Predetermined Chirality in Mono- and Dinuclear Cyclometalated Rhodium(III) Complexes

Liana Ghizdavu,[a] Brunhilde Kolp,[a] Alex von Zelewsky,*[a] and Helen Stoeckli-Evans[b]

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Dinuclear and polynuclear metal complexes with octahedral centers coordinated to di- or polydentate ligands are often obtained as complicated mixtures of various stereoisomers. Stereospecific synthesis of such species is therefore of high current interest. Chiral derivatives of pyridine can be used for this purpose. Dinuclear μ-chloro-bridged Rh^{III} complexes with two didentate, cyclometalated thienylpyridine-type ligands at each metal center are formed stereoselectively when pinene groups are fused to the pyridine rings. The two octahedral Rh^{III} centers have homochiral configurations, ΔΔ and ΛΛ. The heterochiral diastereomer ΔΛ is not observed. With (8*R*,10*R*)-2-(2′-thienyl)-4,5-pinenopyridine [Hth4,5-(*R*,*R*)ppy] the ΔΔ to ΛΛ ratio is 9:1 when the separation eluent contains NaCl. Modeling the ΛΛ and the ΔΔ isomers of the dinuclear species shows crowding of the pinene groups in both cases; however, the strain can be released by relatively small distortions only in the case of the ΛΛ isomer. NO_3^- cleaves the dichloro bridge, yielding the mononuclear species Δ[$Rh(L_2)_2(NO_3)$] (**2**) in a completely stereoselective manner when NaCl is replaced by KNO_3 in the eluent mixture. The molecular structure has been determined by X-ray structure analysis for both the ΔΔ and the mononuclear complex Δ[$Rh(L_2)_2(NO_3)$] (**2**) in order to confirm the configuration at the metal center. ^{1}H-NMR, ^{13}C-NMR and CD spectra were measured and the latter shows that the CD activity is solely due to the chirality at the metal center.

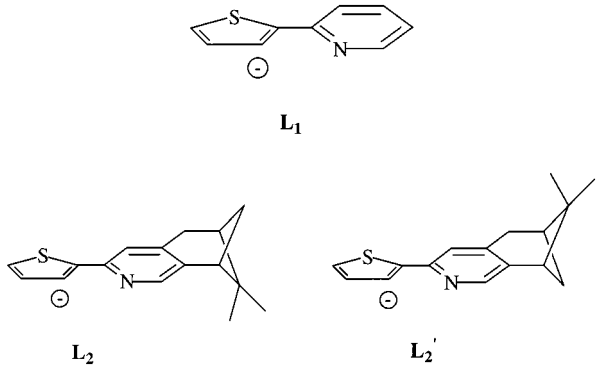
Introduction

The selective generation of chiral metal centers in a predetermined configuration has been reported already in 1920 by Smirnoff,[1] who worked with A. Werner. In contrast to organic chemistry, where *stereoselective synthesis* was developed to a high degree of sophistication, progress in this field was rather slow in coordination chemistry. A recent, fairly comprehensive review[2] on the subject reveals a strongly increased interest in metal-centred chirality in recent years.

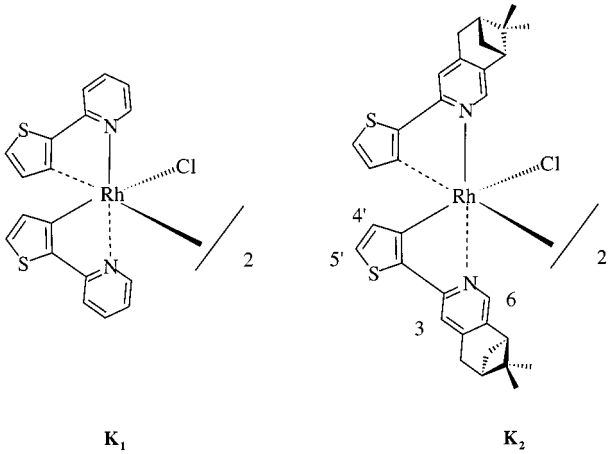
In earlier contributions, we reported the formation of dinuclear cyclometalated Rh^{III} complexes with thienylpyridine[3] or phenylpyridine.[4] 2-(2-Thienyl)pyridine (**L$_1$**, Scheme 1) gives, through a spontaneous cyclometalation, the dinuclear complex di-μ-chlorobis{bis[2-(thien-2′-yl)pyridinato-*N*,*C*$^{3'}$]rhodium} (**K$_1$**, Scheme 2).

It was shown that the formation of this complex is completely regioselective, i.e. only *C*,*C*-*cis*,*N*,*N*-*trans* isomers are obtained. The chirality at the metal centers follows an almost statistical distribution, yielding a ratio of ΔΔ/ΛΛ/ΔΛ of 1:1:2.[5][6] The two enantiomers ΔΔ and ΛΛ occur, of course, in an exact 1:1 ratio.

