Carbon-13 Nuclear Magnetic Resonance Studies on Platinum(II) Complexes of Alicyclic 1,2-Diamines

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A series of new *cis*-diammino(diamine)platinum(II) chlorides, where the diamines are seven different 1,2-cycloaliphatic diamines, have been prepared, and the ^{13}C NMR spectra have been obtained. ^{13}C chemical shifts resemble those of the diamine dihydrochlorides with a *ca.* 10 ppm downfield shift of C(a) due to the platinum binding.

$^{2}J_{PtNC}$ in the chelate rings varies from 0 to 13.5 Hz, increasing with the strain in the chelate ring. $^{3}J_{PtNCC}$ values of 0 to 53.7 Hz were obtained. From these data and the relevant X-ray crystal data a Karplus-type dependence was found for $^{3}J_{PtNCC} = 54 \cos^2 \phi$ where ϕ is the dihedral angle Pt–N–C–C.

The fact that the three-bond coupling constants $^{3}J_{PtNCC}$ normally are easily determined in the proton-decoupled carbon-13 NMR spectra of platinum(II) diamine complexes has resulted in several investigations on the conformational behavior of diamine and amino acid complexes of platinum(II).[1−5] The data have been interpreted by assuming a Karplus-type angular dependence with the dihedral angles in the four atom fragments Pt–N–C–C. It has been suggested that the variation of $^{3}J_{PtNCC}$ fits the simple relationship:

$$^{3}J_{PtNCC} = k \cos^2 \phi$$

ϕ being the dihedral angle between the planes Pt–N–C and N–C–C[2−4] and k being a constant. As most of the investigated complexes undergo rapid conformational inversion on the NMR time scale, the reported coupling constants represent average values of at least two conformers. In order to explore the true dihedral angle dependence of $^{3}J_{PtNCC}$ we have examined the ^{13}C NMR spectra of

several new square–planar platinum(II) complexes with cyclic aliphatic 1,2-diamines. For these complexes, the range of possible geometries are restricted even in solution. Using reported X-ray crystal structural data it has been possible to find the relevant dihedral angles and check the reliability of the Karplus relationship for this kind of system.

Stereochemistry. As for the alicyclic condensed ring systems (hydrindanes and pentalanes) the systems obtained by fusing a five-membered chelate ring to an aliphatic ring give two strainless modifications differing in the type of locking (*cis*- or *trans*-) at the bridge. Cyclic *cis*-1,2-diamines lead to *cis*-fused systems and *trans*-1,2-diamines to *trans*-fused systems. In the fused ring systems several constrains are put on the involved angles. Especially the range of dihedral angles are far more restricted than for single ring systems. For the *cis*-fused systems the chelate ring will be least puckered when the alicyclic ring is nearly planar, whereas for the *trans*-fused systems the opposite trend will be seen. The *trans*-1,2-diamines are chiral and will only be able to coordinate with both the amino–groups in equatorial positions. For a given chirality of the 1,2-diamine the conformation (δ or λ) of the chelate ring is defined and no conformational inversions are possible in the complex. The *cis*-1,2-diamines are *meso* ligands with one amino-group axial and the other equatorial, the complexes will be *enantiotopic*, and in a *symmetrical* environment the potential energy of the δ and λ conformations of the chelate ring will be equal and the inversions are expected to occur easily.

RESULTS AND DISCUSSION

Preparations. The dihydrochlorides of the cyclic 1,2-diamines were prepared according to methods reported in the literature,[6-8] except for the two isomers of *trans*-trimethyl-1,2-cyclohexanediamine (3,5,5-tmchxn and 3,3,5-tmchxn), which were separated from a commercial isomer mixture of "isophoronediamines".[9]

