were tetragonal, space group $P4_2bc$, with unit cell parameters a = 12.368 (5) Å, c = 18.623 (8) Å, V = 2849 (2) Å^3, and Z = 8.

Table III. Selected Bond Distances (Å) and Angles (deg) in the Five-Coordinate Compounds[a]

2c-*trans1*		**2d**-*trans*	
Pt–Cl	2.286 (4)	Pt–Cl(1)	2.301 (7)
		Pt–Cl(2)	2.319 (5)
Pt–N	2.27 (1)	Pt–N(1)	2.28 (2)
		Pt–N(2)	2.25 (2)
Pt–C(10)	2.05 (2)	Pt–C(19)	2.05 (2)
		Pt–C(20)	2.08 (2)
C(10)–C(10′)	1.47 (4)	C(19)–C(20)	1.43 (4)
N–C(1)	1.47 (2)	N(1)–C(1)	1.49 (3)
N–C(2)	1.50 (2)	N(1)–C(3)	1.51 (3)
C(1)–C(1′)	1.52 (1)	C(1)–C(2)	1.54 (3)
		N(2)–C(2)	1.53 (3)
		N(2)–C(5)	1.51 (3)
C(2)–C(3)	1.52 (3)	C(3)–C(4)	1.53 (4)
C(2)–C(4)	1.50 (2)	C(3)–C(7)	1.49 (4)
		C(5)–C(6)	1.54 (3)
		C(5)–C(13)	1.48 (4)
N–Pt–N′	76.9 (5)	N(1)–Pt–N(2)	78.0 (6)
N–Pt–C(10)	120.6 (9)	N(1)–Pt–C(20)	123.3 (8)
		N(2)–Pt–C(19)	118.3 (8)
C(10)–Pt–C(10′)	42.2 (8)	C(19)–Pt–C(20)	40.5 (9)
Cl–Pt–N	88.0 (4)	Cl(1)–Pt–N(1)	85.6 (4)
		Cl(1)–Pt–N(2)	92.2 (4)
Cl–Pt–C(10)	90.6 (5)	Cl(1)–Pt–C(19)	91.5 (6)
		Cl(1)–Pt–C(20)	91.0 (7)
		Cl(2)–Pt–N(1)	91.3 (5)
		Cl(2)–Pt–N(2)	87.6 (4)
		Cl(2)–Pt–C(19)	91.4 (7)
		Cl(2)–Pt–C(20)	90.3 (7)
Cl–Pt–Cl′	179.5 (4)	Cl(1)–Pt–Cl(2)	176.8 (2)
Pt–N–C(1)	109 (1)	Pt–N(1)–C(1)	108 (1)
Pt–N–C(2)	115 (1)	Pt–N(1)–C(3)	116 (1)
C(1)–N–C(2)	111 (1)	C(1)–N(1)–C(3)	112 (2)
		Pt–N(2)–C(2)	110 (1)
		Pt–N(2)–C(5)	116 (1)
		C(2)–N(2)–C(5)	110 (1)
N–C(1)–C(1′)	108 (1)	N(1)–C(1)–C(2)	109 (2)
		N(2)–C(2)–C(1)	107 (2)
N–C(2)–C(3)	107 (1)	N(1)–C(3)–C(4)	108 (2)
N–C(2)–C(4)	112 (1)	N(1)–C(3)–C(7)	113 (2)
C(3)–C(2)–C(4)	114 (1)	C(4)–C(3)–C(7)	112 (2)
		N(2)–C(5)–C(6)	114 (2)
		N(2)–C(5)–C(13)	108 (2)
		C(6)–C(5)–C(13)	111 (2)

[a] Primed atoms are related to unprimed ones by a 2-fold axis (transformation: $-x, y, -z$).

protons give a broad resonance with unresolved ^{195}Pt satellites that is shifted 3 ppm upfield with respect to the NH resonance in four-coordinate **1a**-*cis* and **1a**-*trans* and 1.3 ppm downfield with respect to the free ligand. The olefinic protons give a sharp resonance, flanked by ^{195}Pt satellites with sizable coupling constant, shifted to higher field with respect both to the free ethylene and to the coordinated olefin in a square-planar arrangement.[23-26] Thus, both the olefinic and the NH protons are more shielded in five-coordinate complexes than in four-coordinate species. A still smaller shielding is found in six-coordinate complexes of platinum(IV).[4,27]

Lowering the temperature to −80 °C splits the CH_3 signal in **2a** into two doublets of equal intensity while the olefin and the en CH_2 proton signals split into AA′BB′ multiplets completely similar to those observed, at room temperature, for the complex [Pt(η^2-C_2H_4)Cl_2(*R*,*R*-mben)] (**2c**) (see below). In **2c**, because of the presence of chiral substituents at the nitrogens (–CHMePh in place of *i*-Pr) only trans hydrogens of the olefin are chemically equivalent even under the conditions of fast inversion of configuration at the nitrogens and fast rotation of the olefin. On this basis we conclude that at low temperature the nitrogen atoms of the bidentate ligand become stable chiral centers. This idea also explains the diastereotopic splitting of the CH_3 groups of *i*-Pr; moreover, the multiplicity of the olefin and of the en CH_2 protons is in accord with a trans conformation of the ligand which requires the two nitrogens to have equal configuration (either *R* or *S*). Under these circumstances a fast or slow rotation of the olefin would not affect the proton multiplicity. Other weak resonances observed in the low-temperature NMR spectrum account for less than 5% of the bulk.

The complex [Pt(η^2-C_2H_4)Cl_2(*t*-Bu_2en)] (**2b**) is also obtained, in the solid state, in a single form, which also exhibits a temperature-variable NMR spectrum. At 20 °C only one chemical shift is observed for each type of proton. Lowering the temperature leaves the spectrum almost unchanged until −40 °C. At this point it starts broadening, and at −60 °C, with the single exception of an intense resonance due to the *t*-Bu protons, all resonances merge in a broad absorption between 2.5 and 3.5 ppm. At −80 °C the resonances begin to sharpen again; there is still only one signal for the *t*-Bu protons, while the CH_2 protons of the ethylene and of the diamine give rise to overlapping multiplets. The change of the NMR spectrum with the temperature indicates that a dynamic process involving the diamine and the olefin takes place; the single resonance for *t*-Bu observed in the low-temperature spectrum agrees with the presence of only one isomer, which most probably (by comparison with the case of **2a**) has a trans conformation.

