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**Asymmetric Synthesis of Coordination Compounds: Back to the Roots.**

**Diastereoselective Synthesis of Simple Platinum(IV) Complexes.**

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A publication by Alexander P. Smirnoff in *Helvetica Chimica Acta* in 1920 [6] describes the first synthesis of a coordination species, i.e. [platinum(IV)(1,2-diaminopropane)<sub>3</sub>]<sup>4+</sup>, where it was shown that the configuration of a chiral centre in the ligand can influence the configuration at the metal. Although this paper can thus be considered to be at the origin of stereoselective synthesis in coordination chemistry, it was never cited for 76 years. The present investigation was carried out by NMR spectroscopy, where all nuclei in the metal complex were used as sources of information, i.e. <sup>1</sup>H, <sup>13</sup>C, <sup>15</sup>N, and <sup>195</sup>Pt. <sup>13</sup>C-NMR, and <sup>15</sup>N-NMR (isotopically enriched complex) were especially informative for the analysis of isomer distribution. Stereoselectivity in the formation reaction of the complexes is rather modest, whereas  $\Delta$ -, and  $\Lambda$ -isomers can be separated efficiently by crystallization. A mixture of [Pt(*S*-pn)<sub>3</sub>]<sup>4+</sup>, and [Pt(*R*-pn)<sub>3</sub>]<sup>4+</sup> 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 carbon centers in one preferential configuration 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 in 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 carbon atoms, nowadays called stereogenic carbon 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 Werners coordination theory for which he was awarded the Nobel prize in 1913. In 1914 Werner demonstrated that a completely inorganic coordination compound, containing no carbon atoms, a tetranuclear cobalt 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 Werners laboratory at the University of Zürich continued. All "asymmetric" coordination compounds that were obtained in optically active form in Werners 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, 1,2-diaminopropane abbreviated (pn). It

is quite clear that also this work was initiated by Alfred Werner, since Smirnov 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". Smirnov quotes two publications of E. Fischer [7] on the stereoselective formation of sugar derivatives as analogous examples in organic reactions. *Indeed, the paper by Smirnov 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 Smirnov was completely overlooked by researchers in the field, who took up the subject much later [8]. It seems that the publication by Smirnov has never been cited for 76 years until 1996 [9]. Stereoselective synthesis of coordination species has only recently started to become a subject of increased importance [10]. Since the work of Smirnov has never been repeated in detail, we decided to investigate the platinum-1,2-diaminopropane systems with modern methods, with an emphasis on NMR spectroscopy.

1,2-Diaminopropane, which is generally named propylene-diamine (pn) in coordination chemistry, can be considered to be a "chiralized" form of the archetype of all amine chelate ligands, 1,2-diaminoethane, which is still designated as ethylenediamine (en) in almost all textbooks. en was one of the preferred ligands studied by Alfred Werner, especially with respect to its ability to form chiral coordination species (*Scheme 1*).

Scheme 1.

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  $\Delta$  and  $\Lambda$ , respectively, the situation concerning stereoisomers is much more involved for  $M(pn)_3$  species. Racemic *rac*-pn forms 24 stereoisomers of OC-6  $M(pn)_3$  species (*Table 1*).

Table 1.

The corresponding *mer/fac* diastereoisomers appear with relative statistical weights of 3:2. Although, in principle, a complete analysis of the species formed by *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 enantiopure pn facilitates the analysis enormously. If only one enantiomer of the ligand is used, only four diastereoisomeric complexes are formed (*Table 2*).

Table 2.

In addition, chiroptical methods can now be used, since the solution contains no longer racemic pairs of enantiomers, and it is therefore optically active. This in mind, Smirnoff conducted the study of the formation of  $Pt^{IV}$  complexes with the enantiopure *S*-pn, and *R*-pn ligand respectively, being particularly interested by the question, whether a center of "asymmetry" @ligand can induce "asymmetry"@metal. He concluded that the synthesis is completely stereoselective<sup>1)</sup>.

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<sup>1)</sup> "Da im vorliegenden Fall keine weiteren Isomeren aufgefunden worden sind, so ist man gezwungen anzunehmen, dass optisch-aktive Diaminmolekeln von bestimmter räumlicher Gestalt 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.** - Since  $\text{Pt}^{\text{IV}}$ , as low spin  $5d^6$  system, forms exclusively diamagnetic complexes, NMR spectroscopy is the method of choice for the elucidation of the stereochemistry of the coordination species. We have exploited the spectra of all nuclei in the complex  $\text{Pt}(\text{pn})_3^{4+}$ , i.e.  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{15}\text{N}$ , and  $^{195}\text{Pt}$ . Except for  $^{15}\text{N}$ , where enriched samples were prepared, all nuclei were studied in their natural abundances.

$^{13}\text{C}$ -NMR Spectroscopy. - The most straightforward results are obtained from the  $^{13}\text{C}$  proton-decoupled spectra of  $[\text{Pt}(\text{pn})_3]^{4+}$ . (*Fig. 1*) shows an overview of these spectra for the isomeric mixtures obtained with *rac*-pn **1b** a), and with *S*-pn **2b** b).

Figure 1.

The strong reduction in complexity of the complexes formed by *S*-pn, as discussed in the introduction, is obvious. (*Fig. 2*) shows the details of the spectrum. (*Fig. 2*) a) gives the signals for the  $^{13}\text{CH}$  group in the *S*-pn ligand with the assignment to the four diastereoisomers of the complex. The decent in symmetry from the *fac* ( $\text{C}_3$ ) to the *mer* ( $\text{C}_1$ ) isomer is obvious. The former yields single signals for the *fac*- $\Delta$ - $\text{M}(\text{S-pn})_3$  and the *fac*- $\Lambda$ - $\text{M}(\text{S-pn})_3$ , respectively, whereas the  $\text{C}_1$  *mer*-isomers, *mer*- $\Delta$ - $\text{M}(\text{S-pn})_3$  and *mer*- $\Lambda$ - $\text{M}(\text{S-pn})_3$ , appear as three distinct lines with 1:1:1 relative intensities [11]. The  $^{195}\text{Pt}$ -

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 (*Fig. 2* b) for  $^{13}\text{CH}_2$ , with the difference that here the  $^{195}\text{Pt}$  coupling is clearly resolved and it amounts to ca. 3.5 Hz for all signals in this range. Finally, also the  $^{13}\text{CH}_3$  signals (*Fig. 2* c) confirm the presence of the four diastereoisomers. The  $^{195}\text{Pt}$ -coupling here is much larger, i.e. 13.7 Hz, again for all signals. It is noteworthy that the  $^{13}\text{C}$ - $^{195}\text{Pt}$  coupling is significantly larger for the more distant  $\text{CH}_3$  group as compared to the  $\text{CH}$ , and the  $\text{CH}_2$  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 geometrical diastereoselectivity for the *mer/fac* ratio is approximatively 3:1 for the  $\Delta$ -family and about 5:1 for the  $\Lambda$ -family (statistical ratio 3:2), whereas the configurational diastereoselectivity  $\Delta$ : $\Lambda$  is approximately 2:1.

#### Figure 2.

$^{15}\text{N}$ -NMR Spectroscopy. – (*Fig. 3*) shows the proton-decoupled  $^{15}\text{N}$ -NMR spectrum of  $[\text{Pt}(\text{R-pn}^*)_3]^{4+}$  **4**, measured at 50.68 MHz. Since only one of the two amino groups was enriched with  $^{15}\text{N}$  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  $\text{C}_3$  – symmetric species, *fac*- $\Delta$ - $[\text{Pt}(\text{R-pn}^*)_3]^{4+}$  and *fac*- $\Lambda$ - $[\text{Pt}(\text{R-pn}^*)_3]^{4+}$  show one single signal, whereas the two  $\text{C}_1$  – complexes, *mer*- $\Delta$ - $[\text{Pt}(\text{R-pn}^*)_3]^{4+}$  and *mer*- $\Lambda$ - $[\text{Pt}(\text{R-pn}^*)_3]^{4+}$ , give 3 signals each. Each of these signals is split by a large  $^{15}\text{N}$  –  $^{195}\text{Pt}$  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  $\Delta$ -family and 5 to 8 the  $\Lambda$ -family. In addition, some

of the signals are split by a  $^{15}\text{N} - ^{15}\text{N}$  coupling of 4.4 Hz to form doublets (seen e.g. in the signal 1, 3, 7 and 8, which repeats in several places in the spectrum as the Pt-satellites). Signals showing such a coupling must be due to *mer*-isomers, since only  $^{15}\text{N}$ -nuclei in *trans*-positions show couplings of this magnitude [12].