To ensure high solubility of all the samples used in the NMR experiments and to avoid complications due to steric or chemical interactions from other ligands, we have chosen a homologous series of *cis*-diammino(1,2-diamine)platinum(II) chlorides in our investigation. These salts were prepared in two steps. First the slightly soluble *cis*-dichloro(1,2-diamine)platinum(II) compounds were prepared by neutralization of a 70 °C warm aqueous solution of equimolar amounts of 1,2-diamine dihydrochloride and potassium tetrachloroplatinate(II) with sodium hydroxide (1 M). The *cis*-diammino(1,2-diamine)-platinum(II) chlorides were prepared by suspending the *cis*-dichloro(1,2-diamine)platinum(II) compounds in a 60 °C warm ammonia solution (2 M) until a complete dissolution was achieved. The *cis*-dichloro-*trans*(trimethyl-1,2-cyclohexanediamine)-platinum(II) compounds turned out to be too insoluble for this procedure to be usefull, so in these cases we reacted *cis*-dichlorodiamminoplatinum(II) with the pertinent diamines. For the two 1,2-

Table 1. ^{13}C NMR chemical shifts for cyclic 1,2-diammonium chlorides.

Compound	ppm			
	C(a)	C(b)	C(c)	CH$_3$
(*c*-cbnH$_2$)$^{2+}$	48.49	23.45		
(*t*-cbnH$_2$)$^{2+}$	49.38	21.73		
(*c*-cptnH$_2$)$^{2+}$	53.75	28.07	20.01	
(*t*-cptnH$_2$)$^{2+}$	56.10	30.68	22.62	
(*c*-chxnH$_2$)$^{2+}$	50.96	26.77	21.25	
(*t*-chxnH$_2$)$^{2+}$	53.18	30.31	23.80	
(3,3,5-tmchxnH$_2$)$^{2+}$	61.09	38.85	47.76	26.15
	51.04	35.70	28.88	21.57
				19.91
(3,5,5-tmchxnH$_2$)$^{2+}$	59.33	42.74	45.86	31.89
	50.92	31.89	31.17	24.81
				18.58

cyclohexanediamines (chxn) the bis(chxn)platinum-(II) complexes were also prepared. Using optically pure *trans*-*R*,*R*-chxn only one isomer is possible.[11] For the bis(*cis*-*R*,*S*-chxn)platinum(II) complex two isomers exist, distinguished by the spatial arrangement (*cis* or *trans*) of the optical centers. Only one of these isomers, probably the "*trans*" isomer, was isolated. *trans*-[Pt(RR-chxn)$_2$Cl$_2$]Cl$_2$ was obtained by chlorination of the corresponding platinum(II) salt, as described earlier.[11]
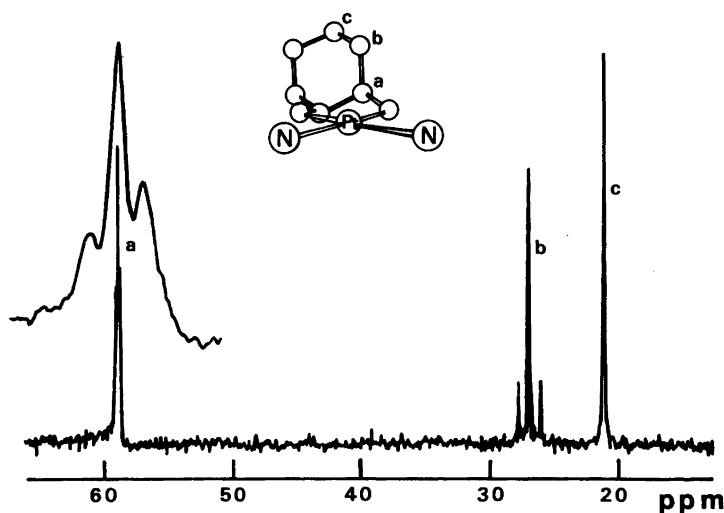
The elemental analyses (Pt,C,H,N,Cl) were all

Fig. 1. The proton-decoupled 15.03 MHz ^{13}C NMR spectrum of *cis*-diammino-*cis*-1,2-cyclohexanediamine platinum(II) chloride in D$_2$O (0.5 M).

Table 2. ^{13}C NMR chemical shifts (ppm) and coupling constants (^{195}Pt$-^{13}$C; Hz) for [Pt(1,2-diamine)(NH$_3$)$_2$]$^{2+}$ complexes.