The *i*-Pr_2en and *t*-Bu_2en ligands in four-coordinate complexes give examples in which the donor nitrogens are stable chiral centers, allowing the separation of the cis and trans isomers, which are formed in comparable yields. In the five-coordinate complexes, under similar conditions, the nitrogens undergo rapid inversion of configuration; lowering the temperature slows the rate of inversion, and the trans conformation apparently is preferred. Nothing can be said about the rotation rate of the olefin, on the basis of the low-temperature spectra of these five-coordinate species, because the resonance patterns would remain unchanged.

In the compounds so far examined the configuration of the nitrogens is inferred from the relative stability of the cis versus that of the trans conformation of the diamine ligand in a four- and a five-coordinate environment. We shall now examine the case of diamine ligands bearing chiral groups in place of *i*-Pr and *t*-Bu and see if there is a certain degree of asymmetric induction upon the nitrogens.

Four-Coordinate Complexes with Chiral Ligands. As before, the nitrogen atoms become, upon coordination, stable chiral centers and the ligand can assume both cis and trans conformations.[11] In the case of *R*,*R*-mben one cis and two trans isomers, trans1 and trans2, can form (see Chart II). All three have been isolated and characterized.[28]

1c-*cis* exhibited, in the NMR spectrum, two chemical shifts for CH_3 and two for CH protons, indicating that the halves of the ligand molecule are not in equivalent environments. The CH_2 protons gave rise to four well-separated multiplets while the NH protons gave two overlapping resonances with sizable ^{195}Pt coupling constants.

Each of the other two species, **1c**-*trans1* and **1c**-*trans2*, exhibited one chemical shift for CH_3 and CH protons, indicating that the ligand is symmetric and the conformation trans. One multiplet was observed for the CH_2 protons and a broad resonance flanked by ^{195}Pt satellites for the NH protons.

If the asymmetric carbon atoms influenced, to some extent, the configuration of the adjacent nitrogens, we might expect isomers **1c**-*trans1* and **1c**-*trans2* to form in dfferent yields. This was not the case, at least under our reaction conditions, so that, before their separation by HPLC, only the ^{195}Pt NMR spectra could tell

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(28) The following discussion will not be concerned with complexes of *S*,*S*-mben since they are completely similar to those with *R*,*R*-mben.

Table IV. Proton Chemical Shifts (δ, Downfield from $SiMe_4$) of Four- and Five-Coordinate Complexes

complex	solvent	temp, °C	C_2H_4[e]	N–H[e]	N–CH_2	C–H	C–Me	C–Ph[f]
1a-*cis*	*a*	+20		6.28 (72)	2.32	3.50	1.32	
					2.49		1.12	
	b	+20		5.85 (72)	2.51	3.94	1.19	
					3.00		1.43	
1a-*trans*	*a*	+20		6.22 (72)	2.22[g]	3.73	1.08	
							1.31	
1b-*cis*	*a*	+20		5.99 (66)	2.53		1.36	
					2.67			
	b	+20		5.20 (80)	2.68		1.48	
					3.40			
1b-*trans*	*a*	+20		5.44 (66)	2.59[g]		1.38	
2a	*b*	+20	3.10 (70)	2.62 br	2.92	3.30	1.38	
	b	−80	2.86	2.63	2.44	3.24	1.15	
			3.04		3.20		1.48	
2b	*b*	+20	3.22 (70)	2.82 br	2.98		1.38	
	b	−80	2.92	2.63	2.73		1.35	
			3.08		3.20			
1c-*cis*	*c*	+24		6.24 (80)	1.27	4.96	1.37	7.15 [2]
				6.28 (80)	1.65	5.24	1.63	7.26 [3]
					2.40			7.51 [3]
					3.38			8.14 [2]
1c-*trans1*	*d*	+24		5.66 (78)	2.05	5.08	1.56	7.38 [3]
					2.56			8.00 [2]
1c-*trans2*	*d*	+24		5.51 (78)	2.22	5.10	1.81	7.18 [3]
					2.30			7.35 [2]
1d-*cis1*	*a*	+20		6.76 (80)	2.10	3.53	1.35	7.40 [6]
					2.44			7.60 [4]
1d-*cis2*	*a*	+20		6.58	1.92	4.62	1.80	7.36
					2.36			
1d-*trans*	*a*	+20		6.37 (78)	1.56	4.74	1.51	7.36 [8]
				6.57 (78)	1.88	5.02	1.81	7.86 [2]
					2.31			
					2.44			
2c	*b*	+20	3.26 (68)	3.11 br	2.44[g]	4.18	1.91	7.29
			3.43 (68)					
	b	−60	3.07	3.15	2.32[g]	4.06	1.81	7.24
			3.24					
2d	*b*	+24	2.81 (71)	3.23 br	2.61	4.23	1.70	7.32
					2.84			
	b	−20	2.59	3.19	2.53	4.14	1.62	7.23
			2.70		2.77			
	b	−80	1.91	3.10	2.45	4.02	1.40	7.29
			2.00	3.30	2.48	4.20	1.74	
			2.84		2.62			
			3.38		2.66			

[a] DMSO-d_6. [b] CD_2Cl_2. [c] $CDCl_3$. [d] Acetone-d_6. [e] Values of *J*(Pt–H) in Hz are given in parentheses. [f] Integral values are given in brackets when needed. [g] Signal related to an AA′BB′ multiplet.

us that there were two different platinum species and not a single species with a dissymmetric ligand.

In the case of *R*,*S*-mben the presence of the two chiral centers on carbons allows the formation of two cis isomers, cis1 and cis2, and a trans racemate (Chart II).

