Asymmetric Synthesis of Coordination Compounds: Back to the Roots. Diastereoselective Synthesis of Simple Platinum(IV) Complexes

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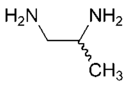
Dedicated to Professor *André Merbach* on the occasion of his 65th birthday

A publication by *Alexander P. Smirnoff* in *Helvetica Chimica Acta* in 1920 [6] describes the first synthesis of a coordination species, *i.e.*, of tris(propane-1,2-diamine-$\kappa N^1,\kappa N^2$)platinum(4+) ([$\mathrm{Pt^{IV}(pn)_3}]^{4+}$), where it was shown that the configuration of a chiral center in the ligand can influence the configuration at the metal. The present investigation of [$\mathrm{Pt^{IV}(pn)_3}]^{4+}$ was carried out by NMR spectroscopy, where all nuclei in the metal complex were used as sources of information, *i.e.*, ^{1}H, ^{13}C, ^{15}N, and ^{195}Pt. ^{13}C-NMR and ^{15}N-NMR spectroscopy (of isotopically enriched complex) were especially informative for the analysis of isomer distribution. Stereoselectivity in the formation reaction of the complexes is rather modest, whereas Δ-, and Λ-isomers can be separated efficiently by crystallization. A mixture of [Pt{(*S*)-pn}$_3$]$^{4+}$ and [Pt{(*R*)-pn}$_3$]$^{4+}$ shows no scrambling of the enantiomeric ligands, thus proving the inertness of the complexes.

1. Introduction. – Asymmetric synthesis, *i.e.*, the building up of chiral C-centers in one preferential configuration by using a chiral auxiliary, has been an extremely important tool in organic chemistry for more than a century. Natural-product synthesis, one of the main topics of 20th-century organic chemistry, would not have been possible without an arsenal of highly elaborate stereoselective reaction methods. The basis of asymmetric synthesis in organic chemistry was led by *Emil Fischer* in the late 19th century. At that time, it was believed that optical activity of chemical compounds is always due to asymmetric C-atoms, nowadays called stereogenic C-atoms, as postulated in 1874 by *van't Hoff* [1] and *Le Bel* [2]. *Alfred Werner* conjectured in 1899 [3] that also coordination compounds with octahedral geometry could exhibit optical activity. This was experimentally demonstrated 12 years later [4]. The discovery of optically active metal complexes represented the ultimate proof of *Werner*'s coordination theory for which he was awarded the *Nobel* prize in 1913. In 1914, *Werner* demonstrated that a completely inorganic coordination compound, containing no C-atoms, a tetranuclear Co-complex, could also be resolved into optically active enantiomers [5]. *Werner* was not able to continue his work for long, due to ill health. Yet the research with optically active compounds in *Werner*'s laboratory at the University of Zürich continued. All 'asymmetric' coordination compounds that were obtained in optically active form in *Werner*'s laboratory had been prepared without any chiral auxiliary, thus leading to racemates. Only for the resolution into enantiomers, chiral auxiliaries in the form of enantiomerically pure anions or cations were employed. Only in 1920, a publication appeared, with *Alexander P. Smirnoff* as single author [6], describing the synthesis of coordination compounds starting with an enantiomerically pure ligand, propane-1,2-

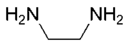
diamine, abbreviated (pn). It is quite clear that also this work was initiated by *Alfred Werner*, since *Smirnoff* writes as in introduction to the publication 'Die vorliegende, aus äusseren Gründen bis jetzt unveröffentlicht gebliebene Untersuchung ist zum grössten Teil im wissenschaftlichen Laboratorium des Herrn Prof. Dr. *A. Werner* noch im Sommer 1917 ausgeführt worden; mit dem herzlichsten Gefühle tiefen Dankes für die Arbeitsmöglichkeit und die mir z. T. überlassenen kostbaren Materialien gedenke ich meines nun verschiedenen Meisters'. *Smirnoff* quotes two publications of *E. Fischer* [7] on the stereoselective formation of sugar derivatives as analogous examples in organic reactions. *Indeed, the paper by* Smirnoff *can be considered as the first report of an asymmetric synthesis, where chirality at the metal is induced by chiral centers located in the ligands.* Unfortunately, the work of *Smirnoff* was completely overlooked by researchers in the field, who took up the subject much later [8]. It seems that the publication by *Smirnoff* has never been cited for 76 years until 1996 [9]¹). Stereoselective synthesis of coordination species has only recently started to become a subject of increased importance [10]. Since the work of *Smirnoff* has never been repeated in detail, we decided to investigate the propane-1,2-diamine platinum systems with modern methods, with an emphasis on NMR spectroscopy.

Propane-1,2-diamine (**1**), which was formerly named propylenediamine (pn) in coordination chemistry, can be considered to be a 'chiralized' form of the archetype of all amine chelate ligands, ethane-1,2-diamine (**2**), which is still designated as ethylenediamine (en) in almost all textbooks. The ligand en was one of the preferred ligands studied by *Alfred Werner*, especially with respect to its ability to form chiral coordination species.



1 pn

rac-**1**
(*R*)-**1**
(*S*)-**1**



2 en

While en forms chiral octahedral (*OC*-6) complexes [M(en)$_3$] showing D_3 symmetry (disregarding conformers of the chelate rings), which exist in two enantiomeric forms, generally designated by the chiral descriptors Δ and Λ, the situation concerning stereoisomers is much more involved for [M(pn)$_3$] species. Their racemic ligand *rac*-pn (*rac*-**1**) forms 24 stereoisomers of (*OC*-6)-[M(pn)$_3$] species (*Table 1*).

The corresponding *mer*/*fac* diastereoisomers (*Fig. 1*) appear with relative statistical weights of 3 : 2. Although, in principle, a complete analysis of the species formed by

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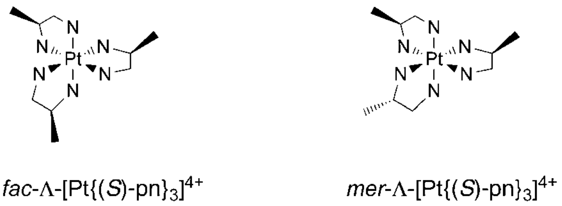
¹) Note added in proof: Despite a careful literature search in the beginning of this project, it turned out that we missed four references [18–21] to *Smirnoff*'s publication. They do not appear, for reasons unknown to us, if the latter is searched in *SciFinder* for 'Citing References'. None of these publications treat the stereochemical properties of the [Pt(pn)$_3$]$^{4+}$ complexes in the same thorough manner, as is done in the present publication. The four references date from 1959–1971, when NMR spectroscopy was by far not as developed as today.

Table 1. *Stereoisomers of [M(en)$_3$] and of [M(*rac-*pn)$_3$] Coordination Species. Columns 1* and *2* contain the enantiomer pairs of a given species, the rows correspond to different diastereoisomers.