### Figure 3.

$^1\text{H}$ -NMR Spectroscopy. – As already shown by  $^{13}\text{C}$ -NMR, the isomeric mixture (12 diastereoisomers) of *rac*-[Pt(pn)<sub>3</sub>]<sup>4+</sup> **1b** results in highly complex NMR spectra, which is also clearly seen in (Fig. 4) a). (Fig. 4) b) shows the much more simple pattern of the  $^1\text{H}$ -NMR spectrum of [Pt(*S*-pn)<sub>3</sub>]<sup>4+</sup> **2b**. This can be even further simplified by recording a  $^{195}\text{Pt}$ -decoupled proton spectrum (Fig. 4) c). Not all signals can be assigned unambiguously. It is obvious that the two diastereotopic protons of the CH<sub>2</sub> groups appear in the range of 3.12 to 3.35 ppm for the axial and the equatorial positions, as indicated in (Fig. 4) c). The CH<sub>3</sub> protons do not show any particularly interesting features, since it is a composite signal of a number of doublets due to the coupling with the CH proton. The latter appears for the major species  $\Lambda$ -[Pt(*S*-pn)<sub>3</sub>]<sup>4+</sup> 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 ( $\Delta$ -[Pt(*S*-pn)<sub>3</sub>]<sup>4+</sup>) 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<sup>III</sup> 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 methyl group [14], [15].

### Figure 4.

$^{195}\text{Pt}$ -NMR Spectroscopy. – The  $^{195}\text{Pt}$ -NMR spectra (see experimental 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  $^{195}\text{Pt}$ -NMR line at  $-863.65$  ppm (vs.  $\text{Na}_2\text{PtCl}_6$ ) could be observed, which is probably due to the two diastereoisomers  $\Lambda$ - and  $\Delta$ - $[\text{Pt}(\text{S-pn})_3]^{4+}$ , respectively.

As discussed above, the stereoselectivity claimed by Smirnov (in 1920) [6], is in general quite modest. We therefore investigated the behaviour of the complexes upon crystallization from solutions containing a mixture of isomers. Indeed, upon slow crystallization (see experimental part) of the raw product, yielding rather small crystals, the isomeric purity could be improved considerably. (*Fig. 5*) shows the  $^1\text{H}$ -NMR, and the proton-decoupled  $^{13}\text{C}$ -NMR spectra of the product after slow recrystallization. In comparison with the spectra discussed earlier, it is obvious that the all  $\Delta$ -isomers have been completely removed by the crystallization process.

#### Figure 5.

Comparing  $[\alpha]_{\text{D}}$  values of our products with that published by Smirnov also indicates that his preparations were only partially stereoselective. Smirnov measured  $[\alpha]_{\text{D}}$  values of the complexes of  $-170^\circ$  to  $-180^\circ$ . We found in the “raw” product a value of only  $-97^\circ$ , whereas it increased to  $-131^\circ$ , when Smirnov’s experimental conditions were applied. Our final value, after careful recrystallization was  $-218.5^\circ$ .

Since both enantiomers of pn are easily accessible, we prepared an “artificial” racemate containing equimolar quantities of  $[\text{Pt}(\text{S-pn})_3]^{4+}$ , and  $[\text{Pt}(\text{R-pn})_3]^{4+}$ , respectively. Observing the  $^{13}\text{C}$ -NMR spectra of  $\text{D}_2\text{O}$  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 platinum complexes. Even heating to  $60^\circ\text{C}$  for several hours did not change this situation.

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### Experimental Part

*General.* NMR spectra were measured on a Bruker DRX 500 or Bruker Avance 400 in deuterium oxide (99.9%D) (Cambridge Isotope Laboratories). Bruker Avance 400 ( $^1\text{H}$  : 400.13 MHz,  $^{13}\text{C}$  : 100.62 MHz), Bruker DRX 500 ( $^1\text{H}$  : 500.13 MHz,  $^{13}\text{C}$  : 125.76 MHz,  $^{15}\text{N}$  : 50.68 MHz,  $^{195}\text{Pt}$  : 107.42 MHz). Chemical shifts ( $\delta$ -scale, ppm) are given relative to external  $\text{Me}_4\text{Si}$  ( $^1\text{H}$ ,  $^{13}\text{C}$ ),  $\text{MeNO}_2$  ( $^{15}\text{N}$ ) and  $\text{Na}_2\text{PtCl}_6$  ( $^{195}\text{Pt}$ ) standards. Assignment of the NMR signal is based on  $^1\text{H}$ ,  $^1\text{H}\{^{195}\text{Pt}\}$ ,  $^{13}\text{C}\{^1\text{H}\}$ ,  $^{13}\text{C}$  APT,  $^{195}\text{Pt}\{^1\text{H}\}$ ,  $^{15}\text{N}\{^1\text{H}\}$ , COSY,  $^{13}\text{C}$  HMQC, ROESY. UV/VIS spectra were recorded in water solution on a Perkin-Elmer Lambda 25 spectrometer. CD spectra were recorded at 25°C in water on a Jasco J-715 spectropolarimeter. Optical rotations were measured on an automatic polarimeter Autopol III (Rudolph Research, New Jersey) or on a Perkin-Elmer 241 MC polarimeter and are given in  $\text{deg.cm}^3.\text{g}^{-1}.\text{dm}^{-1}$ . Mass spectra were recorded on a Bruker Bio Apex II (ESI) or on a VG Instruments 7070E (EI). A diffractometer STOE IPDS-2 was used to record X-ray diffractions. The “Ecole d’ingénieurs et d’architectes de Fribourg” accomplished the elemental analysis.  $^{15}\text{N}$  labeled ammonia solution ( $^{15}\text{N}$ , 98%+) (6M in  $\text{H}_2\text{O}$ ) for the synthesis of labeled (*R*)-1,2-diaminopropane was purchased from Cambridge Isotope Laboratories.

#### *Hydrogen hexachloroplatinate(IV), $\text{H}_2\text{PtCl}_6$ (6).*

Metallic platinum (99.999%) (9.9835 g) was dissolved in aqua regia (100 ml) during one week at 70°C under stirring. The resulting solution was poured into a porcelain evaporating dish placed on a water bath and the liquid was evaporated. A concentrated

HCl solution (30 ml) (37%, puriss. p.a.) was then added and evaporated again. The cycle was repeated 10-times with HCl and 5-times with distilled water finally. The product was transferred quantitatively into a volumetric flask (250 ml) and filled up with distilled water. The stock solution ( $c = 0.20471 \text{ mol.dm}^{-3}$ ) was used in all further experiments.

*rac*-1,2-Diaminopropane (**7**) (*rac*-pn) was purchased from Fluka.

(*R*)-1,2-Diaminopropane (**8**) and (*S*)-1,2-Diaminopropane (**9**) (*R*-pn and *S*-pn) were purchased as dihydrochlorides from Aldrich. The free bases were obtained by distillation of the hydrochlorides with an excess of powdered sodium hydroxide.

(*R*)-1,2-Diaminopropane\* - *R*-pn\* ( $^{15}\text{N}$  labeled ( $^{15}\text{N}$ , 98%+) aminogroup  $-\text{CH}_2-\text{NH}_2^*$ ) (**10**).