The NMR spectra of **1d**-*cis1* and **1d**-*cis2* showed one chemical shift for the CH and CH_3 protons in accord with the symmetric environment of the ligand. The CH_2 protons gave two distinct multiplets and the NH a single resonance flanked by ^{195}Pt satellites. It was not easy, at this stage, to tell which of the two species was cis1 and which was cis2. For this reason an X-ray investigation of one of the two compounds was undertaken (see below).

Also in this case the two cis isomers were obtained in comparable yield.

The NMR spectrum of **1d**-*trans* gave two chemical shifts for the CH and CH_3 protons and a broad resonance for the NH protons in accord with the magnetic nonequivalence of the halves of the ligand molecule.

The results show that in four-coordinate complexes there is neither a marked preference for one conformation of the ligand (cis versus trans) nor an influence by the asymmetric carbon of a N-substituent upon the configuration of the nitrogen on coordination to platinum.

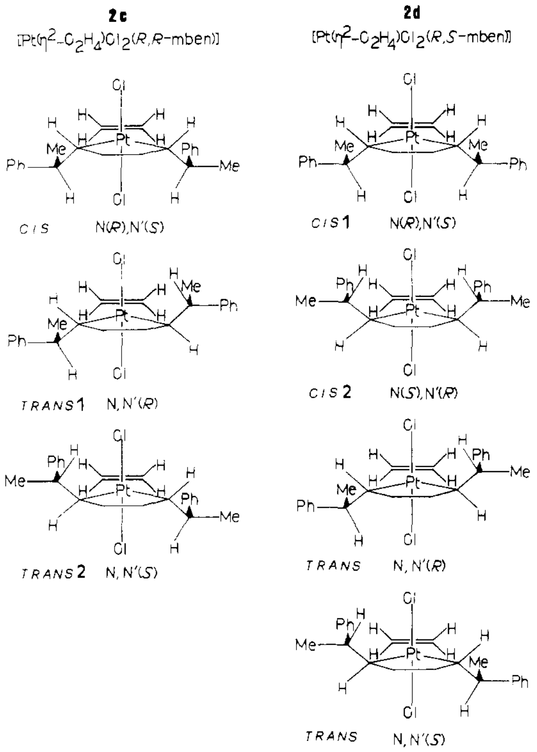
The situation could be different in five-coordinate complexes that are sterically more restricted and labile and can better evince small differences in energy among different configurations.

Five-Coordinate Complexes with Chiral Ligands. These complexes were prepared by using the procedure already reported for the preparation of the complexes with *i*-Pr_2en and *t*-Bu_2en. They have comparable stabilities in solution.

The NMR spectrum of $[Pt(\eta^2\text{-}C_2H_4)Cl_2(R,R\text{-mben})]$ (**2c**) had one chemical shift for CH and CH_3 and an AA′BB′ multiplet for the olefin protons. It did not change in the range of temperature +20 to −60 °C. This feature is in accord either with fast inversion of configuration at the coordinated nitrogens (inspection of the different conformations drawn in Chart III indicates that only trans hydrogens of the olefin become equivalent even in the fast-rotation limit) or with slow inversion at nitrogens but with the ligand being in one of the two possible trans conformations (if the ligand conformation were cis, the olefin multiplet would be of AA′BB′ type in the fast-rotation limit and of ABCD type in the slow-rotation limit). By comparison to the previous results and the discussion (see below) of the *R*,*S*-mben complex we can conclude that the first situation (rapid inversion of configuration at the nitrogens) applies to the room-temperature spectrum, while the latter situation (the two nitrogens having fixed and equal configuration) applies to the low-temperature spectrum.

Of the two possible trans isomers only one ought to be present in solution at low temperature and probably it has the same structure as the compound isolated in the solid state, upon which

Chart III. Schematic Drawings of the Different Stereoisomers of $[Pt(\eta^2\text{-}C_2H_4)Cl_2(R,R\text{-mben})]$ (**2c**) and $[Pt(\eta^2\text{-}C_2H_4)Cl_2(R,S\text{-mben})]$ (**2d**)[a]



[a] The less bulky protons of CHMePh are directed toward the apical chlorine atoms.

an X-ray crystal structure determination was performed (see below).

The NMR spectrum of $[Pt(\eta^2\text{-}C_2H_4)Cl_2(R,S\text{-mben})]$ (**2d**) changed with temperature. At +20 °C single resonances were observed for the CH and CH_3 protons of the ligand and for the olefin protons. This is in accord with fast rotation of the olefin and rapid inversion of configuration at the nitrogen atoms (from inspection of the different conformations shown in Chart III it appears that a slow rotation of the olefin would render nonequivalent the CH_2's hydrogens even in the hypothesis of fast inversion of configuration at the nitrogens, while a fast rotation of the olefin accompanied by a slow change of configuration at the nitrogens would render the hydrogens of the olefin equivalent in the case of a cis conformation of the ligand and nonequivalent in the case of a trans conformation).

When the temperature is lowered to −20 °C, single resonances are still observed for the CH and CH_3 protons of the ligand while the olefin resonance splits into two multiplets, 0.1 ppm apart, related to an AA′BB′ system. This is a clear indication that the olefin is in the slow-rotation limit while the nitrogens still rapidly invert (the same type of spectrum would have been obtained also in the case of slow rotation of the olefin accompanied by slow inversion at the nitrogens if the ligand assumed only one of the two possible cis conformations; however, this disagrees not only with the preferred trans conformation but also with spectroscopic changes observed at still lower temperature).

At −80 °C the NMR spectrum exhibits two resonances for both the CH and CH_3 protons of the ligand and also an ABCD type of spectrum for the olefin (four nonequivalent protons). The equal intensity of the resonances into which the CH and CH_3 protons have been split points to a nonequivalence of these protons inside the same molecule rather than the presence of two isomers with symmetrical ligands (cis1 and cis2) in equal amount. Therefore, once again, the ligand assumes the trans conformation, which implies that the two nitrogens have equal configurations while the two adjacent carbons have different chiralities (absence of asymmetric induction).