Δ-Enantiomer	Λ-Enantiomer	Symmetry
Δ-[M(en)$_3$]	Λ-[(M(en)$_3$]	D_3
fac-Δ-[M{(*S*)-pn}$_3$]	*fac*-Λ-[M{(*R*)-pn}$_3$]	C_3
mer-*Δ*-[M{(*S*)-pn}$_3$]	*mer*-Λ-[M{(*R*)-pn}$_3$]	C_1
fac-Δ-[M{(*S*)-pn}$_2${(*R*)-pn}]	*fac*-Λ-[M{(*R*)-pn}$_2${(*S*)-pn}]	C_1
3 *mer*-Δ-[M{(*S*)-pn}$_2${(*R*)-pn}]	3 *mer*-Λ-[M{(*R*)-pn}$_2${(*S*)-pn}]	C_1
fac-Δ-[M{(*S*)-pn}{(*R*)-pn}$_2$]	*fac*-Λ-[M{(*R*)-pn}{(*S*)-pn}$_2$]	C_1
3 *mer*-Δ-[M{(*S*)-pn}{(*R*)-pn}$_2$]	3 *mer*-Λ-[M{(*R*)-pn}{(*S*)-pn}$_2$]	C_1
fac-Δ-[M{(*R*)-pn}$_3$]	*fac*-Λ-[M{(*S*)-pn}$_3$]	C_3
mer-Δ-[M{(*R*)-pn}$_3$]	*mer*-Λ-[M{(*S*)-pn}$_3$]	C_1



fac-Λ-[Pt{(*S*)-pn}$_3$]$^{4+}$ *mer*-Λ-[Pt{(*S*)-pn}$_3$]$^{4+}$

Fig. 1. *Two of 24 possible stereoisomers* (*Table 1*) *of [Pt(pn)$_3$]$^{4+}$*

rac-pn would yield comprehensive results concerning the stereoselectivity of the complex formation of this type, the relatively large number of stereoisomers makes an investigation of this system unattractive.

However, the use of enantiomerically pure pn facilitates the analysis enormously. When only one enantiomer of the ligand is used, only four diastereoisomeric complexes are formed (*Table 2*).

Table 2. *Four Diastereoisomers for an* (OC-6) *Coordination Species with Enantiomerically Pure* (S)*-pn as Ligand*

fac-Δ-[M{(*S*)-pn}$_3$]	*fac*-Λ-[M{(*S*)-pn}$_3$]	C_3
mer-Δ-[M{(*S*)-pn}$_3$]	*mer*-Λ-[M{(*S*)-pn}$_3$]	C_1

In addition, chiroptical methods can now be used, since the solution contains no longer racemic pairs of enantiomers, and it is, therefore, optically active. With this in mind, *Smirnoff* conducted the study of the formation of Pt^{IV} complexes with the enantiomerically pure (*S*)-pn((*S*)-**1**) and (*R*)-pn((*R*)-**1**) ligands, respectively, being particularly interested by the question whether a center of 'asymmetry' at the ligand can induce 'asymmetry' at the metal. He concluded that the synthesis is completely stereoselective.^{2})

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^{2}) 'Da im vorliegenden Fall keine weiteren Isomeren aufgefunden worden sind, so ist man gezwungen anzunehmen, dass optisch-aktive Diaminmolekeln von bestimmter räumlicher Gestaltung nur je eine bestimmte räumliche Lagerung um das Platinatom einnehmen und so direkt nur eine bestimmte von den zwei möglichen spiegelbildisomern Formen bilden'.

As will be shown in our contribution, the statement of *Smirnoff* cannot be maintained in its absolute form. There is stereoselectivity, but it is far from being complete. Surprisingly, *Smirnoff* does not mention the possibility of *fac*/*mer* diastereoisomerism. Despite these shortcomings, *Smirnoff*'s paper should be considered to be an important step in the development of coordination chemistry.

2. Results and Discussion. – *Preamble.* Since Pt^{IV}, as low-spin $5d^6$ system, forms exclusively diamagnetic complexes, NMR spectroscopy is the method of choice for the elucidation of the configuration of the coordination species. We exploited the spectra of all nuclei in the complex $[Pt(pn)_3]^{4+}$, *i.e.*, ^1H, ^{13}C, ^{15}N, and ^{195}Pt. Except for ^{15}N, where enriched samples were prepared, all nuclei were studied in their natural abundances.

^{13}C-NMR Spectroscopy. The most-straightforward results are obtained from the ^{1}H-decoupled ^{13}C-NMR spectra of $[Pt(pn)_3]^{4+}$. *Fig. 2* shows an overview of these spectra for the isomer mixtures **3** and **4** obtained with *rac*-pn (*rac*-**1**) and with (*S*)-pn ((*S*)-**1**), respectively. The strong reduction in complexity of the mixture **4** formed by (*S*)-pn, as discussed in the introduction, is obvious. *Fig. 3* shows the details of the spectrum of **4**. *Fig. 3,a*, gives the signals for the CH group in the (*S*)-pn ligand with the assignment to the four diastereoisomers of the complex mixture **4**. The descent in symmetry from the *fac*-**4** (C_3) to the *mer*-**4** (C_1) isomers is obvious. The former yield a single signal for the *fac*-Δ-$[M\{(S)\text{-pn}\}_3]$ and the *fac*-Λ-$[M\{(S)\text{-pn}\}_3]$, respectively, whereas the C_1 *mer*-isomers **4**, *mer*-Δ-$[M\{(S)\text{-pn}\}_3]$ and *mer*-Λ-$[M\{(S)\text{-pn}\}_3]$, appear as three distinct lines with 1:1:1 relative intensities [11]. The ^{13}C,^{195}Pt-coupling in all signals is just at the brink of resolution, being of the order of 1 Hz for all species. The same pattern can be observed in *Fig. 3,b*, for the CH_2 signals, with the difference that here the ^{13}C,^{195}Pt coupling is clearly resolved and amounts to *ca.* 3.5 Hz for all signals in this range. Finally, also the CH_3 signals (*Fig. 3,c*) confirm the presence of the four diastereoisomers **4**. The ^{13}C,^{195}Pt-coupling here is much larger, *i.e.*, 13.7 Hz, again for all signals. It is noteworthy that the ^{13}C,^{195}Pt coupling is significantly larger for the more-distant CH_3 group as compared to the CH and the CH_2 groups, respectively. Since integration of signals of this kind is not necessarily very precise, a definite statement about stereoselectivity cannot be made on the basis of these measurements. Semi-quantitatively, however, it can be said that the geometric diastereoselectivity for the *mer*-**4**/*fac*-**4** ratio is *ca.* 3:1 for the Δ-family and *ca.* 5:1 for the Λ-family (statistical ratio 3:2), whereas the configurational diastereoselectivity $\Delta:\Lambda$ is *ca.* 2:1.

$[Pt^{IV}(rac\text{-}pn)_3]^{4+}$	$[Pt^{IV}\{(S)\text{-}pn\}_3]^{4+}$	$[Pt^{IV}\{(R)\text{-}pn\}_3]^{4+}$
3	**4**	**5**

^{15}N-NMR Spectroscopy. – *Fig. 4* shows the ^{1}H-decoupled ^{15}N-NMR spectrum of $[Pt\{(R)\text{-pn*}\}_3]^{4+}$ ((^{15}N)-**5**), measured at 50.68 MHz. Since only one of the two amino groups was enriched with the ^{15}N isotope, up to 98%, relatively simple spectra result. The signals numbered 1 to 8 are due to the four diastereoisomers given in (*Table 2*). Again the two C_3 – symmetric species *fac*-($^{15}N_3$)-**5**, *fac*-Δ-$[Pt\{(R)\text{-pn*}\}_3]^{4+}$ and *fac*-Λ-$[Pt\{(R)\text{-pn*}\}_3]^{4+}$, show one single signal, whereas the two C_1 complexes *mer*-($^{15}N_3$)-**5**, *mer*-Δ-$[Pt\{(R)\text{-pn*}\}_3]^{4+}$ and *mer*-Λ-$[Pt\{(R)\text{-pn*}\}_3]^{4+}$, give three signals each. Each of