Compound	C(a)	C(b)	C(c)	CH$_3$	$^{2,3}J_{PtC}$	$^{3}J_{PtC}$
[Pt(c-cbn)(NH$_3$)$_2$]$^{2+}$	59.50	24.20				<2
[Pt(c-cptn)(NH$_3$)$_2$]$^{2+}$	64.31	29.18	20.97			22.6
[Pt(t-cptn)(NH$_3$)$_2$]$^{2+}$	68.16	23.96	26.31		13.4	37.2
[Pt(c-chxn)(NH$_3$)$_2$]$^{2+}$	58.87	26.92	21.25		3.9	24.7
[Pt(c-chxn)$_2$]$^{2+}$	58.26	26.99	21.34		4	24.9
[Pt(t-chxn)(NH$_3$)$_2$]$^{2+}$	62.57	33.15	24.93		7.1	52.6
[Pt(t-chxn)$_2$]$^{2+}$	62.20	33.17	24.97			50.8
[Pt(t-chxn)$_2$Cl$_2$]$^{2+}$	62.76	32.51	24.51			29.9
[Pt(3,3,5-tmchxn)(NH$_3$)$_2$]$^{2+}$	70.54	41.81	48.53	27.77		50.0
	58.89	36.02	28.90	21.41		44.6
				19.51		
[Pt(3,5,5-tmchxn)(NH$_3$)$_2$]$^{2+}$	68.93	45.57	46.91	31.81		53.7
	59.98	31.84	32.46	25.50		46.4
				18.21		

satisfactory except for the *trans*-1,2-cyclobutanediamine (*trans*-cbn) complex, which contained an excess of nitrogen and chloride. In this case the product probably is polynuclear, due to the inability of *trans*-cbn to function as a bidentate ligand.

^{13}*C NMR spectra.* Typical features of the proton decoupled 15.03 MHz ^{13}C NMR spectra of these compounds are illustrated by the spectrum of [Pt(*cis*-chxn)(NH$_3$)$_2$]Cl$_2$ (0.5 M in D$_2$O), Fig. 1. The fact that only three resonances are seen confirm the bidentate nature of the ligand and shows that the conformational inversion is rapid on the NMR time scale. The data for all the ligands and the platinum complexes are given in Tables 1 and 2. Generally the resonances were assigned through the well-established rule that the C atoms next to the electronegative nitrogen C(a) are shifted more downfield than the other C atoms. These assignments were confirmed by the off-resonance spectra, showing a doublet for C(a) and triplets for the other C atoms. The coupling to ^{195}Pt ($I=\frac{1}{2}$, 33 % abundance) is expected to give rise to two satellite peaks of 17 % intensity, one on each side of the main peak, as indeed is seen in many cases.

^{13}*C chemical shifts.* The ^{13}C chemical shifts of the dihydrochlorides of the 1,2-diamine ligands are characteristic compared to other known diammonium salts.[1-5] On complexation to platinum(II) a downfield shift of about 10 ppm for the C(a) and a few ppm for the other C atoms is seen. The effect on the C atoms neighbour to nitrogen arises in part from electron withdrawal from the N atoms on the

covalent binding to platinum(II). Only in the case of the *trans*-1,2-cyclopentanediamine (*trans*-cptn) platinum(II) complex is a marked deviation from this pattern observed. Most remarkable is the large upfield shift of C(b) (6.7 ppm) causing it to appear at higher field than the C(c). The same trend is observed for the [Co(*trans*-cptn)$_3$]Cl$_3$ salt.[10] It is difficult to rationalize this result within the present knowledge of ^{13}C NMR chemical shifts, but no doubt the effect is connected to the strain introduced in the cyclopentane ring on coordination. It is remarkable that the δ value for C(b) in [Pt(*cis*-cbn)(NH$_3$)$_3$] also is unusually small, here reflecting the strain in the cyclobutane ring. The change of the oxidation state of the platinum from II to IV has practically no influence on the ^{13}C NMR chemical shifts.