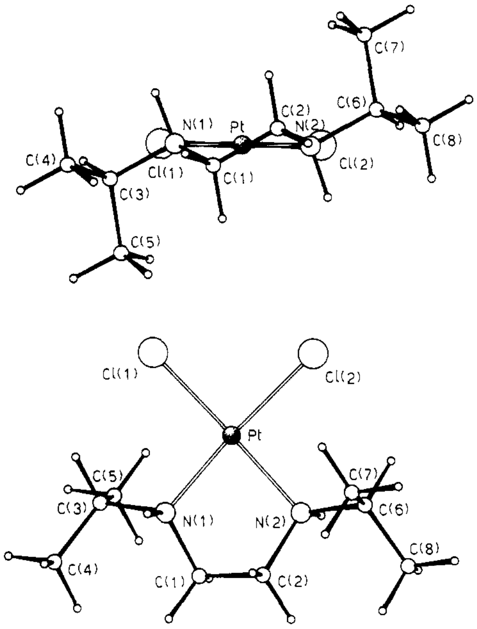


Figure 1. Molecular structure of the comlex $[PtCl_2(i\text{-}Pr_2en)]$ (**1a**-*trans*) viewed along the bisector of the N–Pt–N angle and the perpendicular to the coordination plane.

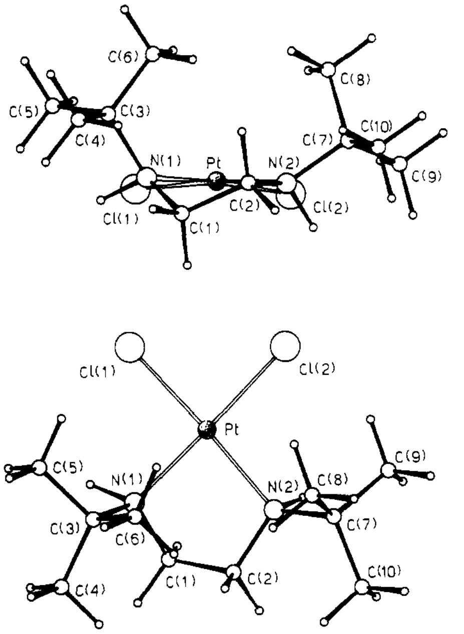


Figure 2. Molecular structure of the complex $[PtCl_2(t\text{-}Bu_2en)]$ (**1b**-*cis*) viewed along the bisector of the N–Pt–N angle and the perpendicular to the coordination plane.

This compound was particularly interesting for two other reasons. First, it allowed us to observe separately the rotation of the ethylene and the inversion of configuration at nitrogens. The activation energies for the two processes were calculated and found to be 13.8 ± 0.2 and 10.4 ± 0.2 kcal mol^{-1}, respectively. Second, it contains in the same molecule two couples of adjacent chiral centers; in one couple carbon and nitrogen have the same configuration, and in the other one they have opposite configurations. From a direct comparison of the two situations it could be worked out if one of them is more destabilized. For this reason an X-ray crystal structure of this complex was performed.

In summary, five-coordinate complexes have a preference for the trans conformation of the ligand, and when two such species are possible, as in the case of **2c**, only one isomer is formed (presence of asymmetric induction).

Comparison of the Structures of 1a-*trans* and 1b-*cis*. Views of the structures of these complexes are given in Figures 1 and

2; selected bond distances and angles are listed in Table II. In **1a**-*trans* the platinum and the coordinated atoms are perfectly coplanar; in **1b**-*cis* the platinum atom is displaced by 0.110 (1) Å from the plane passing through the coordinated atoms, toward the *t*-Bu groups. The bond distances in the coordination sphere of Pt are comparable, only the Pt–N bonds appear to be slightly shorter in **1a**-*trans* [2.08 (2) and 2.05 (2) Å] than they are in **1b**-*cis* [2.097 (9) and 2.078 (8) Å]. More remarkable differences are found in the Cl–Pt–Cl bond angle, which is regular in **1a**-*trans* [89.3 (2)°] but significantly smaller in **1b**-*cis* [86.3 (1)°]. Also, the Cl–Pt–N angles are nearly equal in **1a**-*trans* [94.6 (5) and 93.2 (5)°] and appreciably different in **1b**-*cis* [91.4 (3) and 96.6 (3)°].

These differences are well-understood on the basis of different sterical requirements of the two ligands. In general the chelate ring of ethylenediamine is markedly puckered, which allows an essentially strain-free structure with hydrogen substituents on adjacent carbon atoms almost completely staggered.[29] The substituents attached to the nitrogen atoms have a different degree either of "axial" or "equatorial" character. The conformation of ethylenediamine (en) in **1a**-*trans* is almost perfectly staggered with the two trans *i*-Pr groups in a "quasi-equatorial" position as indicated by the values of torsion angles C(3)–N(1)–C(1)–C(2), N(1)–C(1)–C(2)–N(2), and C(1)–C(2)–N(2)–C(6), which are 177 (2), –59 (2), and 178 (2)°, respectively (theoretical values: 180, –60, and 180°). The C(1) and C(2) atoms between the two nitrogens are nearly equally displaced, on opposite sides, from the coordination plane [0.35 (3) and –0.41 (3) Å, respectively]. The presence of the *i*-Pr groups on the two nitrogens does not cause a significant steric hindrance inside the coordination sphere since they are rotated in such a way as to direct the less bulky tertiary hydrogen atom toward the cis chlorine atoms.