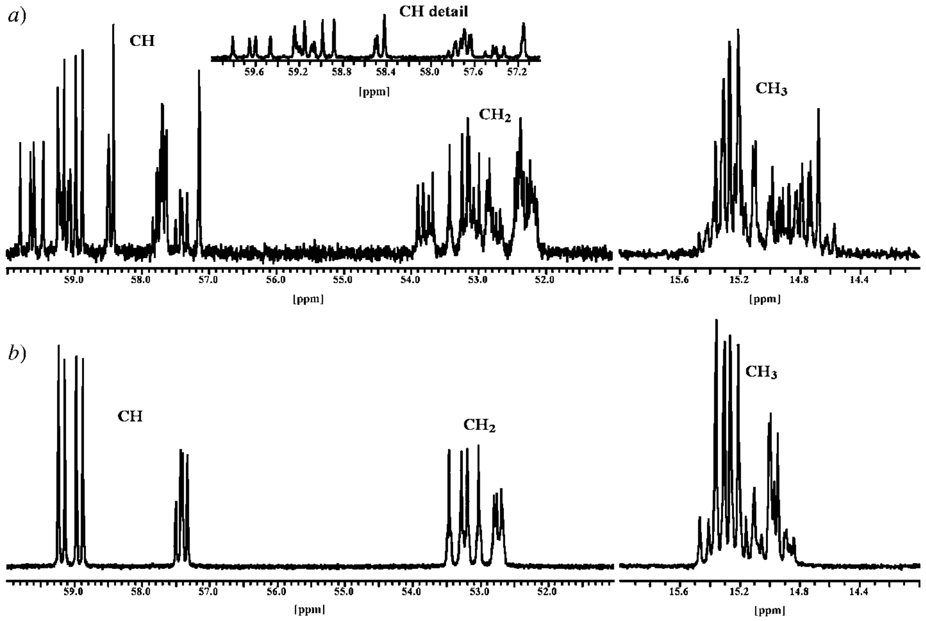


Fig. 2. *^{1}H-Decoupled ^{13}C-NMR spectra of* a) *[Pt(*rac-*pn)$_3$]$^{4+}$* (**3**) (twelve enantiomer pairs of diastereoisomers) *and* b) *[Pt{(*S*)-pn}$_3$]$^{4+}$* (**4**) (four diastereoisomers)

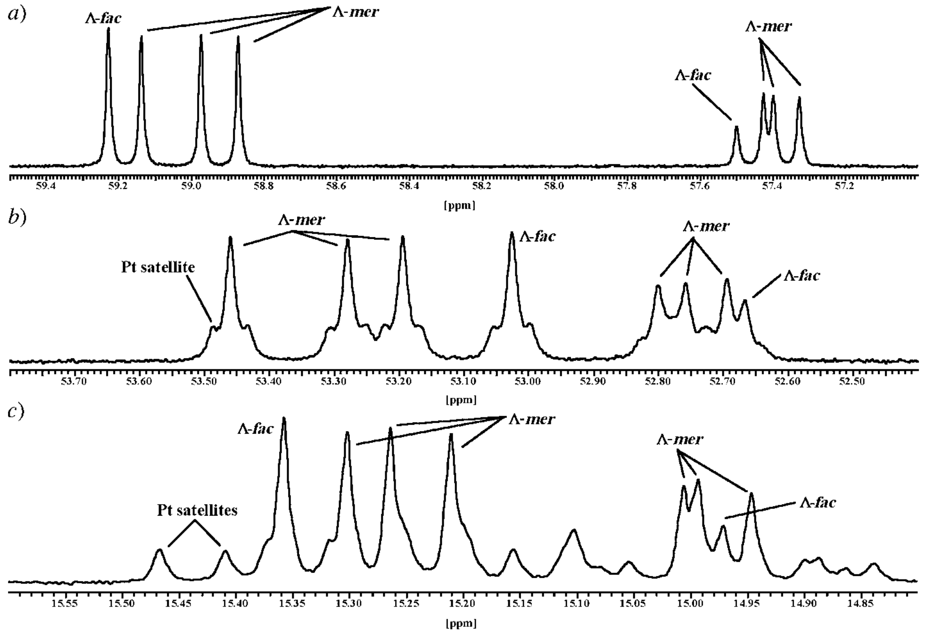


Fig. 3. *Details of ^{1}H-decoupled ^{13}C-NMR spectra of mixture [Pt{(*S*)-pn}$_3$]$^{4+}$* (**4**). a) *CH group,* b) *CH$_2$ group, and* c) *CH$_3$ group*

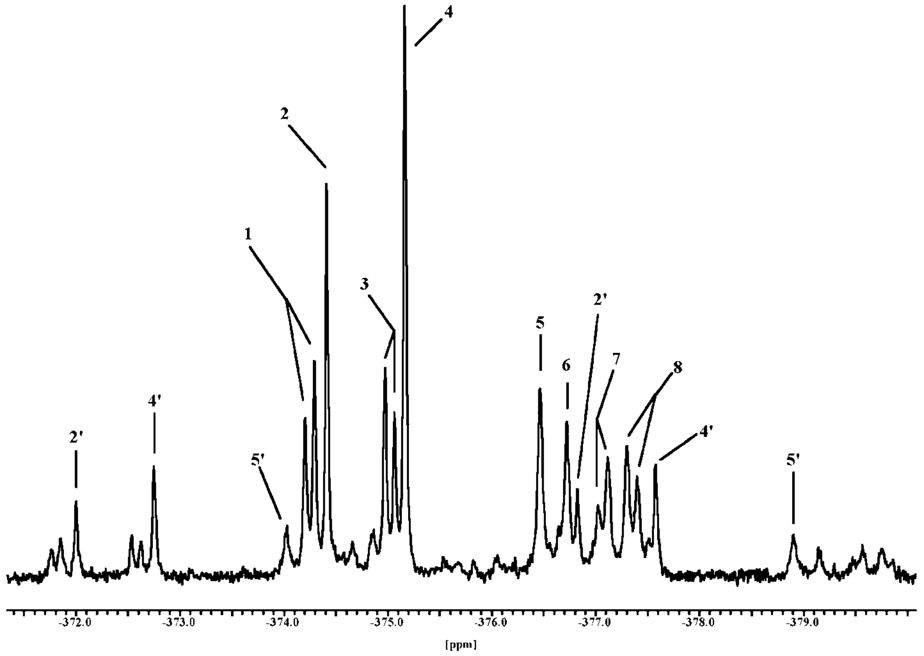
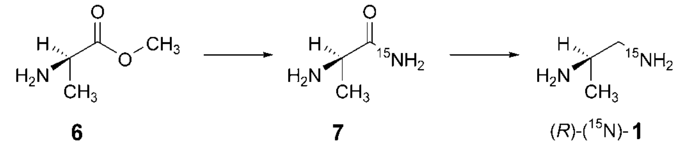


Fig. 4. *^{1}H-Decoupled ^{15}N-NMR spectra of [Pt{(*R*)-$NH_2CH(CH_3)CH_2{}^{15}NH_2$}$_3$]$^{4+}$* ($^{15}N_3$)-**5**) (98% ^{15}N at N^1).

these signals is split by a large ^{15}N,^{195}Pt coupling of 122 Hz to form Pt-satellites (*e.g.*, lines 2′, 4′, 5′, not all numbers are given for clarity reasons). Lines 1 to 4 represent the Δ-family and 5 to 8 the Λ-family. In addition, some of the signals are split by a ^{15}N,^{15}N coupling of 4.4 Hz to form *d* (seen, *e.g.*, in the signal 1, 3, 7, and 8, which is repeating in several places in the spectrum as the Pt-satellites). Signals showing such a coupling must be due to *mer*-isomers, since only ^{15}N-nuclei in *trans*-positions show couplings of this magnitude [12].