The introduction of a new family of chiral, enantiomerically pure pyridine-type ligands[7] prompted us to investigate the ability of these versatile molecules to form the dinuclear complexes in a stereoselective manner and to obtain derived mononuclear species with predetermined chirality at the metal center. For this purpose we used (8*R*,10*R*)-



Scheme 1. 2-(2-Thienyl)pyridine [thpy] (**L$_1$**), (8*R*,10*R*)-2-(2′-thienyl)-4,5-pinenopyridine [th4,5(*R*,*R*)ppy] (**L$_2$**) and (8*S*,10*S*)-2-(2′-thienyl)-4,5-pinenopyridine [th4,5(*S*,*S*)ppy] (**L$_2$′**)



Scheme 2

[a] Contribution from the Institute of Inorganic Chemistry, University of Fribourg,
Pérolles, CH-1700 Fribourg, Switzerland
[b] Institute of Chemistry, University of Neuchâtel,
Avenue de Bellevaux 51, CH-2000 Neuchâtel, Switzerland

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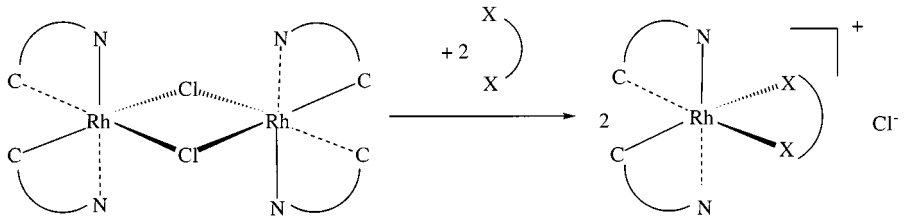

Scheme 3

2-(2′-thienyl)-4,5-pinenopyridine (**L_2**, in Scheme 1) for the preparation of dinuclear complexes. This ligand forms SP-4 Pt^{II} complexes, which significantly deviate from planarity.[8] The enantiomeric purity of **L_2** is due to its synthesis from a chiral-pool precursor, (−)-myrtenal, which is commercially available in high enantiomeric purity. A first question was the stereochemical outcome of the formation of **K_2** (Scheme 2). If we assume the same regioselectivity as in the case of **K_1** (this assumption is a posteriori justified by our investigations), the three isomers ΔΔ, ΛΛ, ΔΛ are now all diastereomers.

In order to obtain more information about the stereochemistry of such complexes, cleaving reactions (Scheme 3) can be carried out with chiral and nonchiral diimines, diamines and other chelating ligands.[3] Further investigations of such reactions and their products are in progress. Cleavage of the dinuclear species with NO_3^- occurred unintentionally upon separation on TLC plates, and also with acetonitrile in an attempt to obtain crystals of an artificial racemate (vide infra).

Results and Discussion

The replacement of the achiral 2-(2-thienyl)pyridine **L_1** by the enantiomerically pure (8*R*,10*R*)-2-(2′-thienyl)-4,5-pinenopyridine **L_2** renders the ΔΔ/ΛΛ isomers of the dinuclear species diastereomers. Separation with ordinary chromatographic methods becomes therefore possible. TLC (preparative thin layer chromatography, with a mixture of solvents and NaCl) gave the ΔΔ.ΛΛ isomers in a ratio of ca. 9:1, indicating that no cleavage occurred. When replacing NaCl with KNO_3, (see Experimental Section) three products in a mass ratio of 61:28:11 are obtained. The major product can clearly be identified as the ΔΔ isomer.

Single-crystal structure determination of this shows a D_2-symmetric species, where the sterical constraints of ligand/ligand interactions are relatively small. Figure 1 is a representation of the experimentally determined structure (see Table 1 for detailed structural information). The two minor products isolated (28% and 11%) were found to be the Δ[Rh(L$_2$)$_2$(NO$_3$)] (**2**) and the Λ[Rh(L$_2$)$_2$(NO$_3$)] (**3**) complexes, respectively. Both species were examined by X-ray diffraction, and the structures are shown in Figures 3 and 4. These two monomeric, isomerically pure compounds behave in some respects almost as enantiomers, in others, however, their diastereomeric nature is quite evident. Since the CD activity is mainly determined by the configuration around the metal center, the respective spectra are almost mirror images (Figure 7). The NMR spectra are also very similar, small differences in shift values are, however, noticeable. The two compounds behave quite differently with respect to crystallization, which shows the importance of intermolecular interactions in the crystal packing.