The cis conformation of the ligand in **1b**-*cis* requires one *t*-Bu group to be in a "quasi-equatorial" and the other to be in a "quasi-axial" position. The latter interacts with the en bridge, causing a distortion of the ligand chain as indicated by values of the torsion angles C(3)–N(1)–C(1)–C(2), N(1)–C(1)–C(2)–N(2), and C(1)–C(2)–N(2)–C(7), which are 84 (1), 56 (1), and –169 (1)°, respectively (theoretical values: 60, 60, and –180°).[30] Moreover, the substitution of the tertiary hydrogen atom of *i*-Pr by the bulkier methyl group of *t*-Bu causes a much stronger steric interaction between the *t*-Bu groups and the cis chlorine atoms. As a consequence of this, the Cl–Pt–Cl angle is narrowed; the two Cl atoms are pushed below the N–Pt–N plane, causing a pyramidal distortion of the square coordination plane and the frame of the chelate ligand is rotated around the N(1)–N(2) direction, bringing both C(1) and C(2) atoms of the en bridge to the same side of the coordination plane (opposite to that of the metal atom) displaced from this by 0.95 (1) and 0.33 (1) Å, respectively.

Comparison of the Cis and Trans Conformations of *R*,*S*-mben in Four-Coordinate 1d-*cis2* and Five-Coordinate 2d-*trans* Complexes. Views of the structures of these complexes are given in Figures 3 and 4; selected bond distances and angles are listed in Tables II (**1d**-*cis2*) and III (**2d**-*trans*).

The coordination parameters of **1d**-*cis2* resemble those of the other four-coordinate complexes already discussed.

The ligand has a cis conformation, as in **1b**-*cis*, and the "axial" CHMePh group sterically interacts with the en bridge (torsion angles C(3)–N(1)–C(1)–C(2), N(1)–C(1)–C(2)–N(2), and C(1)–C(2)–N(2)–C(5) of 97.3 (8), 51.7 (8), and –175.8 (6)°, respectively). The CHMePh groups, like the *i*-Pr's of **1a**-*trans*, direct the less bulky proton toward the cis chlorine atoms with consequent release of steric strain [the C(1) and C(2) atoms of the en bridge are symmetrically displaced by 0.342 (8) and –0.349 (8) Å from the coordination plane].

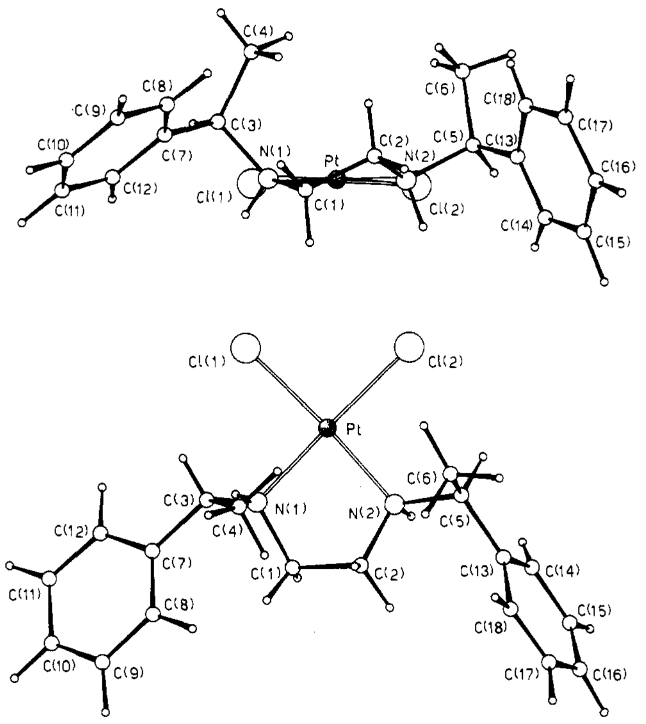


Figure 3. Molecular structure of the complex $[PtCl_2(R,S\text{-mben})]$ (**1d**-*cis2*) viewed along the bisector of the N–Pt–N angle and the perpendicular to the coordination plane.

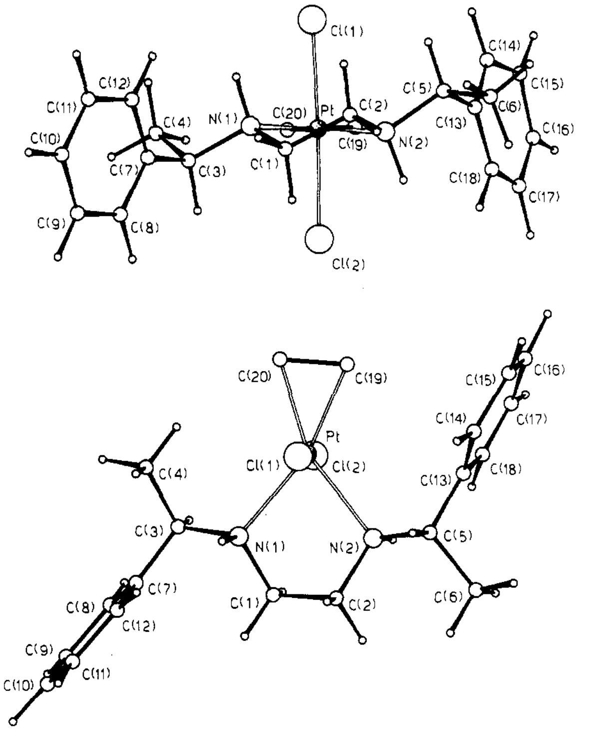


Figure 4. Molecular structure of the complex $[Pt(\eta^2\text{-}C_2H_4)Cl_2(R,S\text{-mben})]$ (**2d**-*trans*) viewed along the bisector of the N–Pt–N angle and the perpendicular to the equatorial plane.

The Pt atom is displaced by 0.053 (2) Å from the plane of the coordinated atoms toward the CHMePh substituents. This pyramidal distortion is caused by a repulsion between the platinum atoms of two centrosymmetrically related complexes linked together by four hydrogen bonds between the NH groups of one unit and the Cl atoms of the other unit [N(1)···Cl(2′) = 3.232

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[29] Corey, E. J.; Bailar, J. C., Jr. *J. Am. Chem. Soc.* **1959**, *81*, 2620–2629. Hawkins, C. J. *Absolute Configurations of Metal Complexes*; Wiley-Interscience: New York, 1971; Chapter 6. Beattie, J. K. *Acc. Chem. Res.* **1971**, *4*, 253–259. Erickson, L. E.; McDonald, J. M.; Howie, J. K.; Clow, R. P. *J. Am. Chem. Soc.* **1968**, *90*, 6371–6382. Appleton, T. G.; Hall, J. R. *Inorg. Chem.* **1970**, *9*, 1800–1806, 1807–1814; **1971**, *10*, 1717–1725. Erickson, L. E.; Erickson, M. D.; Smith, B. L. *Inorg. Chem.* **1973**, *12*, 412–422. Erickson, L. E.; Sarneski, J. E.; Reilley, C. N. *Inorg. Chem.* **1975**, *14*, 3007–3017.