The ^{15}N-labeled ligand (*R*)-(15N)-**1** was prepared from D-alamine methyl ester (**6**) *via* amide **7** (*Scheme*; see *Exper. Part*).

Scheme. *Preparation of the ^{15}N-Labeled (*R*)-pn** ((*R*)-(^{15}N)-**1**)



^{1}*H-NMR Spectroscopy.* As already shown by ^{13}C-NMR, the isomer mixture **3** (12 diastereoisomers) of [Pt(*rac*-pn)$_3$]$^{4+}$ results in highly complex NMR spectra, which is also clearly seen in *Fig. 5,a*. *Fig. 5,b* shows the much simpler pattern of the ^{1}H-NMR spectrum of [Pt{(*S*)-pn}$_3$]$^{4+}$ (**4**). This can be even further simplified by recording a ^{195}Pt-decoupled ^{1}H-NMR spectrum (*Fig. 5,c*). Not all signals can be assigned unambiguously. It is obvious that the two diastereotopic protons of the CH_2 groups appear in the range 3.12 to 3.35 ppm for the axial and the equatorial positions, as indicated in *Fig. 5,c*. The CH_3 protons do not show any particulary interesting features since they give rise to a composite signal of a number of *d* due to the coupling with the CH proton. The latter appears for the major species Λ-[Pt{(*S*)-pn}$_3$]$^{4+}$ again as a superposition of four signals (*fac* + 3 *mer*), each coupling with the protons in the ligand. The signals of the CH protons of the minor species (Δ-[Pt{(*S*)-pn}$_3$]$^{4+}$) are split over a larger range (3.79–3.87 ppm). This might be due to the appearance of several conformers of similar energy, as it has been described for analogous Co^{III} complexes [13]. We assume, in accordance with the cited literature, that the conformation in the major species is fixed in an all equatorial position for the CH_3 group [14][15].

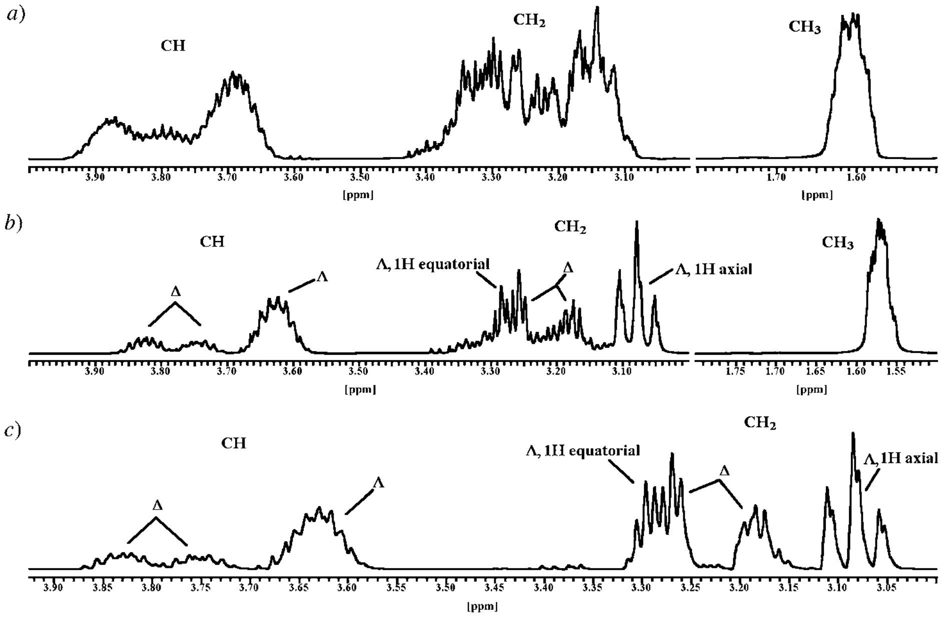


Fig. 5. *^{1}H-NMR Spectra* a) *of [Pt(*rac*-pn)$_3$]$^{4+}$* (**3**), b) *of [Pt{(*S*)-pn}$_3$]$^{4+}$* (4), *and* c) *of [Pt{(*S*)-pn}$_3$]$^{4+}$* (**4**), *under ^{195}Pt decoupling*

^{195}Pt-NMR Spectroscopy. The ^{195}Pt-NMR spectra (see *Exper. Part*) are not of particular value for these investigations since, disappointingly, the signals are rather broad (*ca.* 3 kHz at 107.52 MHz). A splitting of the ^{195}Pt-NMR line at −863.65 ppm (*vs.* Na_2PtCl_6) could be observed, which is probably due to the two diastereoisomers Λ- and Δ-[Pt(*S*)-pn)$_3$]$^{4+}$, respectively.

As discussed above, the stereoselectivity claimed by *Smirnoff* (in 1920) [6], is in general quite modest. We, therefore, investigated the behavior of the complexes upon crystallization from solutions containing a mixture of isomers. Indeed, upon slow crystallization (see *Exper. Part*) of the crude product **4**, yielding rather small crystals, the isomeric purity could be improved considerably. *Fig. 6* shows the ^{1}H-NMR, and the ^{1}H-decoupled ^{13}C-NMR spectra of the product after slow recrystallization. In comparison with the spectra discussed earlier, it is obvious that the all Δ-isomers have been completely removed by the crystallization process.

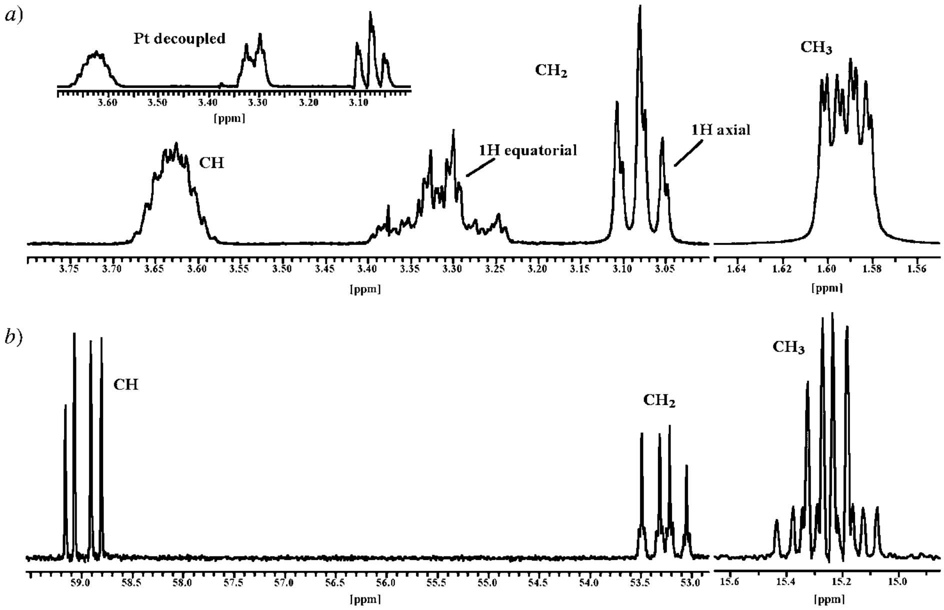


Fig. 6. *NMR Spectra of a carefully recrystallized sample of* $[Pt\{(S)\text{-}pn\}_3]^{4+}$ (**4**): a) *^1H-NMR* (insert: ^{195}Pt-decoupled), b) *^1H-decoupled ^{13}C-NMR*

Comparing $[\alpha]_D$ values of our products with that published by *Smirnoff* also indicates that his preparations were only partially stereoselective. *Smirnoff* measured $[\alpha]_D$ values of the complexes of − 170 to − 180. We found in the 'raw' product **4** · 4Cl a value of only − 97, whereas it increased to − 131, when *Smirnoff*'s experimental conditions were applied. Our final value, after careful recrystallization, was − 218.5.