Synthesis:

D-Alanine methylester hydrochloride (10.42 g) (Aldrich) was dissolved in water (20 ml), sodium hydroxide (2.98 g) was added, and the mixture was extracted with dichloromethane (4 x 20 ml). The organic solution was dried over  $\text{Na}_2\text{SO}_4$  and the solvent was rapidly evaporated at room temperature under vacuum. To the resulting oil  $^{15}\text{N}$  labeled ammonia solution (6M in  $\text{H}_2\text{O}$ ) (20 g) was added immediately and the mixture was stirred at room temperature overnight [16]. The mixture was then evaporated to dryness. The remaining solid was extracted with dichloromethane (30 ml) and the undissolved part was filtered off. The solvent was evaporated from the

clear solution and the crude (*R*)-Alaninamide\* **11** (5 g, 78%) was used in next step without further purification.

#### Scheme 2.

Lithium aluminium hydride (3 g) was suspended in dry THF (100 ml) and the crude (*R*)-Alaninamide\* **11** (5 g) was added sequentially. The stirred mixture was refluxed for 8 hours [17] under argon, diluted with THF (100 ml), and the remaining hydride was decomposed by addition of sodium sulfate decahydrate. The solid part was filtered off and washed with THF. The washings were combined with the filtrate, acidified with concentrated hydrochloric acid and taken to dryness in vacuo. The residue was mixed with an excess of powdered sodium hydroxide and the free base was distilled off and collected. The distillate was dried with small pieces of metallic sodium, the formed sodium hydroxide solution being removed. The product was distilled again, yielding (2.7 g, 65%) of the diamine **10**. b.p. 115 – 120°C.  $[\alpha]_D + 4.4^\circ$  (25°C,  $c = 0.01026$ , H<sub>2</sub>O, measured as dihydrochloride). <sup>1</sup>H-NMR (500.13 MHz, D<sub>2</sub>O) 1.04 (d, 3H, CH<sub>3</sub>,  $J = 6.6$  Hz); 2.52 (m, 2H, CH<sub>2</sub>, coupling with <sup>15</sup>N  $J_{NH} = 0.7$  Hz); 2.86 (m, 1H, CH). <sup>13</sup>C{<sup>1</sup>H}-NMR (125.76 MHz, D<sub>2</sub>O) 19.39 (s, CH<sub>3</sub>); 47.76 (s, CH); 48.37 (d, CH<sub>2</sub>,  $J_{NC} = 4.0$  Hz). <sup>15</sup>N{<sup>1</sup>H}-NMR (50.68 MHz, D<sub>2</sub>O) –364.71 (–CH<sub>2</sub>-NH<sub>2</sub>\*, <sup>15</sup>N labeled). EI-MS: 44 (100%,  $[M - (CH_2-NH_2)]^+$ ).

*rac*-tris-(1,2-Diaminopropane)platinum(IV) tetrachloride – *rac*-[Pt(pn)<sub>3</sub>]Cl<sub>4</sub>

**(1a).**

This complex salt was prepared in an analogous way as described by Smirnoff [6].

The stock solution of H<sub>2</sub>PtCl<sub>6</sub> **6** (50 ml, 10.25 mmol ~ 2 g Pt) was evaporated to dryness and the remaining solid was dissolved in absolut ethanol (17 ml). *rac*-1,2-

Diaminopropane **7** (3.2 g, 3.7 ml, 43.4 mmol) was added sequentially to the chilled (ice bath) ethanolic  $\text{H}_2\text{PtCl}_6$  **6** solution to form *rac*-pn. $\text{H}_2\text{PtCl}_6$  as yellow precipitate. The mixture was refluxed for 30 minutes, allowed to cool to room temperature and the solid product was filtered off, washed with ethanol and ether, and dried in air to yield crude complex **1a** (4 g) as white powder.

*rac*-tris-(1,2-Diaminopropane)platinum(IV) tetrachloride monohydrate – *rac*-[Pt(pn)<sub>3</sub>]Cl<sub>4</sub> · H<sub>2</sub>O (**1b**).

The crude complex **1a** (2.5 g) was dissolved in water (5 ml), filtered, and ethanol (30 ml) was added to the filtrate. The pure precipitated product was isolated, washed with ethanol and ether, and dried in air to obtain the complex **1b** as a white powder (2 g).

<sup>1</sup>H-NMR (500.13 MHz, D<sub>2</sub>O) 1.57 – 1.63 (m, CH<sub>3</sub>); 3.11 – 3.37 (m, CH<sub>2</sub>, Pt satellites); 3.67 – 3.89 (m, CH). <sup>13</sup>C{<sup>1</sup>H}-NMR (125.76 MHz, D<sub>2</sub>O) 14.57 – 15.47 (CH<sub>3</sub>, more than 28 signals with Pt satellites J<sub>PtC</sub> = 13.7 Hz); 52.13 – 53.92 (CH<sub>2</sub>, more than 28 signals with Pt satellites J<sub>PtC</sub> = 3.1 Hz); 57.15 – 59.80 (CH, more than 28 signals). <sup>195</sup>Pt{<sup>1</sup>H}-NMR (107.42 MHz, D<sub>2</sub>O) – 862.46 (broad signal, width > 35 ppm). UV/VIS (λ<sub>max</sub>, H<sub>2</sub>O, c = 2.041 · 10<sup>-4</sup> mol · dm<sup>-3</sup>, L = 1 cm): 303.97 nm. ESI-MS (H<sub>2</sub>O/MeCN): 414 (100% [C<sub>9</sub>H<sub>27</sub>N<sub>6</sub>Pt]<sup>+</sup>). For C<sub>9</sub>H<sub>30</sub>N<sub>6</sub>PtCl<sub>4</sub> · H<sub>2</sub>O calculated: 18.72% C, 5.59% H, 14.56% N; found: 18.59% C, 5.95% H, 14.48% N.

*tris*-((S)-1,2-Diaminopropane)platinum(IV) tetrachloride – [Pt(S-pn)<sub>3</sub>]Cl<sub>4</sub> (**2a**).

The stock solution of  $\text{H}_2\text{PtCl}_6$  **6** (25 ml, 5.13 mmol ~ 1 g Pt) was evaporated to dryness and the remaining solid was dissolved in absolut ethanol (9 ml). (S)-1,2-

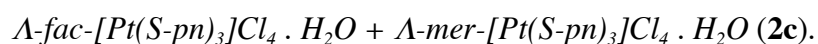
Diaminopropane **9** (2 g, 27 mmol) was added in small portions to the cooled (ice bath)  $\text{H}_2\text{PtCl}_6$  **6** solution and the resulting mixture was refluxed for 30 minutes. The mixture

was allowed to cool to room temperature and ether (35 ml) was added under stirring. The product was isolated by filtration, washed with ether (35 ml) and dried carefully in air to obtain the complex **2a** (2 g) as a white powder.  $[\alpha]_D - 97.0^\circ$  (25°C,  $c = 0.01299$ , H<sub>2</sub>O). ( $\Delta$ -*fac*-[Pt(*S*-pn)<sub>3</sub>]Cl<sub>4</sub> +  $\Delta$ -*mer*-[Pt(*S*-pn)<sub>3</sub>]Cl<sub>4</sub>) : ( $\Delta$ -*fac*-[Pt(*S*-pn)<sub>3</sub>]Cl<sub>4</sub> +  $\Delta$ -*mer*-[Pt(*S*-pn)<sub>3</sub>]Cl<sub>4</sub>) in 1 : 1.3 ratio.