^{195}*Pt*$-^{13}$*C Coupling constants.* The $^{2}J_{PtNC}$ coupling constants for the five-membered chelate diamine rings are given in Table 2. They are usually
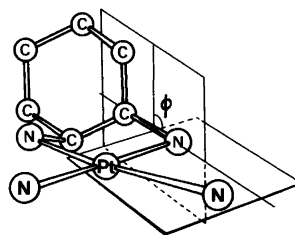

Fig. 2. The *cis*-diammino-(*cis*-1,2-cyclohexane-diamine) platinum(II) ion, where one of the two Pt$-$N$-$C$-$C dihedral angles ϕ are outlined.

small or zero, which can be explained by a multipath coupling mechanism, as suggested by Erickson et al.[2] The coupling is regarded as the sum of couplings via a two-bond and a three-bond path through the chelate ring, where the ^2J and ^3J are assumed to have similar magnitude, but opposite signs. It is remarkable that the largest observed $^{2,3}J_{\text{PtNC}}$ coupling constant (13.4 Hz) is seen for [Pt(trans-cptn)(NH$_3$)$_2$]$^{2+}$, where the chelate ring is expected to be more puckered than usual, due to strain from the nearly planar cyclopentane ring. Among the platinum(II) complexes with cyclic cis-1,2-diamines, only the most strained one, cis-chxn, shows a $^{2,3}J$ coupling (3.5 Hz). In Fig. 3 the observed $^{2,3}J_{\text{PtNC}}$ coupling constants are plotted as a function of $\cos^2 \alpha$, where α is the dihedral angle of the chelate ring, $N - C(a) - C(a)' - N'$ as found in the respective X-ray analysis [11,12,15] (for cis-cbn and cis-cptn, however, only estimated from models). Due to the strain in five-membered chelate rings α will be proportional to the $Pt - N - C(a) - C(a)'$ dihedral angle ϕ, which is expected to determine the $^3J_{\text{PtNCC}}$ coupling via a Karplus relation of the type $J = k \cos^2 \phi$.* The points define a straight line with a slope of -50 Hz. The intercept on the $^{2,3}J$ axis of 24 Hz, corresponding to no contribution from the ^3J path, should reflect the ^2J and this value is actually in good agreement with values found for platinum(II) complexes of aliphatic monamines (appr. 25 Hz).[2,4] Thus the useful relation (1) seems to work. It is remarkable that the relation also holds for aromatic ligands as bipyridine, where $\alpha = 0$ gives $J = -26$ Hz in agreement with the value found by Erickson.[4] (28 -32 Hz.)

$$^{2,3}J_{\text{PtNC}} = {}^2J_{\text{PtNC}} - {}^3J_{\text{PtNCC}} = 24 - 50 \cos^2 \alpha \qquad (1)$$

The $^3J_{\text{PtNCC}}$ coupling constants to C(b) show the largest variation through the series (0 to 53.7 Hz). The coupling constants are smallest for the cis

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*The structure of a five-membered ring is completely specified by 9 independent parameters, so if just 5 distances and 3 angles (e.g. 2 interatomic angles and one dihedral angle) are specified, the remaining angles are interdependent. If it is assumed that the interatomic distances and angles are fixed the conformational changes of the ring can be described with a single dihedral angle and an interdependence will exist between this and the other dihedral angles. With data from the 1,2-diamineplatinum(II) structures,[11,15] the following relation is found for the five-membered chelate ring: $\cos \phi = 0.28 + 0.78 \cos \alpha$. The relation is only defined for α larger than $23°$ ($\phi = 0$), excluding strain-free planar chelate rings.
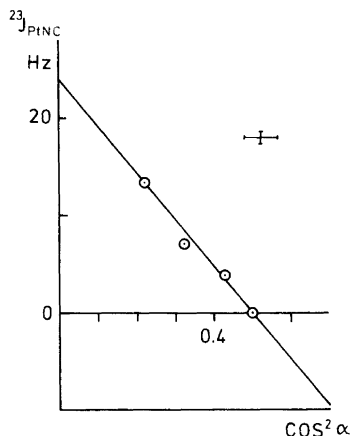