The isomer ΔΔ, where the structure could be determined experimentally, shows a relatively low crowding in the region where the pineno moieties of the ligands of the two Rh centers make their closest approach. The observed angle of 170° for N−Rh−N at one center is the same as in the mononuclear complex Δ[Rh(L$_2$)$_2$(NO$_3$)] (**2**), which will be discussed in more detail later. This indicates that the deviation of the N−Rh−N angle from 180° is a purely "local" phenomenon, due to the bite angle of ca. 81° of the cyclometalated ligand. Because of the relatively low quality of the structural analysis of the ΔΔ dimer (see Experimental Section) an attempt was made to prepare an artificial ΔΔ.ΛΛ racemate, using the enantiomeric ligands L_2 and L_2', respectively. The dimers ΔΔ[Rh(L$_2$)$_2$(μ-Cl)]$_2$ (**1**) and ΛΛ[Rh(L$_2'$)$_2$(μ-Cl)]$_2$ (**5**) behave as true enantiomers and are identical in every respect, except for their CD spectra, which are mirror images. Mixing the two enantiomers in order to form the artificial racemate, however, yielded a product that was no longer soluble in pure CH_2Cl_2. CH_3CN had to be added and crystallization was carried out in a CH_3CN/CH_2Cl_2 solvent mixture. The resulting crystalline material turned out to be {Δ[Rh(L$_2$)$_2$Cl(CH$_3$CN)] Λ[Rh(L$_2'$)$_2$Cl(CH$_3$CN)]} (**6**) (Figure 5), indeed a racemate, but of one of the cleaved dimers, containing the monomeric enantiomers. Thus, the dimers are obviously not sufficiently inert towards the solvent (CH_3CN).

In order to gain more insight into the effects that influence the formation or (non-)formation of the three dinuclear diastereomers, the non-existing configurations were graphically constructed on computer (with the MSI Cerius[2] program) by "manual" manipulation of the X-ray structure of the ΔΔ isomer (Figure 2a). The "models" of the ΔΛ and the ΛΛ diasteromers were obtained using the same coordinates as for the ΔΔ isomer except for the μ-dicloro bridge (vide infra), but changing the absolute configuration at the metal centers to ΔΛ and ΛΛ, respectively. This was done by simply breaking the Rh−C bonds and inverting the ligand′s orientation on both sides of the ΛΛ diasteromer and only for one metal center for ΔΛ diasteromer.

In the ΔΛ and the ΛΛ "models" severe crowding of the pineno groups occurs. Figure 2b represents a structure in which the twist angle of the two N−Rh−N directions,

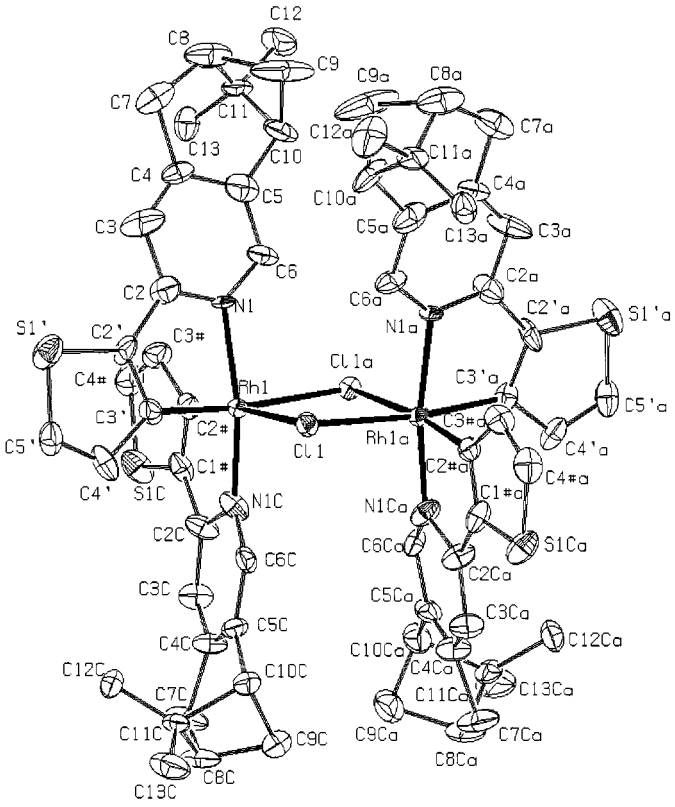

Figure 1a. Numbered ORTEP[18] plot with thermal ellipsoids drawn at 30% probability level of **1**

bution of ΔΔ/Δ/Λ of 61:28:11, mirrors the relative reactivities of the possible diastereomers of the dinuclear species. Only the ΔΔ isomer could be isolated, demonstrating the much higher reactivities towards the cleavage reaction of the ΛΛ and of the ΔΛ isomers that are most probably formed as intermediates.