*tris-((S)-1,2-Diaminopropane)platinum(IV) tetrachloride monohydrate – [Pt(*S*-pn)<sub>3</sub>]Cl<sub>4</sub> · H<sub>2</sub>O (2b).*

The crude complex **2a** (1.5 g) was dissolved in water (1.5 ml), filtered and a mixture of ethanol (10 ml) and ether (5 ml) was added to the filtrate. The pure precipitated product was isolated, washed with ether, and dried carefully in air to give complex **2b** (1.3 g) as a white powder.  $[\alpha]_D - 131.0^\circ$  (25°C,  $c = 0.01130$ , H<sub>2</sub>O). <sup>1</sup>H-NMR (500.13 MHz, D<sub>2</sub>O) 1.55 – 1.58 (m, set of overlapped doublets, CH<sub>3</sub>, 3H,  $\Delta$ -*fac* +  $\Delta$ -*mer* +  $\Delta$ -*fac* +  $\Delta$ -*mer*); 3.08 (m, multiple dd, CH<sub>2</sub>, 1H<sub>axial</sub>,  $J_{\text{gem.}} = J_{\text{vic.-trans}} = 13.3$  Hz,  $\Delta$ -*fac* +  $\Delta$ -*mer*); 3.17 (m, CH<sub>2</sub>, 1H<sub>axial</sub>,  $\Delta$ -*fac* +  $\Delta$ -*mer*); 3.25 – 3.29 (m, CH<sub>2</sub>, 1H<sub>equatorial</sub>, Pt satellites  $J_{\text{PtH}} = 27$  Hz,  $\Delta$ -*fac* +  $\Delta$ -*mer* +  $\Delta$ -*fac* +  $\Delta$ -*mer*); 3.58 – 3.68 (m, CH, 1H,  $\Delta$ -*fac* +  $\Delta$ -*mer*); 3.71 – 3.78 and 3.79 – 3.87 (m and m, CH, 1H). <sup>13</sup>C{<sup>1</sup>H}-NMR (125.76 MHz, D<sub>2</sub>O) 14.99, 15.03, 15.04 (CH<sub>3</sub>, Pt satellites  $J_{\text{PtC}} = 13.5$  Hz,  $\Delta$ -*mer*); 15.01 (CH<sub>3</sub>, Pt satellites  $J_{\text{PtC}} = 13.5$  Hz,  $\Delta$ -*fac*); 15.27, 15.31, 15.35 (CH<sub>3</sub>, Pt satellites  $J_{\text{PtC}} = 13.7$  Hz,  $\Delta$ -*mer*); 15.40 (CH<sub>3</sub>, Pt satellites  $J_{\text{PtC}} = 13.7$  Hz,  $\Delta$ -*fac*); 52.71 (CH<sub>2</sub>, Pt satellites  $J_{\text{PtC}} = 3$  Hz,  $\Delta$ -*fac*); 52.74, 52.81, 52.85 (CH<sub>2</sub>, Pt satellites  $J_{\text{PtC}} = 3$  Hz,  $\Delta$ -*mer*); 53.07 (CH<sub>2</sub>, Pt satellites  $J_{\text{PtC}} = 3.5$  Hz,  $\Delta$ -*fac*); 53.24, 53.34, 53.52 (CH<sub>2</sub>, Pt satellites  $J_{\text{PtC}} = 3.5$  Hz,  $\Delta$ -*mer*); 57.31, 57.39, 57.40 (CH,  $\Delta$ -*mer*); 57.48 (CH,  $\Delta$ -*fac*); 58.80, 58.89, 59.07 (CH,  $\Delta$ -*mer*); 59.15 (CH,

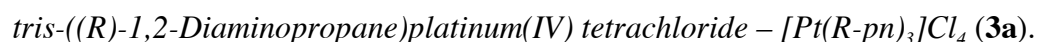
$\Lambda$ -*fac*).  $^{195}\text{Pt}\{^1\text{H}\}$ -NMR (107.52 MHz,  $\text{D}_2\text{O}$ ) – 872.39 (broad signal, unresolved coupling). UV/VIS ( $\lambda_{\text{max}}$ ,  $\text{H}_2\text{O}$ ,  $c = 2.051 \cdot 10^{-4} \text{ mol.dm}^{-3}$ ,  $L = 1 \text{ cm}$ ): 300.48 nm. CD ( $\lambda_{\text{min/max}}$  ( $\Delta\epsilon$ ),  $\text{H}_2\text{O}$ ,  $c = 2.051 \cdot 10^{-4} \text{ mol.dm}^{-3}$ ,  $L = 1 \text{ cm}$ ): 245 nm (+ 0.20); 320 nm (+ 0.25). ESI-MS ( $\text{H}_2\text{O}/\text{MeCN}$ ): 414 (100%  $[\text{C}_9\text{H}_{27}\text{N}_6\text{Pt}]^+$ ). For  $\text{C}_9\text{H}_{30}\text{N}_6\text{PtCl}_4 \cdot \text{H}_2\text{O}$  calculated: 18.72% C, 5.59% H, 14.56% N; found: 18.50% C, 6.00% H, 14.51% N. ( $\Lambda$ -*fac*- $[\text{Pt}(\text{S-pn})_3]\text{Cl}_4$  +  $\Lambda$ -*mer*- $[\text{Pt}(\text{S-pn})_3]\text{Cl}_4$ ) : ( $\Lambda$ -*fac*- $[\text{Pt}(\text{S-pn})_3]\text{Cl}_4$  +  $\Lambda$ -*mer*- $[\text{Pt}(\text{S-pn})_3]\text{Cl}_4$ ) in 1 : 2.4 ratio. ( $\Lambda$ -*fac*- $[\text{Pt}(\text{S-pn})_3]\text{Cl}_4$ ) : ( $\Lambda$ -*mer*- $[\text{Pt}(\text{S-pn})_3]\text{Cl}_4$ ) in 1 : 3 ratio.



The complex  $[\text{Pt}(\text{S-pn})_3]\text{Cl}_4 \cdot \text{H}_2\text{O}$  **2b** (500 mg) was dissolved in water (1 ml) at  $90^\circ\text{C}$  and the resulting solution was allowed to cool to  $4^\circ\text{C}$ . The white precipitate was isolated by filtration, washed with a small amount of cold water, and dried in air to give the complex **2c** (20 mg) as a white powder.  $[\alpha]_{\text{D}} - 218.5^\circ$  ( $25^\circ\text{C}$ ,  $c = 0.00615$ ,  $\text{H}_2\text{O}$ ).

$^1\text{H}$ -NMR (400.13 MHz,  $\text{D}_2\text{O}$ ) 1.49 – 1.51 (m, multiple d,  $\text{CH}_3$ , 3H,  $\Lambda$ -*fac* +  $\Lambda$ -*mer*); 3.00 (m, multiple dd,  $\text{CH}_2$ ,  $1\text{H}_{\text{axial}}$ ,  $\Lambda$ -*fac* +  $\Lambda$ -*mer*); 3.14 – 3.31 (m,  $\text{CH}_2$ ,  $1\text{H}_{\text{equatorial}}$ , Pt satellites  $J_{\text{PtH}} = 27 \text{ Hz}$ ,  $\Lambda$ -*fac* +  $\Lambda$ -*mer*); 3.53 – 3.57 (m, CH, 1H,  $\Lambda$ -*fac* +  $\Lambda$ -*mer*).

$^{13}\text{C}\{^1\text{H}\}$ -NMR (100.62 MHz,  $\text{D}_2\text{O}$ ) 15.17, 15.22, 15.26 ( $\text{CH}_3$ , Pt satellites  $J_{\text{PtC}} = 13.7 \text{ Hz}$ ,  $\Lambda$ -*mer*); 15.32 ( $\text{CH}_3$ , Pt satellites  $J_{\text{PtC}} = 13.7 \text{ Hz}$ ,  $\Lambda$ -*fac*); 53.01 ( $\text{CH}_2$ ,  $\Lambda$ -*fac*); 53.17, 53.26, 53.44 ( $\text{CH}_2$ ,  $\Lambda$ -*mer*); 58.84, 58.94, 59.10 (CH,  $\Lambda$ -*mer*); 59.19 (CH,  $\Lambda$ -*fac*). CD ( $\lambda_{\text{min/max}}$  ( $\Delta\epsilon$ ),  $\text{H}_2\text{O}$ ,  $c = 2.508 \cdot 10^{-4} \text{ mol.dm}^{-3}$ ,  $L = 1 \text{ cm}$ ): 245 nm (+ 1.52); 320 nm (+ 0.25). ( $\Lambda$ -*fac*- $[\text{Pt}(\text{S-pn})_3]\text{Cl}_4$ ) : ( $\Lambda$ -*mer*- $[\text{Pt}(\text{S-pn})_3]\text{Cl}_4$ ) in 1 : 4 ratio.