Fig. 3. A plot of the coupling constant $^{2,3}J_{\text{PtNC}}$ for the chelate ring as a function of $\cos^2 \alpha$, where α is the dihedral angle $N_1 - C_1 - C_2 - N_2$. The bars indicate the uncertainties.

complexes. Because of the rapid conformational inversion of the chelate ring in these complexes an averaged coupling to the methylene groups, spending equal times in equatorial and axial orientations, are seen. The unsymmetrical structure of a coordinated cis-chxn has recently been demonstrated through the X-ray crystal structure of [Pt(cis-chxn)Cl$_2$].[15] The geometry is shown in Fig. 2 for the corresponding cis-diammino complex and the dihedral angle ϕ for the axial methylene is depicted. From the data a value of 98° for the axial and 160° for the equatorial methylene group were calculated. Similar data were found from the crystal analysis of the fac-Δ-[Co(cis-chxn)$_3$]Cl$_3$, by Bernal.[14] Assuming a rapid conformational interchange in solution a time-averaged environment between the two conformers yields an average ϕ of 129°. We tried to estimate the rate of the conformational interchange by recording the ^{13}C NMR spectrum of [Pt(cis-chxn)(NH$_3$)$_2$](CF$_3$COO)$_2$ in methanol at $-100°C$. Apart from some broadening of the lines, no changes were observed in the spectrum compared to that at room temperature. As a separation of about 100 Hz between the resonances of an equatorial and an axial carbon atom is expected we see that even at $-100°C$ the rate is very high. In chelated trans-cptn, trans-chxn, trans-3,3,5-tmchxn and trans-3,5,5-tmchxn the conformational changes are locked and the C(b) are necessarily equatorial all the time. The
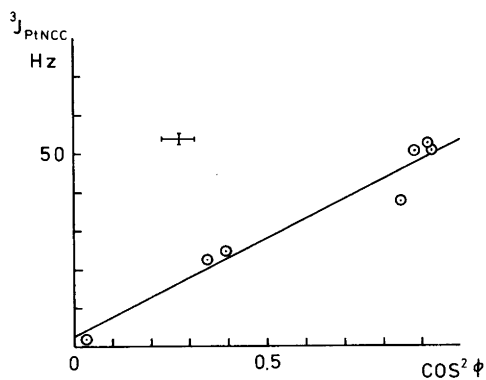
Fig. 4. A plot of the coupling constant $^3J_{\mathrm{PtNCC}}$ as a function of $\cos^2 \phi$, where ϕ is the angle defined in Fig. 2. The bars indicate the uncertainties.

$^3J_{\mathrm{PtNCC}}$ values fall in the range 37.2 to 53.7 Hz. Because of the very stiff nature of the fused ring systems crystallographic data should give quite reliable data for the dihedral angle. Using data reported for $\Lambda(\delta\delta\delta)(lel)_3[\mathrm{Co}(S,S\text{-cptn})_3]\mathrm{Cl}_3,$[12] $\Lambda(\delta\delta\delta)(lel)_3[\mathrm{Co}(RR\text{-chxn})_3]\mathrm{Cl}_3 5\mathrm{H}_2\mathrm{O}$[13] and $[\mathrm{Pt}(R,R\text{-chxn})_2\mathrm{Cl}]\mathrm{Cl}_2,$[11] we calculated ϕ values of 157, 162 and 164°, respectively (suggesting an uncertainty of $+3°$ in the values). No structural data for coordinated *cis*-cbn are available, but by using data for 1,2-*cis*-cyclobutanedicarboxylic acid[17] and again assuming rapid conformational change, an average ϕ value very close to 90° is predicted. An average value for *cis*-cptn of 126° was estimated from molecular models. The validity of the Karplus relationship for the $^3J_{\mathrm{PtNCC}}$ of the cyclic 1,2-diamine platinum(II) complexes is demonstrated by the plot of $^3J_{\mathrm{PtNCC}}$ as a function of $\cos^2 \phi$ in Fig. 4. It is seen that the best straight line through the points passes the origo, showing that no constant term is needed in the expression (2). That the point for *trans*-cptn is significantly below the line, might be due to the considerable strain in this system, weakening the Pt − N bond.