A model of the "*meso*" isomer ΔΛ, which is still chiral due to the pineno groups, is shown in Figure 2c. Here the internal coordinates were taken from the ΔΔ isomer and the configuration at one Rh center was inverted. This reduces the symmetry of the dinuclear complex from D_2 to C_2. Figure 2c shows that the aromatic groups of the ligands on the two different Rh centers are now nearly perpendicular. The concomitant steric strain cannot be avoided through "distortions" of the complex. Experimentally no evidence indicated that the ΔΛ isomer is formed in this synthesis. From these observations it is concluded that only the ΔΔ isomer of the dimer shows a sufficiently low reactivity to be isolable. Another dimer must be formed as intermediate, which, however, reacts rapidly under the experimental conditions to yield the monomeric species Λ[Rh(L$_2$)$_2$(NO$_3$)] (**3**). Most probably this intermediate is the ΛΛ dimer, already observed in small proportions after separation of the raw product.

The third product obtained after separation on the TLC plates (61:*28*:11) was identified by X-ray diffraction methods as a mononuclear species Δ[Rh(L$_2$)$_2$(NO$_3$)] (**2**) (Figures 3a and 3b). Evidently, the enantiomerically pure mononuclear complex is obtained through cleavage of the dichloro

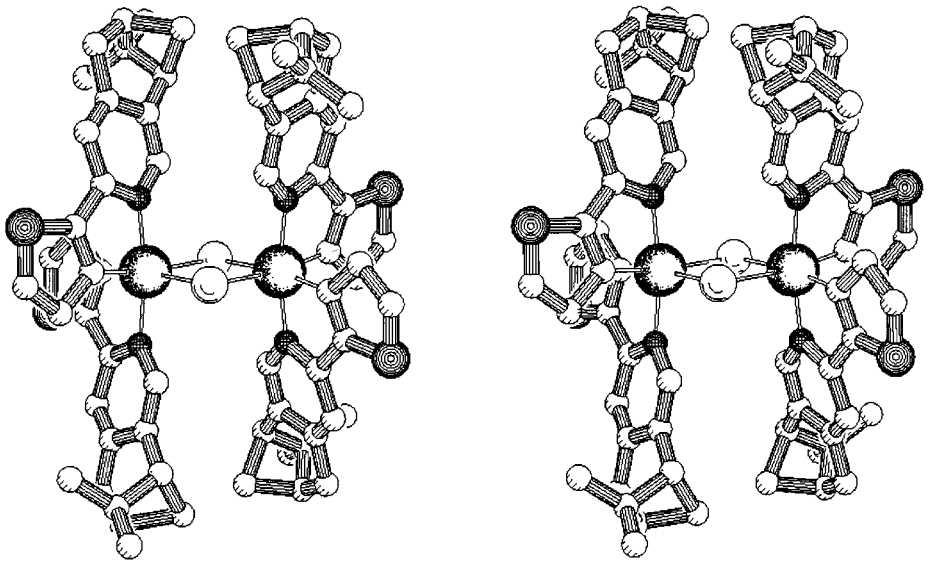

Figure 1b. Stereoview of the molecular structure of ΔΔ[Rh(L$_2$)$_2$(μ-Cl)]$_2$ (**1**); the hydrogen atoms have been omitted for clarity

which is 0° in the ΔΔ isomer, has been changed to 15° in the ΛΛ isomer. This distortion along one of the C_2 axes of the dinuclear species relieves the steric strains due to interligand repulsion considerably. It is therefore predicted that the ΛΛ isomer shows a "distortion" of this type, where the D_2 symmetry is conserved and the parallel orientation of the aromatic parts is maintained, but where the pineno groups are in less crowded positions. The product distribridge by NO_3^- used in the eluent during chromatography. As we will show in a forthcoming publication about a number of mononuclear complexes obtained through cleavage of the dinuclear species, it is a general phenomenon that the former can be obtained in enantiomerically pure form with predetermined chirality. Thus, the complex Δ[Rh(L$_2$)$_2$(NO$_3$)] (**2**) is the first example of a mononuclear species obtained from a diastereoselectively prepared dinuclear