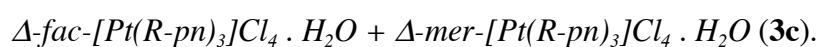
We have applied the same protocol as for the preparation of  $[\text{Pt}(\text{S-pn})_3]\text{Cl}_4$  **2a**. The stock solution of  $\text{H}_2\text{PtCl}_6$  **6** (25 ml) and (*R*)-1,2-diaminopropane **8** (2 g) were used for the preparation to obtain the crude complex **3a** (1.9 g) as a white powder.  $[\alpha]_{\text{D}} + 111.4^\circ$  (25°C, *c* = 0.01176,  $\text{H}_2\text{O}$ ). ( $\Delta$ -*fac*- $[\text{Pt}(\text{R-pn})_3]\text{Cl}_4$  +  $\Delta$ -*mer*- $[\text{Pt}(\text{R-pn})_3]\text{Cl}_4$ ) : ( $\Lambda$ -*fac*- $[\text{Pt}(\text{R-pn})_3]\text{Cl}_4$  +  $\Lambda$ -*mer*- $[\text{Pt}(\text{R-pn})_3]\text{Cl}_4$ ) in 1.3 : 1 ratio.

*tris-((R)-1,2-Diaminopropane)platinum(IV) tetrachloride monohydrate* –  $[\text{Pt}(\text{R-pn})_3]\text{Cl}_4 \cdot \text{H}_2\text{O}$  (**3b**).

The application of the same procedure as for  $[\text{Pt}(\text{S-pn})_3]\text{Cl}_4 \cdot \text{H}_2\text{O}$  **2b** gave pure complex **3b** (1.35 g) as a white powder.  $[\alpha]_{\text{D}} + 128.6^\circ$  (25°C, *c* = 0.01368,  $\text{H}_2\text{O}$ ).  $^1\text{H}$ -NMR (500.13 MHz,  $\text{D}_2\text{O}$ ) 1.58 – 1.62 (m, set of overlaped doublets,  $\text{CH}_3$ , 3H,  $\Delta$ -*fac* +  $\Delta$ -*mer* +  $\Lambda$ -*fac* +  $\Lambda$ -*mer*); 3.12 (m, multiple dd,  $\text{CH}_2$ ,  $1\text{H}_{\text{axial}}$ ,  $J_{\text{gem.}} = J_{\text{vic.-trans}} = 13.3$  Hz,  $\Delta$ -*fac* +  $\Delta$ -*mer*); 3.21 (m,  $\text{CH}_2$ ,  $1\text{H}_{\text{axial}}$ ,  $\Lambda$ -*fac* +  $\Lambda$ -*mer*); 3.28 – 3.35 (m,  $\text{CH}_2$ ,  $1\text{H}_{\text{equatorial}}$ , Pt satellites  $J_{\text{PtH}} = 27$  Hz,  $\Delta$ -*fac* +  $\Delta$ -*mer* +  $\Lambda$ -*fac* +  $\Lambda$ -*mer*); 3.63 – 3.70 (m, CH, 1H,  $\Delta$ -*fac* +  $\Delta$ -*mer*); 3.75 – 3.80 and 3.83 – 3.90 (m and m, CH, 1H).  $^{13}\text{C}\{^1\text{H}\}$ -NMR (125.76 MHz,  $\text{D}_2\text{O}$ ) 14.95, 14.99, 15.01 ( $\text{CH}_3$ , Pt satellites  $J_{\text{PtC}} = 13.5$  Hz,  $\Lambda$ -*mer*); 14.97 ( $\text{CH}_3$ , Pt satellites  $J_{\text{PtC}} = 13.5$  Hz,  $\Lambda$ -*fac*); 15.21, 15.26, 15.30 ( $\text{CH}_3$ , Pt satellites  $J_{\text{PtC}} = 13.7$  Hz,  $\Delta$ -*mer*); 15.36 ( $\text{CH}_3$ , Pt satellites  $J_{\text{PtC}} = 13.7$  Hz,  $\Delta$ -*fac*); 52.67 ( $\text{CH}_2$ , Pt satellites  $J_{\text{PtC}} = 3$  Hz,  $\Lambda$ -*fac*); 52.69, 52.78, 52.80 ( $\text{CH}_2$ , Pt satellites  $J_{\text{PtC}} = 3$  Hz,  $\Lambda$ -*mer*); 53.03 ( $\text{CH}_2$ , Pt satellites  $J_{\text{PtC}} = 3.5$  Hz,  $\Delta$ -*fac*); 53.19, 53.28, 53.46 ( $\text{CH}_2$ , Pt satellites  $J_{\text{PtC}} = 3.5$  Hz,  $\Delta$ -*mer*); 57.33, 57.40, 57.43 (CH,  $\Lambda$ -*mer*); 57.50 (CH,  $\Lambda$ -*fac*); 58.87, 58.97, 59.14 (CH,  $\Delta$ -*mer*); 59.23 (CH,  $\Delta$ -*fac*).  $^{195}\text{Pt}\{^1\text{H}\}$ -NMR (107.52 MHz,  $\text{D}_2\text{O}$ ) – 863.65 and – 871.75 (broad signals, unresolved coupling in ratio ca. 2 : 1 ~  $\Delta$  :  $\Lambda$ ). UV/VIS ( $\lambda_{\text{max}}$ ,  $\text{H}_2\text{O}$ , *c* =



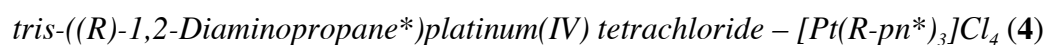
$2.108.10^{-4}$  mol.dm<sup>-3</sup>, L = 1 cm): 300.82 nm. CD ( $\lambda_{\min/\max}$  ( $\Delta\epsilon$ ), H<sub>2</sub>O, c =  $2.051.10^{-4}$  mol.dm<sup>-3</sup>, L = 1 cm): 245 nm (+ 0.40); 320 nm (+ 0.25). ESI-MS (H<sub>2</sub>O/MeCN): 414 (100% [C<sub>9</sub>H<sub>27</sub>N<sub>6</sub>Pt]<sup>+</sup>). For C<sub>9</sub>H<sub>30</sub>N<sub>6</sub>PtCl<sub>4</sub> · H<sub>2</sub>O calculated: 18.72% C, 5.59% H, 14.56% N; found: 18.63% C, 6.10% H, 14.53% N. ( $\Delta$ -*fac*-[Pt(*R*-pn)<sub>3</sub>]Cl<sub>4</sub> +  $\Delta$ -*mer*-[Pt(*R*-pn)<sub>3</sub>]Cl<sub>4</sub>) : ( $\Delta$ -*fac*-[Pt(*R*-pn)<sub>3</sub>]Cl<sub>4</sub> +  $\Delta$ -*mer*-[Pt(*R*-pn)<sub>3</sub>]Cl<sub>4</sub>) in 1 : 2.0 ratio. ( $\Delta$ -*fac*-(Pt(*R*-pn)<sub>3</sub>]Cl<sub>4</sub>) : ( $\Delta$ -*mer*-[Pt(*R*-pn)<sub>3</sub>]Cl<sub>4</sub>) in 1 : 3 ratio.