Since both enantiomers of pn are easily accessible, we prepared an 'artificial' racemate containing equimolar quantities of $[Pt\{(S)\text{-pn}\}_3]^{4+}$ (**4**) and $[Pt\{(R)\text{-pn}\}_3]^{4+}$ (**5**). Observing the ^{13}C-NMR spectra of D_2O solutions at room temperature during several months indicated no scrambling of the (*S*)-pn and (*R*)-pn ligands under these conditions, thus showing the inertness of the Pt-complexes. Even heating to 60° for several hours did not change this situation.

This work was supported by the *Swiss National Science Foundation*.

Experimental Part

General. ^{15}N-Labeled ammonia solution (^{15}N, 98% +; 6M in H_2O) for the synthesis of labeled (2*R*)-propane-1,2-diamine was purchased from *Cambridge Isotope Laboratories.* Optical rotations: automatic polarimeter *Autopol III* (*Rudolph Research*, New Jersey) or *Perkin-Elmer 241-MC* polarimeter; $[\alpha]_D$ in deg · $cm^3 \cdot g^{-1} \cdot dm^{-1}$. UV/VIS Spectra: H_2O soln.; *Perkin-Elmer Lambda 25* spectrometer L = 1 cm; λ_{max} in cm^{-1}. CD Spectra: at 25° in H_2O; *Jasco J-715* spectropolarimeter; $\lambda_{min/max}$ ($\Delta\varepsilon$) in nm. NMR Spectra: *Bruker DRX-500* (^{1}H 500.13 MHz; ^{13}C 125.76 MHz; ^{15}N 50.68 MHz; ^{195}Pt 107.42 MHz) or *Bruker Avance 400* (^{1}H 400.13 MHz; ^{13}C 100.62 MHz) in D_2O (99.9% D; *Cambridge Isotope Laboratories*); Chemical shifts δ in ppm rel. to external

Me_4Si (^{1}H, ^{13}C), $MeNO_2$ (^{15}N), and Na_2PtCl_6 (^{195}Pt), coupling constants *J* in Hz; assignments based on ^{1}H, $^{1}H\{^{195}Pt\}$, $^{13}C\{^{1}H\}$, ^{13}C-APT, $^{195}Pt\{^{1}H\}$, $^{15}N\{^{1}H\}$, COSY, ^{13}C-HMQC, and ROESY experiments. Mass spectra *Bruker Bio-Apex II* (ESI) or *VG-Instruments 7070E* (EI); spectrometer in *m*/*z* (rel. %). The 'Ecole d'ingénieurs et d'architectes de Fribourg' accomplished the elemental analysis.

Dihydrogen Hexachloroplatinate(2+) (H_2PtCl_6). Metallic platinum (99.999%; 9.9835 g) was dissolved in aqua regia (100 ml) during one week at 70° under stirring. The resulting soln. was poured into a porcelain evaporating dish placed on a water bath, and the liquid was evaporated. A 37% HCl soln. (30 ml; *puriss. p.a.*) was then added and the mixture evaporated again. The cycle was repeated 10 times with HCl and 5 times with distilled H_2O. The product was transfered quantitatively into a volumetric flask (250 ml) and filled to the mark with dist. H_2O. The stock soln. ($c = 0.20471\ \mathrm{mol \cdot dm^{-3}}$) was used in all further experiments.

rac-*Propane-1,2-Diamine* (*rac*-**1**; *rac*-pn) was purchased from *Fluka*.

*(2*R*)- and (2*S*)-Propane-1,2-diamine* ((*R*)- and (*S*)-**1**; (*R*)-pn and (*S*)-pn) were purchased as dihydrochlorides from *Aldrich*. The free bases were obtained by distillation of the hydrochlorides in the presence of an excess of powdered NaOH.

*(2*R*)-Propane-1,2-(*N^{1-15}*N)diamine* ((*R*)-(^{15}N)-**1**; (*R*)-pn*). D-Alanine methylester hydrochloride (**6** · HCl; 10.42 g; *Aldrich*) was dissolved in H_2O (20 ml), NaOH (2.98 g) was added, and the mixture was extracted with CH_2Cl_2 (4 × 20 ml). The org. soln. was dried (Na_2SO_4), and the solvent was rapidly evaporated at r.t. under vacuum. To the resulting oil, 6M aq. ^{15}N-labeled ammonia (20 g) was added immediately, and the mixture was stirred at r.t. overnight [16]. The mixture was then evaporated, the remaining solid extracted with CH_2Cl_2 (30 ml), and the undissolved part filtered off. The solvent was evaporated from the clear soln. and the crude R-alanina(^{15}N)mide (**7**; 5 g, 78%) was used in the next step without further purification.

Lithium aluminium hydride (3 g) was suspended in dry THF (100 ml) and crude **7** (5 g) was added sequentially. The stirred mixture was refluxed for 8 h [17] under Ar, diluted with THF (100 ml), and the remaining hydride was decomposed by addition of $Na_2SO_4 \cdot 10\,H_2O$. The solid part was filtered off and washed with THF. The washings were combined with the filtrate, acidified with conc. HCl soln., and evaporated. The residue was mixed with an excess of powdered NaOH, and the free base was distilled off and collected. The distillate was dried with small pieces of metallic Na, the formed NaOH soln. being removed. The product was distilled again: (*R*)-(^{15}N)-**1** (2.7 g, 65%). B.p. 115–120°. $[\alpha]_D = +4.4$ (25°, $c = 0.01026$, H_2O, measured as dihydrochloride). ^{1}H-NMR (500.13 MHz, D_2O): 1.04 (*d*, $J = 6.6$, Me); 2.52 (*m*, $J(N,H) = 0.7$, CH_2); 2.86 (*m*, CH). $^{13}C\{^{1}H\}$-NMR (125.76 MHz, D_2O); 19.39 (*s*, Me); 47.76 (*s*, CH); 48.37 (*d*, $J(N,C) = 4.0$, CH_2). $^{15}N\{^{1}H\}$-NMR (50.68 MHz, D_2O): −364.71 ($^{15}NH_2$). EI-MS: 44 (100, $[M - CH_2NH_2]^+$).

*Tris(*rac*-propane-1,2-diamine-κ*N*¹,κ*N*²)platinum(4+)Tetrachloride* (*[Pt(*rac*-pn)₃]Cl₄*; **3** · 4Cl). This complex salt was prepared in an analogous way as described by *Smirnoff* [6]. The stock soln. of H_2PtCl_6 (50 ml; *ca.* 2 g Pt, 10.25 mmol) was evaporated and the remaining solid dissolved in abs. EtOH (17 ml). Then *rac*-**1** (3.2 g, 3.7 ml, 43.4 mmol) was added sequentially to the chilled (ice bath) H_2PtCl_6 soln. in EtOH to form *rac*-pn · H_2PtCl_6 as yellow precipitate. The mixture was refluxed for 30 min and allowed to cool to r.t. and the solid product was filtered off, washed with Et_2O and Et_2O, and dried in air: crude **3** · 4Cl (4 g). White powder.