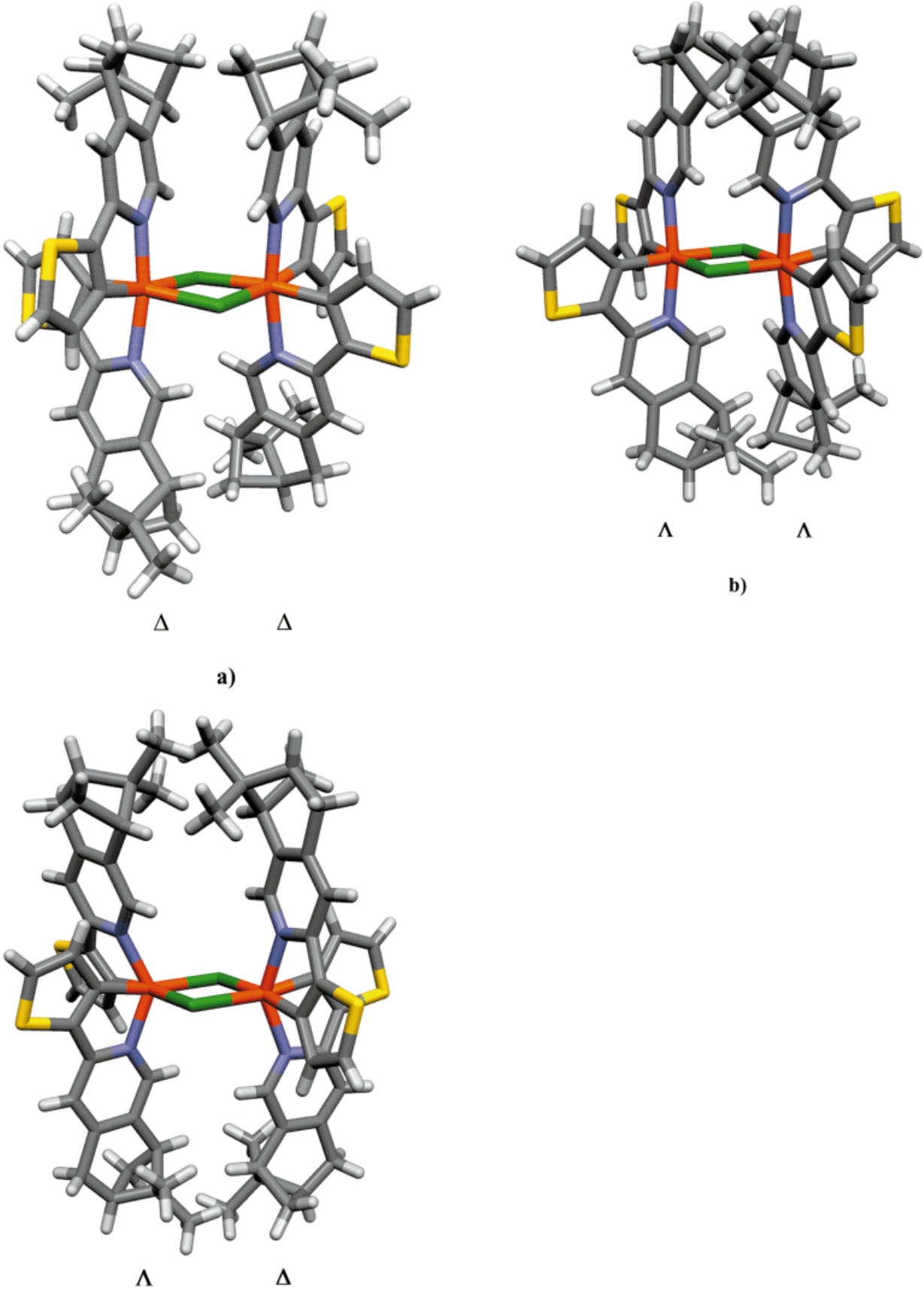

Figure 2. Cylinder plot of the molecular structure of ΔΔ[Rh(L_2)$_2$(μ-Cl)]$_2$ (**1**) (a), models of the ΛΛ structures (b) and ΔΛ (c) using the same internal coordinates as those measured in the ΔΔ isomer

compound that shows a *completely* predetermined chirality at the metal center.

NMR Spectroscopy

Figure 6 illustrates the aromatic region of the ^{1}H-NMR spectra for the $\Delta\Delta[Rh(L_2)_2(\mu\text{-}Cl)]_2$ (**1**), $\Delta[Rh(L_2)_2(NO_3)]$

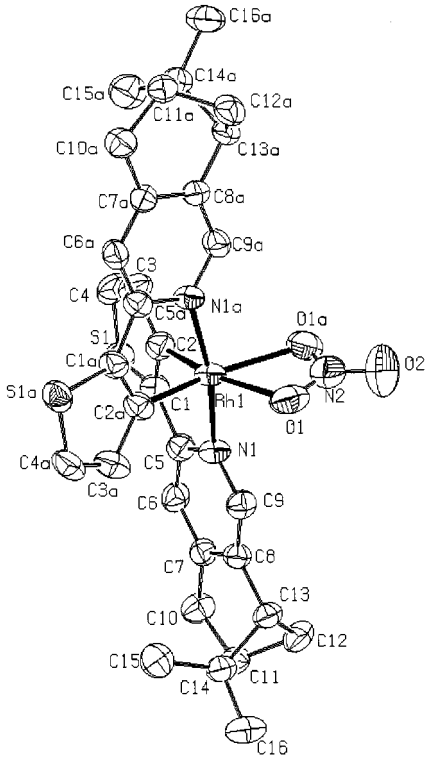

Figure 3a. Numbered ORTEP[18] plot with thermal ellipsoids represented at 50% probability level of **2**