The complex [Pt(*R*-pn)<sub>3</sub>]Cl<sub>4</sub> · H<sub>2</sub>O **3b** (500 mg) was dissolved in water (1 ml) at 90°C and the resulting solution was allowed to cool to 4°C. The white precipitate was isolated by filtration, washed with small amount of cold water, and dried in air to give the complex **3c** (26 mg) as a white powder. [ $\alpha$ ]<sub>D</sub> + 217.3° (25°C, c = 0.00635, H<sub>2</sub>O).

<sup>1</sup>H-NMR (400.13 MHz, D<sub>2</sub>O) 1.50 – 1.51 (m, multiple d, CH<sub>3</sub>, 3H,  $\Delta$ -*fac* +  $\Delta$ -*mer*); 3.01 (m, multiple dd, CH<sub>2</sub>, 1H<sub>axial</sub>,  $\Delta$ -*fac* +  $\Delta$ -*mer*); 3.14 – 3.31 (m, CH<sub>2</sub>, 1H<sub>equatorial</sub>, Pt satellites J<sub>PtH</sub> = 27 Hz,  $\Delta$ -*fac* +  $\Delta$ -*mer*); 3.53 – 3.57 (m, CH, 1H,  $\Delta$ -*fac* +  $\Delta$ -*mer*).

<sup>13</sup>C{<sup>1</sup>H}-NMR (100.62 MHz, D<sub>2</sub>O) 15.18, 15.23, 15.27 (CH<sub>3</sub>, Pt satellites J<sub>PtC</sub> = 13.7 Hz,  $\Delta$ -*mer*); 15.33 (CH<sub>3</sub>, Pt satellites J<sub>PtC</sub> = 13.7 Hz,  $\Delta$ -*fac*); 53.02 (CH<sub>2</sub>,  $\Delta$ -*fac*); 53.19, 53.28, 53.45 (CH<sub>2</sub>,  $\Delta$ -*mer*); 58.84, 58.94, 59.10 (CH,  $\Delta$ -*mer*); 59.19 (CH,  $\Delta$ -*fac*). CD ( $\lambda_{\min/\max}$  ( $\Delta\epsilon$ ), H<sub>2</sub>O, c =  $1.819.10^{-4}$  mol.dm<sup>-3</sup>, L = 1 cm): 245 nm (+ 1.48); 320 nm (+ 0.25). ( $\Delta$ -*fac*-(Pt(*R*-pn)<sub>3</sub>]Cl<sub>4</sub>) : ( $\Delta$ -*mer*-[Pt(*R*-pn)<sub>3</sub>]Cl<sub>4</sub>) in 1 : 4 ratio.



„(R)-1,2-diaminopropane <sup>15</sup>N (98% +) labeled at –CH<sub>2</sub>-NH<sub>2</sub>\*“.

We have applied the same protocol for the synthesis and for the crystallization as we have used for  $[\text{Pt}(\text{S-pn})_3]\text{Cl}_4$  **2a**. The stock solution of  $\text{H}_2\text{PtCl}_6$  **6** (25 ml) and (*R*)-1,2-diaminopropane\* **10** (2 g,  $^{15}\text{N}$  labeled) were used for the preparation. The pure complex  $[\text{Pt}(\text{R-pn}^*)_3]\text{Cl}_4 \cdot \text{H}_2\text{O}$  **4** (1.2 g) was obtained as a white powder.  $[\alpha]_{\text{D}} + 136.5^\circ$  (25°C,  $c = 0.01546$ ,  $\text{H}_2\text{O}$ ).  $^1\text{H}$ -NMR (500.13 MHz,  $\text{D}_2\text{O}$ ) 1.57 – 1.60 (m,  $\text{CH}_3$ , 3H,  $\Delta$ -*fac* +  $\Delta$ -*mer* +  $\Lambda$ -*fac* +  $\Lambda$ -*mer*); 3.09 (m, multiple dd,  $\text{CH}_2$ ,  $1\text{H}_{\text{axial}}$ ,  $J_{\text{gem.}} = J_{\text{vic.-trans}} = 13.3$  Hz,  $\Delta$ -*fac* +  $\Delta$ -*mer*); 3.18 (m,  $\text{CH}_2$ ,  $1\text{H}_{\text{axial}}$ ,  $\Lambda$ -*fac* +  $\Lambda$ -*mer*); 3.25 – 3.31 (m,  $\text{CH}_2$ ,  $1\text{H}_{\text{equatorial}}$ , Pt satellites, coupling with  $^{15}\text{N}$ ,  $\Delta$ -*fac* +  $\Delta$ -*mer* +  $\Lambda$ -*fac* +  $\Lambda$ -*mer*); 3.59 – 3.70 (m, CH, 1H,  $\Delta$ -*fac* +  $\Delta$ -*mer*); 3.72 – 3.79 and 3.80 – 3.89 (m and m, CH, 1H).  $^{13}\text{C}\{^1\text{H}\}$ -NMR (125.76 MHz,  $\text{D}_2\text{O}$ ) 14.54, 14.56, 14.58, 14.60 ( $\text{CH}_3$ , coupling with  $^{15}\text{N}$ , Pt satellites,  $\Lambda$ -*fac* +  $\Lambda$ -*mer*); 14.82, 14.87, 14.91 ( $\text{CH}_3$ , set of doublets  $J_{\text{NC}} = 2.4$  Hz, Pt satellites  $J_{\text{PtC}} = 13.7$  Hz,  $\Delta$ -*mer*); 14.96 ( $\text{CH}_3$ , doublet  $J_{\text{NC}} = 2.4$  Hz, Pt satellites  $J_{\text{PtC}} = 13.7$  Hz,  $\Delta$ -*fac*); 52.24, 52.27, 52.30, 52.33, 52.38, 52.41 ( $\text{CH}_2$ , coupling with  $^{15}\text{N}$ , Pt satellites,  $\Lambda$ -*fac* +  $\Lambda$ -*mer*); 52.62 ( $\text{CH}_2$ , doublet  $J_{\text{NC}} = 4$  Hz, Pt satellites  $J_{\text{PtC}} = 3.5$  Hz,  $\Delta$ -*fac*); 52.79, 52.89, 53.07 ( $\text{CH}_2$ , set of doublets  $J_{\text{NC}} = 4$  Hz, Pt satellites  $J_{\text{PtC}} = 3.5$  Hz,  $\Delta$ -*mer*); 56.90, 56.97, 56.99 (CH,  $\Lambda$ -*mer*); 57.06 (CH,  $\Lambda$ -*fac*); 58.40, 58.50, 58.67 (CH,  $\Delta$ -*mer*); 58.76 (CH,  $\Delta$ -*fac*).  $^{195}\text{Pt}\{^1\text{H}\}$ -NMR (107.52 MHz,  $\text{D}_2\text{O}$ ) – 869.11 (broad signal, coupling with  $^{15}\text{N}$ ).  $^{15}\text{N}\{^1\text{H}\}$ -NMR (50.68 MHz,  $\text{D}_2\text{O}$ ) – 377.35 (d,  $J_{^{15}\text{N}-^{15}\text{N trans}} = 4.41$  Hz, Pt satellites  $J_{\text{PtN}} = 122$  Hz,  $\Lambda$ -*mer*); – 377.07 (d,  $J_{^{15}\text{N}-^{15}\text{N trans}} = 4.41$  Hz, Pt satellites  $J_{\text{PtN}} = 122$  Hz,  $\Lambda$ -*mer*); – 376.72 (s, Pt satellites  $J_{\text{PtN}} = 122$  Hz,  $\Lambda$ -*fac*); – 376.47 (s, Pt satellites  $J_{\text{PtN}} = 122$  Hz,  $\Lambda$ -*mer*); – 375.16 (s, Pt satellites  $J_{\text{PtN}} = 122$  Hz,  $\Delta$ -*fac*); – 375.02 (d,  $J_{^{15}\text{N}-^{15}\text{N trans}} = 4.41$  Hz, Pt satellites  $J_{\text{PtN}} = 122$  Hz,  $\Delta$ -*mer*); – 374.41 (s, Pt satellites  $J_{\text{PtN}} = 122$  Hz,  $\Delta$ -