$$^3J_{\mathrm{PtNCC}} = 54 \cos^2 \phi \qquad (2)$$

Expressions (1) and (2) might have useful applications in the determination of the conformation of amine platinum(II) complexes, however, the coupling constants show some variation with substitution at the involved atoms.[4] The corrections for methyl substitution at carbon

can be obtained from the isomeric trimethyl-*trans*-1,2-cyclohexanediamine platinum(II) salts. Assuming that the substitution does not lead to large changes in the cyclohexanering geometry, the correction for one CH_3 substitution at C(b) will be a 12% reduction in $^3J_{\mathrm{PtNCC}}$ corresponding to (2'). Substitution of two hydrogens for two CH_3 at the same carbon atom will lead to a 15% reduction of $^3J_{\mathrm{PtNCC}}$ corresponding to (2'').

$$^3J_{\mathrm{PtNCC}} = 47 \cos^2 \phi \qquad (2')$$

$$^3J_{\mathrm{PtNCC}} = 46 \cos^2 \phi \qquad (2'')$$

Similar expressions are expected to work for the J values of methyl-substituted chelate rings. For substitution at a single carbon, eqn. (1') and for dimethyl substitution at one carbon atom, eqn. (1''). The predicted $^{2,3}J_{\mathrm{PtNC}}$ for the 1,2-propylenediamine and isobutanediamine platinum(II) complexes (assuming $\alpha = 51°$ as in the crystal structure of $[\mathrm{Pt}(R\text{-pn})_2]\mathrm{Cl}_2$[19]) are then 7 and 8 Hz respectively, in agreement with the experimental values of 6 and 8 Hz.[4]

$$^{2,3}J_{\mathrm{PtNC}} = 24 - 44 \cos^2 \alpha \qquad (1')$$

$$^{2,3}J_{\mathrm{PtNC}} = 24 - 42 \cos^2 \alpha \qquad (1'')$$

By oxidation of $[\mathrm{Pt}(trans\text{-chxn})_2]^{2+}$ to $[\mathrm{Pt}(trans\text{-chxn})_2\mathrm{Cl}_2]^{2+}$ the $^3J_{\mathrm{PtNCC}}$ is nearly halved. This is understandable if it is assumed that the *s*-character on Pt is shared equally by all ligands. Then a change from square − planar to octahedral coordination should reduce the *s*-character in the Pt − N bonds with a factor of 0.67, not far from the 0.57 found.

EXPERIMENTAL

1. *Preparation of the 1,2-diamines.* cis and trans-*1,2-cyclobutanediamine* (*cis* and *trans*-cbn) were prepared from the 1,2-cyclobutanedicarboxylic acids by double Curtius degradations of the azides according to Buchman.[6] Yields as the dihydrochlorides: 20% (Anal. $C_4H_{12}N_2Cl_2$: C, H, N, Cl).

cis *and* trans-*1,2-cyclopentanediamine* (*cis* and *trans*-cptn) were prepared according to Toftlund[7] by reduction of 1,2-cyclopentanedionedioxime. Yields as the dihydrochlorides: 20% (Anal. $C_5H_{16}N_2Cl_2$: C, H, N, Cl).

cis- *and* trans-*1,2-cyclohexanediamine* (*cis* and *trans*-chxn) were prepared according to Toftlund[8]

and Galsbøl.[16] Yields as the dihydrochlorides: 10 and 60 %. (Anal. $C_6H_{16}N_2Cl_2$: C, H, N, Cl).

trans-3,3,5-Trimethyl-1,2-cyclohexanediamine (3,3,5-tmchxn) and trans-3,5,5-trimethyl-1,2-cyclohexanediamine (3,5,5-tmchxn) were separated from a crude product of "isophoronediamine" purchased from VEBA-Chemie. The work-up was done via the nickel(II) complex chlorides as described elsewhere.[9] Yields as the dihydrochlorides: 8 % (Anal. $C_9H_{22}N_2Cl_2$: C, H, N, Cl).