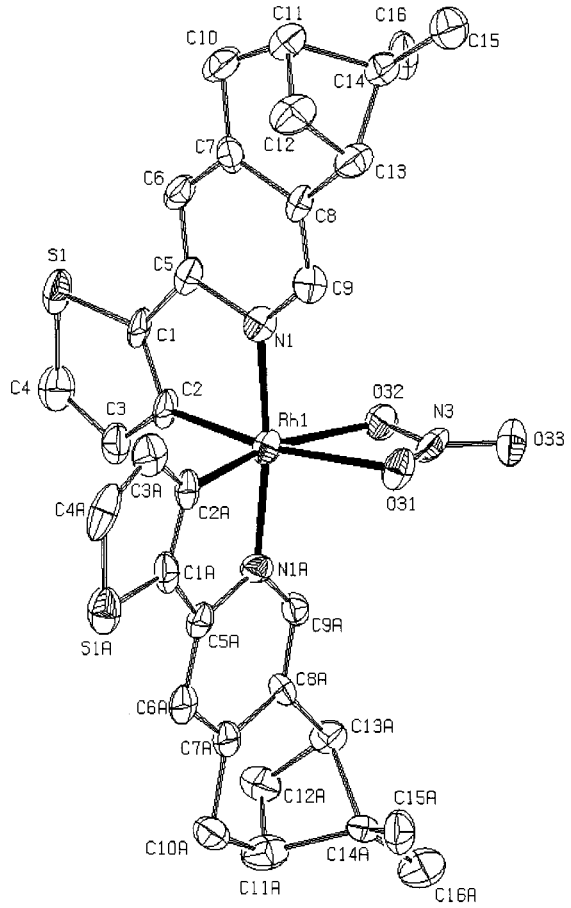

Figure 4. Numbered ORTEP[18] plot with thermal ellipsoids represented at 30% probability level of the molecular structure of $\Lambda[Rh(L_2)_2(NO_3)]$ (**3**); the hydrogen atoms have been omitted for clarity

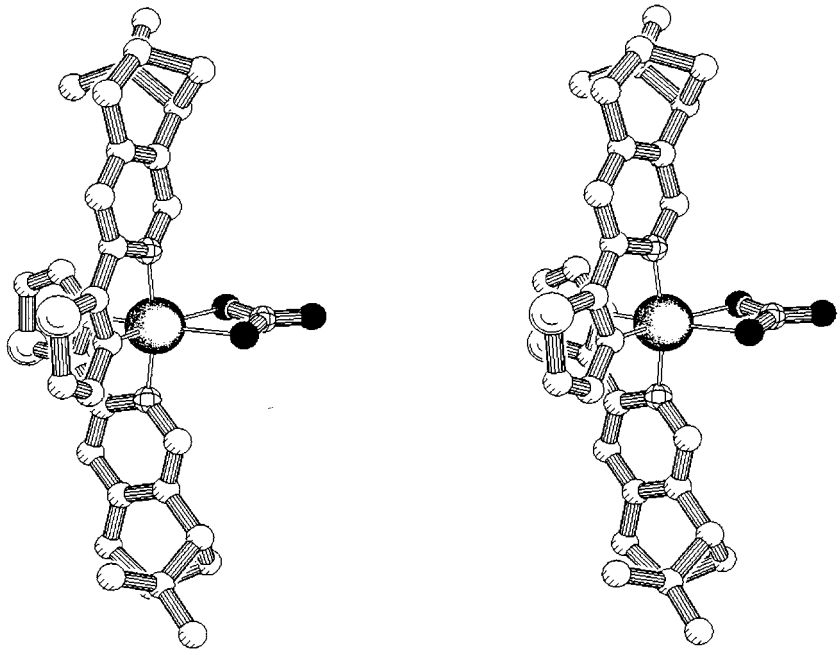

Figure 3b. Stereoview of the molecular structure of $\Delta[Rh(L_2)_2(NO_3)]$ (**2**); the hydrogen atoms have been omitted for clarity

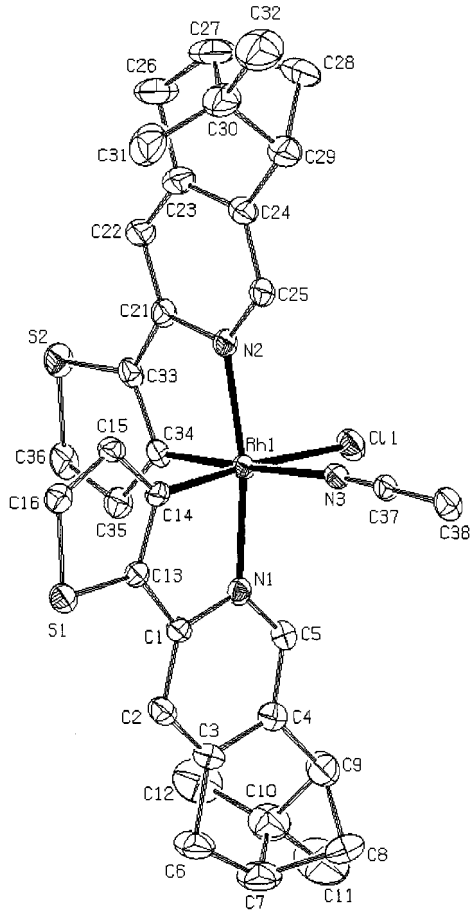

Figure 5. Numbered ORTEP[18] plot with thermal ellipsoids represented at 30% probability level of the molecular structure of $\Lambda[Rh(L_2')_2Cl(CH_3CN)]$ (**6**); the hydrogen atoms have been omitted for clarity