*mer*); - 374.25 (d,  $J_{15N-15N\ trans} = 4.41$  Hz, Pt satellites  $J_{PtN} = 122$  Hz,  $\Delta$ -*mer*). ESI-MS ( $H_2O/MeCN$ ): 417 (100%  $[C_9H_{27}N_3^{15}N_3Pt]^+$ ). For  $C_9H_{30}N_3^{15}N_3PtCl_4 \cdot H_2O$  calculated: 18.64% C, 5.56% H, 15.00% N; found: 18.55% C, 5.82% H, 14.88% N. ( $\Delta$ -*fac*-[Pt(*R*-pn\*)<sub>3</sub>]Cl<sub>4</sub> +  $\Delta$ -*mer*-[Pt(*R*-pn\*)<sub>3</sub>]Cl<sub>4</sub>) : ( $\Delta$ -*fac*-[Pt(*R*-pn\*)<sub>3</sub>]Cl<sub>4</sub> +  $\Delta$ -*mer*-[Pt(*R*-pn\*)<sub>3</sub>]Cl<sub>4</sub>) in 1 : 2.9 ratio. ( $\Delta$ -*fac*-(Pt(*R*-pn)<sub>3</sub>]Cl<sub>4</sub>) : ( $\Delta$ -*mer*-[Pt(*R*-pn)<sub>3</sub>]Cl<sub>4</sub>) in 1 : 3 ratio.

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Table 1. Stereoisomers of  $M(en)_3$  and of  $rac-M(pn)_3$  coordination species. Column 1, and 2, respectively, contain the enantiomeric pairs of a given species, the lines correspond to different diastereoisomers.

$\Delta$ -enantiomer	$\Lambda$ -enantiomer	Symmetry
$\Delta-M(en)_3$	$\Lambda-M(en)_3$	$D_3$
$fac-\Delta-M(S-pn)_3$	$fac-\Lambda-(M(R-pn)_3)$	$C_3$
$mer-\Delta-M(S-pn)_3$	$mer-\Lambda-(M(R-pn)_3)$	$C_1$
$fac-\Delta-M(S-pn)_2(R-pn)$	$fac-\Lambda-(M(R-pn)_2(S-pn))$	$C_1$
$3\ mer-\Delta-M(S-pn)_2(R-pn)$	$3\ mer-\Lambda-(M(R-pn)_2(S-pn))$	$C_1$
$fac-\Delta-M(S-pn)(R-pn)_2$	$fac-\Lambda-(M(R-pn)(S-pn)_2)$	$C_1$
$3\ mer-\Delta-M(S-pn)(R-pn)_2$	$3\ mer-\Lambda-(M(R-pn)(S-pn)_2)$	$C_1$
$fac-\Delta-(M(R-pn)_3)$	$fac-\Lambda-M(S-pn)_3$	$C_3$
$mer-\Delta-(M(R-pn)_3)$	$mer-\Lambda-M(S-pn)_3$	$C_1$

Table 2. Four diastereoisomers for an OC-6 coordination species with enantiopure *S*-pn as ligand.

<i>fac</i> - $\Delta$ -M( <i>S</i> -pn) <sub>3</sub>	<i>fac</i> - $\Lambda$ -M( <i>S</i> -pn) <sub>3</sub>	C <sub>3</sub>
<i>mer</i> - $\Delta$ -M( <i>S</i> -pn) <sub>3</sub>	<i>mer</i> - $\Lambda$ -M( <i>S</i> -pn) <sub>3</sub>	C <sub>1</sub>

## Legends

Scheme 2. Preparation of the  $^{15}\text{N}$  labeled  $R\text{-pn}^*$ 

Fig. 1. Proton decoupled  $^{13}\text{C}$ -NMR spectra of a)  $\text{rac-}[\text{Pt}(\text{pn})_3]^{4+}$  (12 enantiomeric pairs of diastereoisomers) and b)  $[\text{Pt}(S\text{-pn})_3]^{4+}$  (4 diastereoisomers).

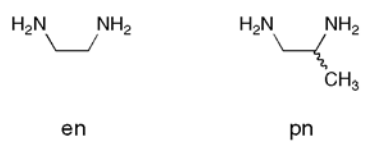
Fig. 2. Details of proton decoupled  $^{13}\text{C}$ -NMR spectra of  $[\text{Pt}(S\text{-pn})_3]^{4+}$ ; a) CH group, b)  $\text{CH}_2$  group, c)  $\text{CH}_3$  group.

Fig. 3. Proton decoupled  $^{15}\text{N}$ -NMR spectra of  $[\text{Pt}((R) \text{NH}_2\text{-CH}(\text{CH}_3)\text{-CH}_2\text{-}^{15}\text{NH}_2^*)_3]^{4+}$  (\*N 98%  $^{15}\text{N}$ ).

Fig. 4.  $^1\text{H}$ -NMR spectra of a)  $\text{rac-}[\text{Pt}(\text{pn})_3]^{4+}$ , b)  $[\text{Pt}(S\text{-pn})_3]^{4+}$ , and c) platinum decoupled  $[\text{Pt}(S\text{-pn})_3]^{4+}$ .

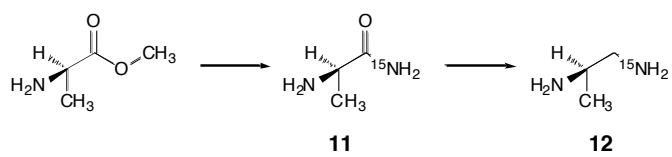
Fig. 5. NMR spectra of a carefully recrystallized sample of  $[\text{Pt}(S\text{-pn})_3]^{4+}$ ; a)  $^1\text{H}$ -NMR (insert Pt decoupled), b) proton decoupled  $^{13}\text{C}$ -NMR.