2. *Preparation of the* cis-diammino(diamine)platinum(II) chlorides. The yellow cis-dichloro(diamine)-platinum(II) compounds were prepared in accordance with the procedure for the corresponding ethylenediamine complex.[18]

The colourless cis-diammino(diamine)platinum-(II) chlorides were obtained by stirring the corresponding cis-dichloro(diamine)platinum(II) compounds with ammonia solutions (2 M) at 70 °C for several hours. The resulting solutions were evaporated in vacuo and the salts were precipitated with ethanol (96 %). Yield: cis-[Pt(cis-cbn)(NH_3)_2]Cl_2 33 %. (Anal. [Pt($C_4H_{10}N_2$)(NH_3)_2]Cl: Pt, C, H, N, Cl), cis-[Pt(cis-cptn)(NH_3)_2]Cl_2 50 % (Anal. [Pt-($C_5H_{12}N_2$)(NH_3)_2]Cl_2: Pt, C, H, N, Cl), cis-[Pt(trans-cptn)(NH_3)_2]Cl_2 60 % (Anal. [Pt-($C_5H_{12}N_2$)(NH_3)_2]Cl_2: Pt, C, H, N, Cl), cis-[Pt-(cis-chxn)(NH_3)_2]Cl_2: 70 % (Anal. [Pt($C_6H_{14}N_2$)-(NH_3)_2]Cl_2: Pt, C, H, N, Cl), cis-[Pt(trans-chxn)-(NH_3)_2]Cl_2: 70 % (Anal. [Pt($C_6H_{14}N_2$)(NH_3)_2]Cl_2: Pt, C, H, N, Cl).

The platinum complex obtained starting from the trans-1,2-cyclobutanediamine was not pure and probably polymeric, as it shows broad ^{13}C NMR lines. Yield: 33 % (Anal. Found: C 12.4: H 4.0: N 10.3: Cl 16.5: Pt 48.6, Calc. for [Pt($C_4H_{10}N_2$)-(NH_3)_2]Cl_2: C 12.4: H 4.14: N 14.5: Cl 18.4: Pt 50.5).

In the case of the two trans-trimethyl-1,2-cyclo-hexanediamines the cis-dichloro(diamine)platinum-(II) compounds were not dissolvable in ammonia solutions, even after stirring for several days at 90 °C. Instead the two cis-diamine salts were obtained by reacting a suspension of cis-dichloro-diamminoplatinum(II) with the trans-trimethyl-1,2-cyclohexanediammonium chlorides and slowly neutralizing the solutions with sodium hydroxide at 70 °C. When cis-dichloro-diamminoplatinum(II) was dissolved, the solutions were evaporated in vacuo and the products were precipitated with ethanol (96 %). Yield of cis-[Pt(3,3,5-tmchxn)-(NH_3)_2]Cl_2: 58 % (Anal. [Pt($C_9H_{20}N_2$)(NH_3)_2]Cl_2: Pt, C, H, N, Cl). Yield of cis-[Pt(3,5,5-tmchxn)-(NH_3)_2]Cl_2: 57 % (Anal. [Pt($C_9H_{20}N_2$)(NH_3)_2]Cl_2: Pt, C, H, N, Cl).

3. *Bis[(−)1R,2R-cyclohexanediamine]platinum-(II) chloride.* This salt was obtained as described by Toftlund.[11] Yield: 84 % (Anal. [Pt($C_6H_{14}N_2$)_2]-Cl_2: Pt, C, H, N, Cl).

Bis[cis-1,2-cyclohexanediamine]platinum(II) chloride. Was prepared analogous to the above compound. Yield: 80 % (Anal. [Pt($C_6H_{14}N_2$)_2]Cl_2: Pt, C, H, N, Cl).

4. trans-Dichloro-bis[(−)-1R,2R-cyclohexanedi-amine]platinum(IV) chloride, was prepared as described by Toftlund.[11] Yield: 75 % (Anal. [Pt-($C_6H_{14}N_2$)_2Cl_2]Cl_2: Pt, C, H, N, Cl).

5. *Measurements.* All the ^{13}C NMR spectra were recorded on a 15.03 MHz JEOL FX-60 NMR spectrometer. The solvent was in every case D_2O (approx. 0.5 M) with a little methanol as reference.

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