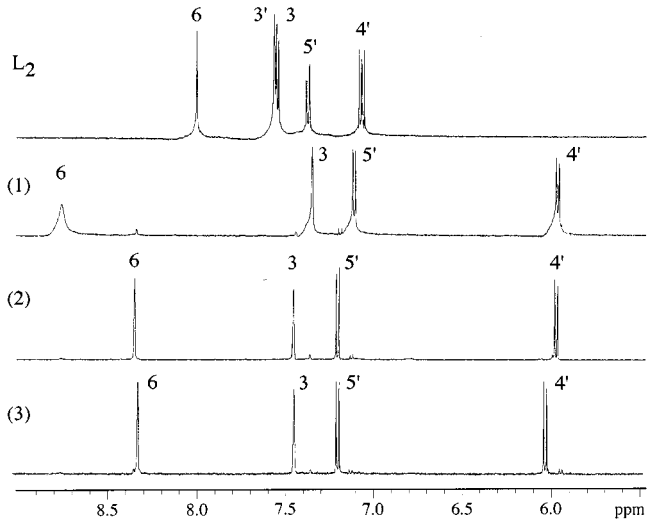

Figure 6. ^{1}H-NMR aromatic region spectra of $\Delta\Delta[Rh(L_2)_2(\mu\text{-}Cl)]_2$ (**1**), $\Delta[Rh(L_2)_2(NO_3)]$ (**2**), $\Lambda[Rh(L_2)_2(NO_3)]$ (**3**), (8*R*,10*R*)-2-(2′-thienyl)-4,5-pinenopyridine ($\mathbf{L_2}$)

(**2**), $\Lambda[Rh(L_2)_2(NO_3)]$ (**3**) complexes and the free ligand $\mathbf{L_2}$: (8*R*,10*R*)-2-(2′-thienyl)-4,5-pinenopyridine. Upon complexation with Rh^{III}, the signal corresponding to the proton 3′-H in the free (8*R*,10*R*)-2-(2′-thienyl)-4,5-pinenopyridine disappears. In agreement with the data from X-ray structure determination, the ^{1}H- and ^{13}C-NMR spectra indicate that the dinuclear complex $\Delta\Delta[Rh(L_2)_2(\mu\text{-}Cl)]_2$ (**1**) has D_2 symmetry and therefore all four ligands are equivalent. The ^{13}C-NMR spectrum of the $\Delta\Delta$ isomer shows 16 resonances; the signal at lowest field attributed to C-3′ is split due to the ^{13}C-^{103}Rh coupling (J_{Rh-C} = 36 Hz). The aromatic region of the ^{1}H-NMR spectra of the complexes is simple: Only four signals are observed due to the high symmetry. Relative to the free-ligand spectrum (see Figure 6) the proton chemical shifts of 4′-H, 5′-H and 3-H in all complexes appear upfield due to the positive ring current of the neighboring ligand coordinated at the same metal center. While the 5′-H and 3-H signals are only slightly shifted upfield, an important shift of ca. 1 ppm occurs for the signal of the 4′-H proton, which is pointing inside the pyridine ring of the neighboring ligand. There are three possible effects on the shift of the proton 6-H: (i) a deshielding by coordination to rhodium, (ii) a close proximity to the bridging Cl ligand, (iii) a negative ring current of the ligand situated at the other metal center. The corresponding signals of the two mononuclear complexes show a small downfield shift, and those of the $\Delta\Delta$ complex a much larger one. It seems therefore that in the mononuclear complexes Δ and Λ the shift of 6-H is mainly determined by the coordination to the rhodium center, whereas in the $\Delta\Delta$ isomer an additional influence in the same direction is observed, which is due to (iii). The limited solubility of the $\Delta[Rh(L_2)_2(NO_3)]$ (**2**) and $\Lambda[Rh(L_2)_2(NO_3)]$ (**3**) complexes in CD_3CN renders ^{13}C-NMR measurements impossible.

Electronic Spectra

The UV/Vis spectra of the dinuclear and mononuclear complexes show essentially two absorption bands at 282 and at 375 nm. These bands are likely to be due to charge transfer transitions.[5,9,10] Figure 7 shows the CD spectra of the Δ and Λ diastereomers of the mononuclear species. The near mirror symmetry of these spectra shows that the whole CD activity in this spectral range is mainly determined by the chiral configuration of the metal center.