*Tris(*rac*-propane-1,2-diamine-κ*N*¹,κ*N*²)platinum(4+) Tetrachloride Monohydrate* (*[Pt(*rac*-pn)₃]Cl₄ · H₂O*; **3** · 4Cl · H_2O). The crude **3** · 4Cl (2.5 g) was dissolved in H_2O (5 ml), the soln. filtered, and EtOH (30 ml) added to the filtrate. The pure precipitated product was isolated, washed with EtOH and Et_2O, and dried in air: **3** · 4Cl · H_2O (2 g). White powder. UV/VIS (H_2O, $c = 2.041 \cdot 10^{-4}\ \mathrm{mol \cdot dm^{-3}}$: 303.97. ^{1}H-NMR (500.13 MHz, D_2O): 1.57–1.63 (*m*, Me); 3.11–3.37 (*m*, Pt satellites, CH_2); 3.67–3.89 (*m*, CH). $^{13}C\{^{1}H\}$-NMR (125.76 MHz, D_2O): 14.57–15.47 (more than 28 signals with Pt satellites, $J(Pt,C) = 13.7$, Me); 52.13–53.92 (more than 28 signals with Pt satellites, $J(Pt,C) = 3.1$, CH_2); 57.15–59.80 (more than 28 signals, CH). $^{195}Pt\{^{1}H\}$-NMR (107.42 MHz, D_2O): −862.46 (br., width > 35 ppm). ESI-MS (H_2O/MeCN): 414 (100, $C_9H_{27}N_6Pt^+$). Anal. calc. for $C_9H_{30}Cl_4N_6Pt \cdot H_2$: C 18.72, H 5.59, N 14.56; found: C 18.59, H 5.95, N 14.48.

*Tris[(2*S*)-propane-1,2-diamine-κ*N*¹,κ*N*³]platinum(4+) Tetrachloride* (*[Pt{(*S*)-pn}₃]Cl₄*; **4** · 4Cl). The stock soln. of H_2PtCl_6 (25 ml; *ca.* 1 g Pt, 5.13 mmol) was evaporated and the remaining solid dissolved in abs. EtOH (9 ml). Then (*S*)-**1** (2 g, 27 mmol) was added in small portions to the cooled (ice bath) H_2PtCl_6 soln., and the resulting mixture was refluxed for 30 min. The mixture was allowed to cool to r.t. and Et_2O (35 ml) was added under stirring. The product was isolated by filtration, washed with Et_2O (35 ml) and dried carefully in air: **4** · 4Cl (2 g). White powder. $[\alpha]_D = -97.0$ (25°, $c = 0.01299$, H_2O). (Δ-*fac*-$[Pt\{(S)\text{-pn}\}_3]Cl_4$ + Δ-*mer*-$[Pt\{(S)\text{-pn}\}_3]Cl_4$)/(Λ-*fac*-$[Pt\{(S)\text{-pn}\}_3]Cl_4$ + Λ-*mer*-$[Pt\{(S)\text{-pn}\}_3]Cl_4$) ratio 1 : 1.3.

*Tris[(2*S*)-propane-1,2-diamino-κ*N*¹,κ*N*²]platinum(4+) Tetrachloride Monohydrate* (*[Pt{(*S*)-pn}₃]Cl₄ · H₂O*; **4** · 4Cl · H_2O). The crude **4** · 4Cl (1.5 g) was dissolved in H_2O (1.5 ml), the soln. filtered, and a mixture of EtOH (10 ml) and Et_2O (5 ml) added to the filtrate. The pure precipitated product was isolated, washed with

Et$_2$O, and dried carefully in air: **4** · 4Cl · H_2O (1.3 g). White powder. $[\alpha]_{\mathrm{D}} = -131.0$ (25°, *c* = 0.01130, H_2O). UV/VIS (H_2O, *c* = 2.051 · 10^{-4} mol · dm^{-3}): 300.48. CD (H_2O, *c* = 2.051 · 10^{-4} mol · dm^{-3}): 245 (+0.20), 320 (+0.25). ^{1}H-NMR (500.13 MHz, D_2O): 1.55 – 1.58 (*m*, set of overlapping *d*, 3 H, Me, Λ-*fac* + Λ-*mer* + Δ-*fac* + Δ-*mer*); 3.08 (*m*, multiple *dd*, $J_{\mathrm{gem}} = J_{\mathrm{vic},trans} = 13.3$, 1 H$_{\mathrm{ax}}$, CH$_2$, Λ-*fac* + Λ-*mer*); 3.17 (*m*, 1 H$_{\mathrm{ax}}$, CH$_2$, Δ-*fac* + Δ-*mer*); 3.25 – 3.29 (*m*, Pt satellites, *J*(Pt,H) = 27, 1 H$_{\mathrm{eq}}$, CH$_2$, Λ-*fac* + Λ-*mer* + Δ-*fac* + Δ-*mer*); 3.58 – 3.68 (*m*, 1 H, CH, Λ-*fac* + Λ-*mer*); 3.71 – 3.78, 3.79 – 3.87 (2*m*, 1 H, CH). ^{13}C{^{1}H}-NMR (125.76 MHz, D_2O): 14.99, 15.03, 15.04 (Pt satellites, *J*(Pt,C) = 13.5, Me, Δ-*mer*); 15.01 (Pt satellites, *J*(Pt,C) = 13.5, Me, Δ-*fac*); 15.27, 15.31, 15.35 (Pt satellites, *J*(Pt,C) = 13.7, Me, Λ-*mer*); 15.40 (Pt satellites, *J*(Pt,C) = 13.7, Me, Λ-*fac*); 52.71 (CH$_2$, Pt satellites, *J*(Pt,C) = 3, CH$_2$, Δ-*fac*); 52.74, 52.81, 52.85 (Pt satellites, *J*(Pt,C) = 3, CH$_2$, Δ-*mer*); 53.07 (Pt satellites, *J*(Pt,C) = 3.5, CH$_2$, Λ-*fac*); 53.24, 53.34, 53.52 (Pt satellites, *J*(Pt,C) = 3.5, CH$_2$, Λ-*mer*); 57.31, 57.39, 57.40 (CH, Δ-*mer*); 57.48 (CH, Δ-*fac*); 58.80, 58.89, 59.07 (CH, Λ-*mer*); 59.15 (CH, Λ-*fac*). ^{195}Pt{^{1}H}-NMR (107.52 MHz, D_2O): −872.39 (br. signal, unresolved coupling). ESI-MS (H_2O/MeCN): 414 (100, $C_9H_{27}N_6Pt^+$). Anal. calc. for $C_9H_{30}Cl_4N_6Pt \cdot H_2O$: C 18.72, H 5.59, N 14.56; found: C 18.50, H 6.00, N 14.51. (Δ-*fac*-[Pt{(*S*)-pn}$_3$]Cl$_4$ + Δ-*mer*-[Pt{(*S*)-pn}$_3$]Cl$_4$)/(Λ-*fac*-[Pt{(*S*)-pn}$_3$]Cl$_4$ + Λ-*mer*-[Pt{(*S*)-pn}$_3$]Cl$_4$) ratio 1 : 2.4. Λ-*fac*-(Pt{(*S*)-pn}$_3$]Cl$_4$)/Λ-*mer*-[Pt{(*S*)-pn}$_3$]Cl$_4$ ratio 1 : 3.