[30] Tapscott, R. E.; Mather, J. D.; Them, T. F. *Coord. Chem. Rev.* **1979**, *29*, 87–127.

(7) Å, H(1)···Cl(2′) = 2.50 Å, N(1)-H(1)-Cl(2′) = 143°; N(2)···Cl(1′) = 3.250 (6) Å, H(2)···Cl(1′) = 2.33 Å, N(2)-H(2)-Cl(1′) = 149°].[31] The two related complexes form a dimer with a Pt···Pt separation of 3.344 (2) Å.

In **2d**-*trans* bond distances and angles in the coordination sphere of platinum resemble those of the five-coordinate complexes having the same arrangement of donor atoms, in particular [Pt(C_2H_4)Cl_2(HMeN—N=CMe—CMe=N—NHMe)], which was the first to be reported,[5b] [Pt(C_2H_4)Cl_2(*N,N′*-Me_2-*R,R*-mben)], in which the residual *N*-hydrogen atoms of mben have been substituted by methyl groups,[9a] and [$PtCl_2$(HMeC=CH_2)(*N,N′*-Me_2-*R,R*-mben)] and [$PtCl_2$(HPhC=CH_2)(*t*-Bu—N=CH—CH=N—*t*-Bu)], which have an olefin other than ethylene.[9a,10a] All of these have a trigonal-bipyramidal arrangement with apical chlorine atoms and the olefin and the two nitrogen atoms of the ligand in the equatorial plane. They are characterized by Pt–Cl bond distances similar to those found in four-coordinate complexes, longer Pt–N bonds, and smaller N–Pt–N bite angles. In a previous work the notion that in five-coordinate trigonal-bipyramidal complexes the platinum atom exhibits an axial covalent radius similar to that in four-coordinate Pt^{II} species and an equatorial covalent radius similar to that in three-coordinate Pt^0 species was used.[5b]

The substituted en shows a strain-free trans conformation with both substituents in equatorial positions as indicated by the C(3)–N(1)–C(1)–C(2), N(1)–C(1)–C(2)–N(2), and C(1)–C(2)–N(2)–C(5) torsion angles of 176 (2), −59 (2), and 169 (2)°, respectively. The C(1) and C(2) atoms are displaced symmetrically, by 0.44 (2) and −0.32 (2) Å, from the mean equatorial plane.

In both the four- and the five-coordinate complexes the CHMePh group is rotated in such a way as to direct the less bulky proton toward the cis chlorine atoms. This observation gives a clue to the preferred conformation of the ligand in the two cases. In four-coordinate complexes the two chlorine atoms are coplanar with the chelate ligand and contacts between the Cl's and the N-substituents can be avoided with either a cis or a trans conformation of the ligand. In the five-coordinate species the two chlorine atoms are in the apical positions of a trigonal bipyramid. The ligand is then forced to extend into the equatorial plane and can be accommodated only in a trans conformation that brings the two N-substituents into equatorial positions.

Asymmetric Induction in 2c-*trans1*. An X-ray investigation of this complex was carried out to ascertain which of the two possible trans structures, both in accord with the NMR data, was the preferred one. The two alternatives, trans1 and trans2 in Chart III, are by no means equivalent, in fact assuming that the ligand has a trans conformation with the N-substituents in equatorial positions and the less bulky proton of CHMePh directed toward the axial Cl ligands, the structure with equal configurations on adjacent C and N atoms (trans1) brings the Me groups near the equatorial olefin ligand while that with different configurations on adjacent atoms (trans2) brings the more bulky phenyls.

The molecular structure of **2c**-*trans1* is shown in Figure 5; bond distances and angles are reported in Table III. The complex has a crystallographically imposed C_2 symmetry and shows only the λ conformation of the chelate ring, while in all other compounds so far examined both the λ and δ conformations were present in the crystals. As expected, the conformation of the ligand is trans with both N-substituents in equatorial positions [C(2)–N–C(1)–C(1′) and N–C(1)–C(1′)–N′ torsion angles of 173 (1) and −61 (1)°, respectively]; moreover, both the CHMePh groups are rotated in such a way as to direct the less bulky proton toward the apical chlorine atoms.

Of the two possibilities, trans1 and trans2, the complex prefers the former; that is, the N atoms adopt the same configuration as their adjacent carbon. This allows the less bulky Me groups to be directed toward the equatorial olefin ligand. In light of these findings small differences in bond lengths and angles observed in **2c**-*trans1* and **2d**-*trans* assume some relevance. These concern the Pt–Cl bond distances, which are slightly shorter in the former than in the latter case [2.286 (4) against 2.301 (7) and 2.319 (5) Å], and the Cl–Pt–Cl axis, which is straight in the case of **2c**-*trans1* and bent (177°) outward in the case of **2d**-*trans*. Both these facts indicate a local destabilization in the case in which the Ph group points toward the coplanar olefin ligand.