Scheme 1





Scheme 2



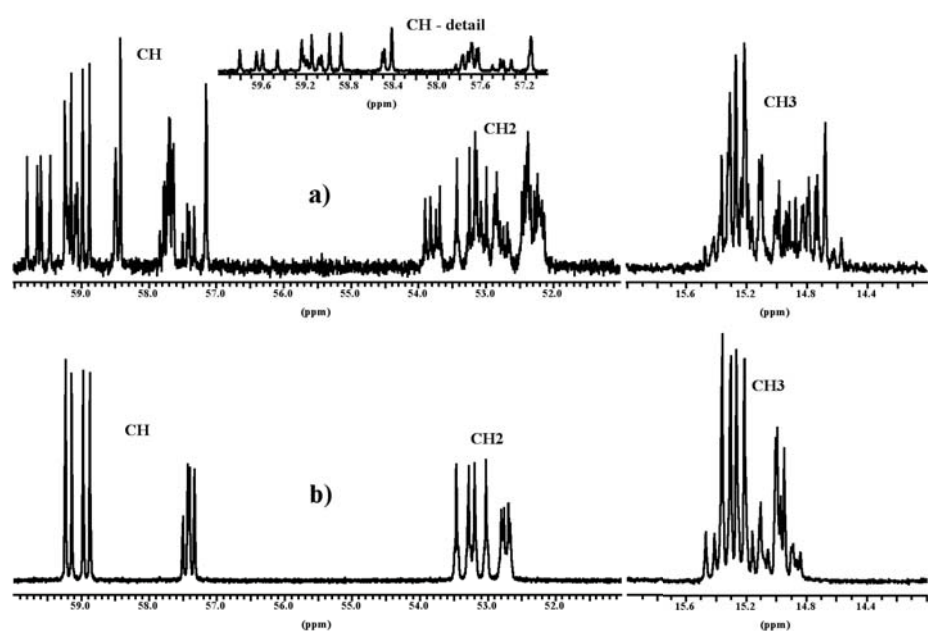


Fig. 1

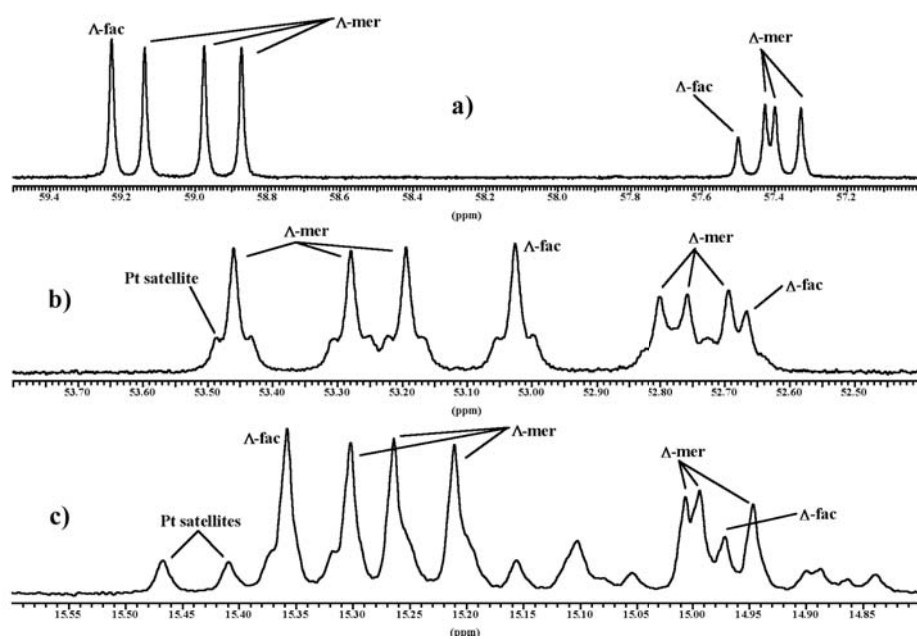


Fig. 2

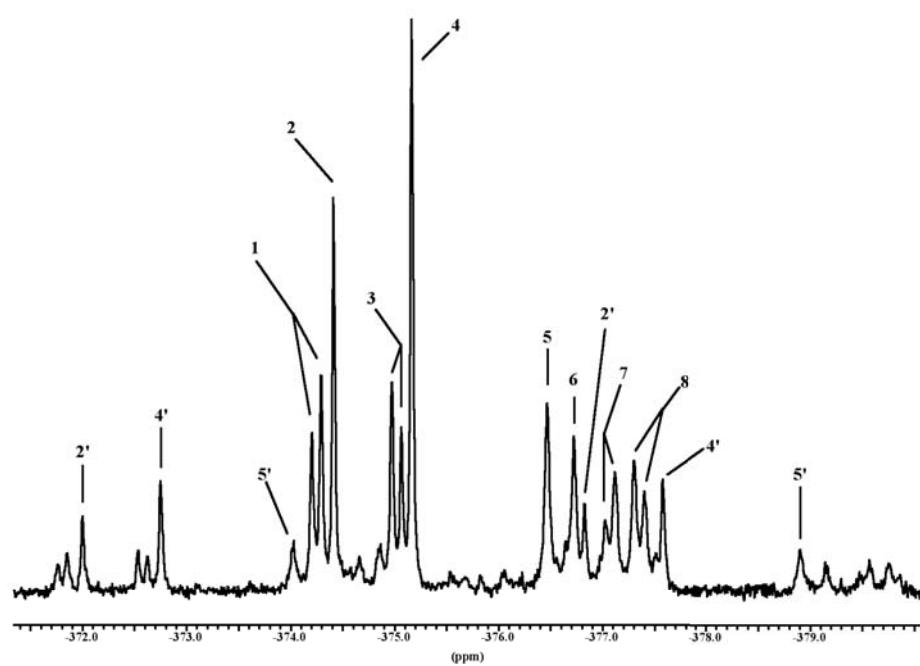


Fig. 3

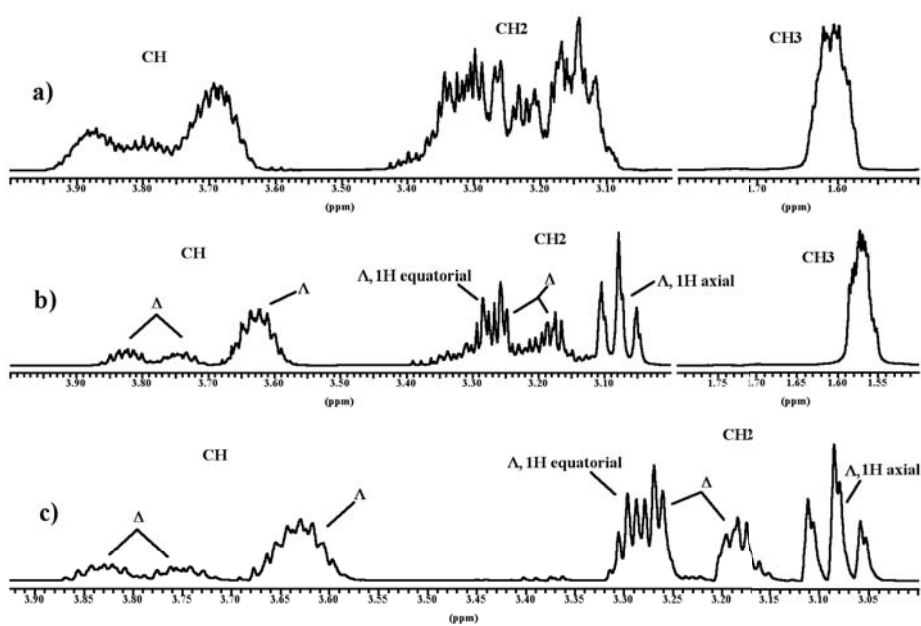


Fig. 4

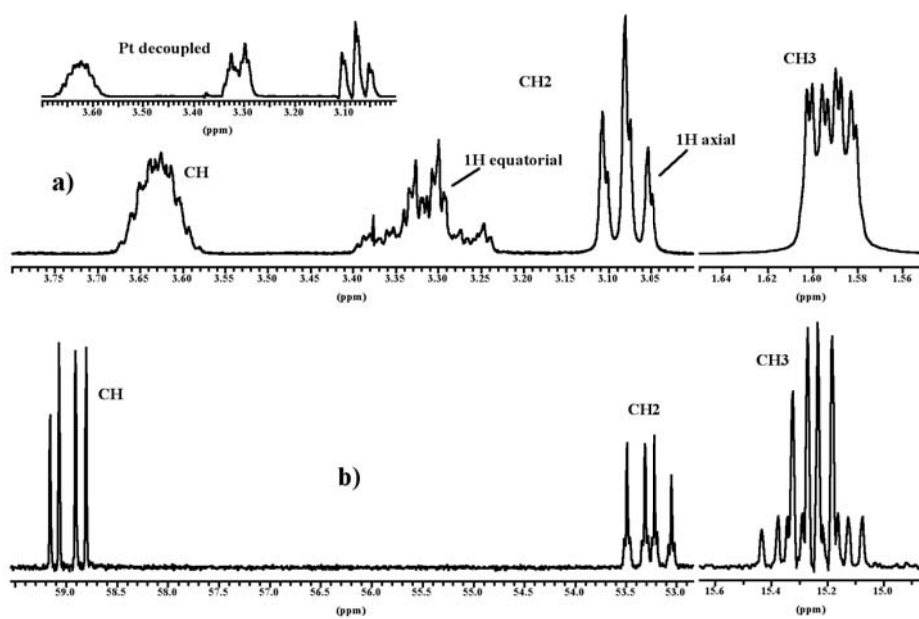


Fig. 5

## Contents