Λ-fac-*[Pt{(*S*)-pn}$_3$]Cl$_4$ · H$_2$O/Λ*-mer-*[Pt{(*S*)-pn}$_3$]Cl$_4$ · H$_2$O* (Λ-*fac*-**4** · 4Cl · H_2O/Λ-*mer*-**4** · 4Cl · H_2O). The complex **4** · 4Cl · H_2O (500 mg) was dissolved in H_2O (1 ml) at 90°, and the resulting soln. was allowed to cool to 4°. The white precipitate was isolated by filtration, washed with a small amount of cold H_2O, and dried in air to give Λ-*fac*-**4** · 4Cl · H_2O/Λ-*mer*-**4** · 4Cl · H_2O (20 mg). White powder. $[\alpha]_{\mathrm{D}} = -218.5$ (25°, *c* = 0.00615, H_2O). ^{1}H-NMR (400.13 MHz, D_2O): 1.49 – 1.51 (*m*, multiple *d*, 3 H, Me, Λ-*fac* + Λ-*mer*); 3.00 (*m*, multiple *dd*, 1 H$_{\mathrm{ax}}$, CH$_2$, Λ-*fac* + Λ-*mer*); 3.14 – 3.31 (*m*, Pt satellites, *J*(Pt,H) = 27, 1 H$_{\mathrm{eq}}$, CH$_2$, Λ-*fac* + Λ-*mer*); 3.53 – 3.57 (*m*, 1 H, CH, Λ-*fac* + Λ-*mer*). ^{13}C{^{1}H}-NMR (100.62 MHz, D_2O): 15.17, 15.22, 15.26 (Pt satellites, *J*(Pt,H) = 13.7, Me, Λ-*mer*); 15.32 (Pt satellites, *J*(Pt,H) = 13.7, Me, Λ-*fac*); 53.01 (CH$_2$, Λ-*fac*); 53.17, 53.26, 53.44 (CH$_2$, Λ-*mer*); 58.84, 58.94, 59.10 (CH, Λ-*mer*); 59.19 (CH, Λ-*fac*). CD (H_2O, *c* = 2.508 · 10^{-4} mol · dm^{-3}): 245 (+1.52), 320 (+0.25). Λ-*fac*-(Pt{(*S*)-pn}$_3$]Cl$_4$/Λ-*mer*-[Pt{(*S*)-pn}$_3$]Cl$_4$ ratio 1 : 4.

*Tris[(2*R*)-propane-1,2-diamine-κ*N^1*,κ*N^2*]platinum(4+) Tetrachloride* (*[Pt{(*R*)-pn}$_3$]Cl$_4$*; **5** · 4Cl). As described for **4** · 4Cl, from the stock soln. of H_2PtCl_6 (25 ml) and (*R*)-**1** (2 g): crude **5** · 4Cl (1.9 g). White powder. $[\alpha]_{\mathrm{D}} = +111.4$ (25°, *c* = 0.01176, H_2O). (Δ-*fac*-[Pt{(*R*)-pn}$_3$]Cl$_4$ + Δ-*mer*-[Pt{(*R*)-pn}$_3$]Cl$_4$)/(Λ-*fac*-[Pt{(*R*)-pn}$_3$]Cl$_4$ + Λ-*mer*-[Pt{(*R*)-pn}$_3$]Cl$_4$) ratio 1.3 : 1.

*Tris[(2*R*)-propane-1,2-diamine-κ*N^1*,κ*N^2*]platinum(4+)Tetrachloride Monohydrate* (*[Pt{(*R*)-pn}$_3$]Cl$_4$ · H$_2$O*; **5** · 4Cl · H_2O). As described for **4** · 4Cl · H_2O pure **5** · 4Cl · H_2O (1.35 g). White powder. $[\alpha]_{\mathrm{D}} = +128.6$ (25°, *c* = 0.01368, H_2O). UV/VIS (H_2O, *c* = 2.108 · 10^{-4} mol · dm^{-3}): 300.82. CD (H_2O, *c* = 2.051 · 10^{-4} mol · dm^{-3}): 245 (+0.40); 320 (+0.25). ^{1}H-NMR (500.13 MHz, D_2O): 1.58 – 1.62 (*m*, set of overlapping *d*, 3 H, Me, Δ-*fac* + Δ-*mer* + Λ-*fac* + Λ-*mer*); 3.12 (*m*, multiple *dd*, $J_{\mathrm{gem}} = J_{\mathrm{vic},trans} = 13.3$, CH$_2$, 1 H$_{\mathrm{ax}}$, Δ-*fac* + Δ-*mer*); 3.21 (*m*, 1 H$_{\mathrm{ax}}$, CH$_2$, Λ-*fac* + Λ-*mer*); 3.28 – 3.35 (*m*, Pt satellites, *J*(Pt,H) = 27, 1 H$_{\mathrm{eq}}$, CH$_2$, Δ-*fac* + Δ-*mer* + Λ-*fac* + Λ-*mer*); 3.63 – 3.70 (*m*, 1 H, CH, Δ-*fac* + Δ-*mer*); 3.75 – 3.80, 3.83 – 3.90 (2*m*, 1 H, CH). ^{13}C{^{1}H}-NMR (125.76 MHz, D_2O): 14.95, 14.99, 15.01 (Pt satellites, *J*(Pt,C) = 13.5 Hz, Me, Λ-*mer*); 14.97 (Pt satellites, *J*(Pt,C) = 13.5, Me, Λ-*fac*); 15.21, 15.26, 15.30 (Pt satellites, *J*(Pt,C) = 13.7, Me, Δ-*mer*); 15.36 (Pt satellites, *J*(Pt,C) = 13.7, Me, Δ-*fac*); 52.67 (Pt satellites, *J*(Pt,C) = 3, CH$_2$, Λ-*fac*); 52.69, 52.78, 52.80 (Pt satellites, *J*(Pt,C) = 3, CH$_2$, Λ-*mer*); 53.03 (Pt satellites, *J*(Pt,C) = 3.5, CH$_2$, Δ-*fac*); 53.19, 53.28, 53.46 (Pt satellites, *J*(Pt,C) = 3.5, CH$_2$, Δ-*mer*); 57.33, 57.40, 57.43 (CH, Λ-*mer*); 57.50 (CH, Λ-*fac*); 58.87, 58.97, 59.14 (CH, Δ-*mer*); 59.23 (CH, Δ-*fac*). ^{195}Pt{^{1}H}-NMR (107.52 MHz, D_2O): −863.65, −871.75 (2br. signals, unresolved coupling, ratio Δ/Δ *ca.* 2 : 1). ESI-MS (H_2O/MeCN): 414 (100, $C_9H_{27}N_6Pt^+$). Anal. calc. for $C_9H_{30}Cl_4N_6Pt \cdot H_2$: C 18.72, H 5.59, N 14.56; found: C 18.63, H 6.10, N 14.53. (Δ-*fac*-[Pt{(*R*)-pn}$_3$]Cl$_4$ + Δ-*mer*-[Pt{(*R*)-pn}$_3$]Cl$_4$)/(Λ-*fac*-[Pt{(*R*)-pn}$_3$]Cl$_4$ + Λ-*mer*-[Pt{(*R*)-pn}$_3$]Cl$_4$) ratio 1 : 2.0. (Δ-*fac*-(Pt{(*R*)-pn}$_3$]Cl$_4$)/(Δ-*mer*-[Pt{(*R*)-pn}$_3$]Cl$_4$) ratio 1 : 3.