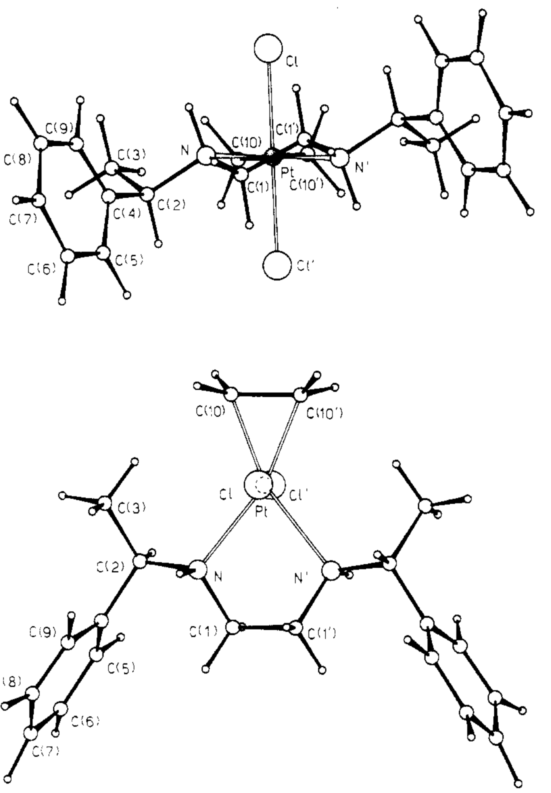

Figure 5. Molecular structure of the complex [Pt(η^2-C_2H_4)Cl_2(*R,R*-mben)] (**2c**-*trans1*) viewed along the bisector of the N–Pt–N angle and the perpendicular to the equatorial plane.

Conclusions

There are several areas in which the five-coordinate complexes differ significantly from the corresponding four-coordinate complexes. These include (i) longer Pt–N bond distances accompanied by smaller N–Pt–N bite angles, (ii) upfield shift of the NH resonance with ill-defined ^{195}Pt satellites, and (iii) higher values of the N–H stretching vibrations.[32] All these features indicate that in five-coordinate species the central metal withdraws less electron charge from the nitrogen and polarizes the N–H bond less.

Although the N–H group is less acidic in the five-coordinate than in the four-coordinate complexes, the rate of proton exchange (in D_2O-saturated chloroform solution) is much higher in the five-coordinate (complete in a few seconds) than in the four-coordinate compounds (negligible after several days). A possible explanation is that in five-coordinate species the coordinated amine, being loosely bound to the metal, can free its lone pair of electrons, allowing the exchange process to take place, as it does in free amines,[33] without the necessity of a preliminary N–H bond dissociation. It has already been shown that in the five-coordinate

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(31) The primed atoms are related to those unprimed by the transformation $-x, -y, 1 - z$.

(32) The IR spectra showed very characteristic N–H stretching bands either in four- or in five-coordinate species. In the isomers with a trans conformation of the ligand only one N–H stretching mode was observed and this occurred at 3120, 3140, 3140, and 3120 cm^{-1} for **1a**, **1b**, **1c**, and **1d**, respectively and at 3240, 3230, 3240, and 3240 cm^{-1} for **2a**, **2b**, **2c**, and **2d**, respectively.

(33) Delpuech, J. J.; Martinet, Y. *Chem. Commun.* **1968**, 478–479. Sudmeier, J. L.; Occupati, G. *J. Am. Chem. Soc.* **1968**, *90*, 154–159. Saunders, M.; Yamada, F. *J. Am. Chem. Soc.* **1963**, *85*, 1882. Delpuech, J. J.; Dechamps, M. N. *Chem. Commun.* **1967**, 1188–1189. Anet, F. A. L.; Brown, M. A. *Tetrahedron Lett.* **1967**, 4881–4884. Anderson, J. E.; Lehn, J. M. *J. Am. Chem. Soc.* **1967**, *89*, 81–87.

platinum complexes $[Pt(C_2H_4)Cl_2\{Me_2N(CH_2)_nNMe_2\}]$ a slight destabilization of the chelate ring of the diamine, such as that caused by increasing the *n* value from 2 to 4, causes a progressive shift from bis- to monocoordination of the ligand.[34] In contrast, in four-coordinate platinum(II) and six-coordinate platinum(IV) species, where the platinum–nitrogen bond is more tight, the proton exchange must necessarily take place through a preliminary N–H bond dissociation. Thus, in these cases, proton exchange and acidity of NH go hand in hand and both relate to the electron-withdrawing ability of the metal center.

The breaking of the Pt–N linkage, instead of N–H bond dissociation, can also be invoked to explain the rapid rate of nitrogen inversion observed in the five-coordinate species. This possibility was ruled out by other authors because the Me groups of the diamine in $[PtCl_2(\eta^2\text{-}PhHC{=}CH_2)\{N,N'\text{-}(EtMe_2C)_2en\}]$ exhibit a diastereotopic splitting (as a consequence of the dissymmetry in the equatorial plane) even under conditions of fast inversion at the nitrogens. In our opinion such a diastereotopic splitting would still be observed if Pt–N bond dissociation and inversion at nitrogen took place while the end of the diamine remained close to platinum. The solution behavior of the five-coordinate complexes $[Pt(\eta^2\text{-}C_2H_4)Cl_2\{N,N'\text{-}Me_2\text{-},N,N'\text{-}i\text{-}Pr_2en\}]$ (**2e**) and $[Pt(\eta^2\text{-}PhHC{=}CH_2)Cl_2\{N,N'\text{-}Me_2\text{-}N,N'\text{-}i\text{-}Pr_2en\}]$ (**2f**) buttresses this opinion.[33] In both complexes the coordinated tertiary amine group can invert configuration only through Pt–N bond dissociation. At room temperature rapid inversion of configuration at nitrogens does take place, as indicated by the equivalence of the ethylene protons and of the Me groups of *i*-Pr in **2e**. Under the same conditions the resonances of the Me groups of *i*-Pr in **2f** exhibit a diastereotopic splitting that can only stem from the dissymmetry in the equatorial plane.

Another point considered in this investigation was the preferred conformation of N,N′-disubstituted ethylenediamines in four- and five-coordinate species. This can be either cis or trans. The cis conformation has one of the N-substituents in an axial and the other in an equatorial position; the trans conformation has both substituents in equatorial positions.[36] Four-coordinate species did not appear to have a marked preference for either of these alternatives.[37] Hence, all different isomers were formed in comparable yield, and the isomers could be separated because the configuration at the nitrogens was rather stable. In all cases the ligands conform themselves to minimize steric hindrance; they rotate the N-substituents to direct the least bulky group toward the cis Cl atoms. This appears to be the most stringent steric requirement, which, however, can be fulfilled in either of the two ligand conformations.