Δ-fac-*[Pt{(*R*)-pn}$_3$]Cl$_4$ · H$_2$O/Δ*-mer-*[Pt{(*R*)-pn}$_3$]Cl$_4$ · H$_2$O* (Δ-*fac*-**5** · 4Cl · H_2O/Δ-*mer*-**5** · 4Cl · H_2O). The complex **5** · 4Cl · H_2O (500 mg) was dissolved in H_2O (1 ml) at 90°, and the resulting soln. was allowed to cool to 4°. The white precipitate was isolated by filtration, washed with a small amount of cold H_2O, and dried in air: Δ-*fac*-**5** · 4Cl · H_2O/Δ-*mer*-**5** · 4Cl · H_2O (26 mg). White powder. $[\alpha]_{\mathrm{D}} = +217.3$ (25°, *c* = 0.00635, H_2O). ^{1}H-NMR (400.13 MHz, D_2O): 1.50 – 1.51 (*m*, multiple *d*, 3 H, Me, Δ-*fac* + Δ-*mer*); 3.01 (*m*, multiple *dd*, 1 H$_{\mathrm{ax}}$, CH$_2$, Δ-*fac* + Δ-*mer*); 3.14 – 3.31 (*m*, 1 H$_{\mathrm{eq}}$, CH$_2$, Pt satellites, *J*(Pt,H) = 27, Δ-*fac* + Δ-*mer*); 3.53 – 3.57 (*m*, 1 H, CH, Δ-*fac* + Δ-*mer*). ^{13}C{^{1}H}-NMR (100.62 MHz, D_2O): 15.18, 15.23, 15.27 (Pt satellites, *J*(Pt,C) = 13.7, Me; Δ-*mer*); 15.33 (Pt satellites, *J*(Pt,C) = 13.7, Me, Δ-*fac*); 53.02 (CH$_2$, Δ-*fac*); 53.19, 53.28, 53.45 (CH$_2$, Δ-*mer*); 58.84, 58.94, 59.10 (CH, Δ-*mer*); 59.19 (CH, Δ-*fac*). CD (H_2O, *c* = 1.819 · 10^{-4} mol · dm^{-3}): 245 (+1.48), 320 (+0.25). Δ-*fac*-(Pt{(*R*)-pn}$_3$]Cl$_4$/Δ-*mer*-[Pt{(*R*)-pn}$_3$]Cl$_4$ ratio 1 : 4.

*Tris[(2*R*)-propane-1,2-(*N$^{1\text{-}15}$*N)diamine-κ*N^1*,κ*N^2*]platinum(4+) Tetrachloride* (*[Pt{(*R*)-pn*}$_3$]Cl$_4$*; ($^{15}N_3$)-**5**·4Cl). As described for **4**·4Cl, from the stock soln. of H_2PtCl_6 and (*R*)-(^{15}N)-**1** (2 g), and as described for **4**·4Cl·H_2O: pure ($^{15}N_3$)-**5**·4Cl·H_2O (1.2 g). White powder. $[\alpha]_D = +136.5$ (25°, $c = 0.01546$, H_2O). ^{1}H-NMR (500.13 MHz, D_2O): 1.57–1.60 (*m*, 3 H, Me, Δ-*fac* + Δ-*mer* + Λ-*fac* + Λ-*mer*); 3.09 (*m*, multiple *dd*, $J_{gem} = J_{vic,trans} = 13.3$, 1 H_{ax}, CH_2, Δ-*fac* + Δ-*mer*); 3.18 (*m*, 1 H_{ax}, CH_2, Λ-*fac* + Λ-*mer*); 3.25–3.31 (*m*, Pt satellites, coupling with ^{15}N, 1 H_{eq}, CH_2, Δ-*fac* + Δ-*mer* + Λ-*fac* + Λ-*mer*); 3.59–3.70 (*m*, 1 H, CH, Δ-*fac* + Δ-*mer*); 3.72–3.79, 3.80–3.89 (2*m*, CH, 1 H). ^{13}C{^{1}H}-NMR (125.76 MHz, D_2O): 14.54, 14.56, 14.58, 14.60 (coupling with ^{15}N, Pt satellites, Me, Λ-*fac* + Λ-*mer*); 14.82, 14.87, 14.91 (set of *d*, *J*(N,C) = 2.4, Pt satellites, *J*(Pt,C) = 13.7, Me, Δ-*mer*); 14.96 (*d*, *J*(N,C) = 2.4, Pt satellites, *J*(Pt,C) = 13.7, Me, Δ-*fac*); 52.24, 52.27, 52.30, 52.33, 52.38, 52.41 (coupling with ^{15}N, Pt satellites, CH_2, Λ-*fac* + Λ-*mer*); 52.62 (*d*, *J*(N,C) = 4, Pt satellites, *J*(Pt,C) = 3.5, CH_2, Δ-*fac*); 52.79, 52.89, 53.07 (set of *d*, *J*(N,C) = 4, Pt satellites, *J*(Pt,C) = 3.5, CH_2, Δ-*mer*); 56.90, 56.97, 56.99 (CH, Λ-*mer*); 57.06 (CH, Λ-*fac*); 58.40, 58.50, 58.67 (CH, Δ-*mer*); 58.76 (CH, Δ-*fac*). ^{195}Pt{^{1}H}-NMR (107.52 MHz, D_2O): −869.11 (br., coupling with ^{15}N). ^{15}N{^{1}H}-NMR (50.68 MHz, D_2O): −377.35 (*d*, $J_{trans}(^{15}N,^{15}N) = 4.41$, Pt satellites, *J*(Pt,N) = 122, Λ-*mer*); −377.07 (*d*, $J_{trans}(^{15}N,^{15}N) = 4.41$, Pt satellites, *J*(Pt,N) = 122, Λ-*mer*); −376.72 (*s*, Pt satellites, *J*(Pt,N) = 122, Λ-*fac*); −376.47 (*s*, Pt satellites, *J*(Pt,N) = 122, Λ-*mer*); −375.16 (*s*, Pt satellites, *J*(Pt,N) = 122, Δ-*fac*); −375.02 (*d*, $J_{trans}(^{15}N,^{15}N) = 4.41$, Pt satellites, *J*(Pt,N) = 122, Δ-*mer*); −374.41 (*s*, Pt satellites, *J*(Pt,N) = 122, Δ-*mer*); −374.25 (*d*, $J_{trans}(^{15}N,^{15}N) = 4.41$, Pt satellites, *J*(Pt,N) = 122, Δ-*mer*). ESI-MS (H_2O/MeCN): 417 (100, $C_9H_{27}N_3{}^{15}N_3Pt^+$). Anal. calc. for $C_9H_{30}Cl_4N_3{}^{15}N_3Pt \cdot H_2O$: C 18.64, H 5.56, N 15.00; found: C 18.55, H 5.82, N 14.88. (Δ-*fac*-[Pt{(*R*)-pn*}$_3$]Cl$_4$ + Δ-*mer*-[Pt{(*R*)-pn*}$_3$]Cl$_4$)/(Λ-*fac*-[Pt{(*R*)-pn*}$_3$]Cl$_4$ + Λ-*mer*-[Pt{(*R*)-pn*}$_3$]Cl$_4$) ratio 1:2.9. Δ-*fac*-[Pt{(*R*)-pn}$_3$]Cl$_4$/Δ-*mer*-[Pt{(*R*)-pn}$_3$]Cl$_4$) ratio 1:3.

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