In contrast to the case for four-coordinate complexes, the five-coordinate species have, at room temperature, variable ligand conformations that "freeze out" as the temperature is lowered. The trans conformation appears to be preferred. The obvious explanation is that the two apical ligands, in a trigonal-bipyramidal arrangement, force the other three ligands to extend into the equatorial plane, whereby the amine is forced to adopt the trans conformation with both N-substituents in equatorial positions.

A final aim of this work was to ascertain if the presence of a chiral N-substituent could determine, to some degree, the configuration on the coordinating nitrogens. No asymmetric induction was observed in the case of four-coordinate species, in which, because the nitrogens are stable chiral centers, the obtainment of a particular isomer can be dictated by factors other than stability (such as a favorable reaction pathway or low solubility in a particular solvent).

The situation is definitely different in the five-coordinate complexes. In these compounds the nitrogen configurations are labile and it is possible to see the preference for a particular isomer by lowering the temperature. Also in this case, however, the conformation of the ligand must be trans (that is, the two nitrogens must have the same configurations) for the reasons seen above. Hence, only when more trans isomers are possible (as in the case of **2c**) is it possible to discriminate between them. We conclude that the preferred configuration is the one that allows the chiral alkyl substituents to direct the least bulky group toward the apical ligands and the one immediately bigger toward the other equatorial ligand. When the priority of the groups for the assignment of the absolute configuration parallels their bulk, this corresponds to equal configurations on adjacent C and N atoms.

Acknowledgment. This work has been supported by the Consiglio Nazionale delle Ricerche (CNR) and Ministero della pubblica Istruzione (MPI), Rome, and by the University of Parma.

Registry No. **1a**-*cis*, 111338-69-3; **1a**-*trans*, 111408-83-4; **1b**-*cis*, 114613-17-1; **1b**-*trans*, 114613-18-2; **1c**-*cis*, 114613-20-6; **1c**-*trans1*, 114613-21-7; **1c**-*trans2*, 114613-22-8; **1d**-*cis1*, 114613-23-9; **1d**-*cis2*, 114613-24-0; **1d**-*trans*, 114613-25-1; **2a**-*trans*, 66945-62-8; **2b**-*trans*, 114613-19-3; **2c**-*trans1*, 114613-26-2; **2d**-*trans*, 114613-27-3; (*R*,*R*)-mben, 76740-22-2; (±)-mben, 19302-22-8; (*R*,*S*)-mben, 103421-77-8; *t*-Bu_2en, 4062-60-6; *i*-Pr_2en, 4013-94-9; (±)-mben·2HCl, 114581-00-9; (*R*,*S*)-mben·2HCl, 114563-80-3; $[PtCl(DMSO)(i\text{-}Pr_2en)]Cl$, 114594-67-1; $[PtCl_2(DMSO)_2]$, 15274-33-6; *cis*-[PtCl(DMSO)(*R*,*R*-mben)]Cl, 114672-88-7; *cis2*-[PtCl(DMSO)(*R*,*S*-mben)]Cl, 114672-89-8; $K_2[PtCl_4]$, 10025-99-7; $K[Pt(\eta^2\text{-}C_2H_4)Cl_3]$, 16405-35-9; N_2, 7727-37-9; α-(*R*)-methylbenzylamine, 3886-69-9; 1,2-dibromoethane, 106-93-4; racemic α-methylbenzylamine, 98-84-0; racemic α-methylbenzylamine hydrobromide, 48104-35-4.

Supplementary Material Available: Listings of atomic coordinates (Tables SI–SIII, SV, SVII, SIX, and SXI) and thermal parameters (Tables SIV, SVI, SVIII, SX, and SXII) (12 pages); listings of observed and calculated structure factors (64 pages). Ordering information is given on any current masthead page.

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(34) A shift from five- to four-coordination has been observed in complexes of this type with less effective chelators such as diimines and bis(hydrazones)[9b] and also in other similar complexes such as $[PtX_2(PR_3)(L\text{-}L)]$ (X = anionic ligand, L-L = bidentate ligand: Dixon, K. R. *Inorg. Chem.* **1977**, *16*, 2618–2624. van der Poel, H.; van Koten, G.; Vrieze, K. *Inorg. Chem.* **1980**, *19*, 1145–1151. van der Poel, H.; van Koten, G.; Grove, D. M.; Pregosin, P. S.; Ostoja Starzewski, K. *Helv. Chim. Acta* **1981**, *64*, 1174). Moreover, a change of the chelate bonding mode (σ,σ′-N,N′) of the dinitrogen ligand to a σ-N unidentate mode has been proposed in the study of olefin and ligand exchange in five-coordinate complexes.[10c]

(35) The synthesis and spectroscopy of compound **2e** were in accord with ref 6. Compound **2f** was prepared by the usual procedure starting from the styrene analogue of Zeise's salt;[10a] the ^1H NMR spectrum in $CDCl_3$ solution and at 20 °C gave resonances (δ, downfield from TMS) at 7.16 (2 H), 7.39 (1 H), and 7.66 (2 H) (Ph group of styrene), 5.68 (1 H), 4.37 (1 H), and 3.63 (1 H) (olefinic protons of styrene), 3.94 (2 H), 1.44 (6 H), and 1.18 (6 H) (*i*-Pr groups), 2.46 (6 H) (N–Me groups), and 2.79 (m, 2 H) and 2.90 (m, 2 H) (NCH_2CH_2N protons).

(36) A δ–λ inversion of the puckered ring would, however, bring the N-substituents from an equatorial to an axial position.

(37) Erickson, L. E.; Fritz, H. L.; May, R. J.; Wright, D. A. *J. Am. Chem. Soc.* **1969**, *91*, 2513–2518.