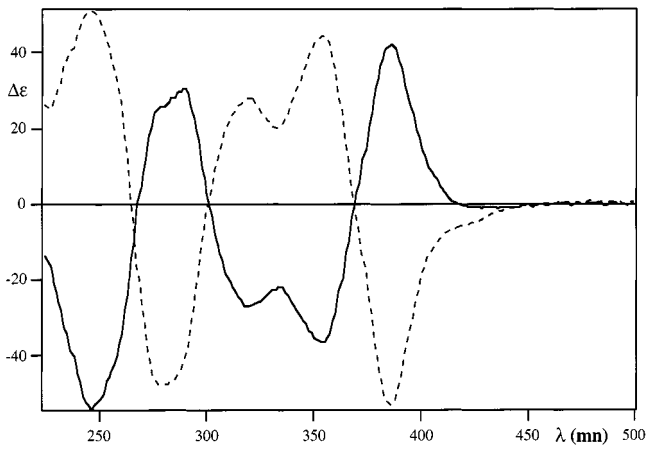

Figure 7. CD spectra of −−− $\Delta[Rh(L_2)_2(NO_3)]$ (**2**) and ---- $\Lambda[Rh(L_2)_2(NO_3)]$ (**3**) (c = 1.45 10^{-5} M in CH_3CN)

Conclusions and Outlook

The synthesis of the rhodium complexes with chiral thienylpyridine ligands yields two homochiral dimers (ΔΔ and ΛΛ), which are diastereomers, in a ratio of 9:1. The heterochiral dinuclear complex (ΔΛ) does not occur in measurable amounts. Through interactions between chiral ligands located at two adjacent metal centers, the absolute configurations of the latter are determined with a high selectivity. Cleavage of the dichloro bridge with NO_3^- or CH_3CN yields mononuclear species with predetermined chirality, since the configuration is retained during the cleavage reaction. As preliminary results indicate, stereochemically especially interesting reactions of this type occur with chiral diimines and diamines. The use of easily accessible chiral ligands thus gives the possibility of preparing stereoselectively Rh^{III} chelate complexes of various compositions. Such complexes may have interesting applications in the fields of bioinorganics[11] and photochemistry,[12][13] as well as in catalysis.

Experimental Section

General: All chemicals and reagent-grade products were obtained from Fluka, Aldrich or Merck and used, unless noted, without further purification. (+)-α-Pinene (> 97%; $[\alpha]_D^{20} = +45$), and (1*R*)-(−)-myrtenal (> 97%, $[\alpha]_D^{20} = -14.6$) were obtained from Fluka. The ligand $\mathbf{L_2}$ [(8*R*,10*R*)-2-(2′-thienyl)-4,5-pinenopyridine] and (2-thienylacetyl)pyridinium bromide were prepared according to literature procedures.[8] The enantiomer of $\mathbf{L_2}$ [(8*S*,10*S*)-2-(2′-thienyl)-4,5-pinenopyridine (abbreviated $\mathbf{L_2}'$)] was obtained analogously, starting from (+)-α-pinene, which was transformed into (+)-(*S*)-myrtenal by known procedures.[14] The product of crystallization of the artificial racemate {ΔΔ[Rh(L_2)$_2$Cl]$_2$ **(1)** ΛΛ[Rh(L_2')$_2$Cl]$_2$ **(5)**} was, in fact, {Δ[Rh(L_2)$_2$Cl(CH_3CN)] Λ[Rh(L_2')$_2$Cl(CH_3CN)]} (**6**) (see Results and Discussion), and was only characterized by X-ray structure analysis (see Figure 5).

Measurements: UV/Vis spectra were recorded with a Perkin-Elmer Lambda 5 and Perkin-Elmer Lambda 40 spectrometers; λ_{max} in nm, ε in <emphasis type="scaps">m^{-1} cm^{-1}. − NMR spectra were measured with a Varian Gemini-300 spectrometer operating at 300 MHz (for ^{1}H) and 75.46 MHz (for ^{13}C); δ in ppm with solvent as internal standard relative to $SiMe_4$, *J* in Hz. CD spectra: Jobin-Yvon and JASCO J-715 specropolarimeters; λ_{max} (Δε) in nm. − IR-spectral data were obtained with Perkin−Elmer 683 and Perkin−Elmer 16 PC FT-IR spectrometers; samples (1%) were compressed KBr pellets. − MS: VG-Instruments 7070E mass spectrometer equipped with an FAB inlet system. The elemental analyses were performed by CIBA Specialty Chemicals, Marly, Switzerland.

X-ray Structure Determination of ΔΔ[Rh(L_2)$_2$(μ-Cl)]$_2$ (1), Δ[Rh(L_2)$_2$(NO_3)] (2), Λ[Rh(L_2)$_2$(NO_3)] (3) and {Δ[Rh(L_2)$_2$Cl(CH_3CN)] Λ[Rh(L_2')$_2$Cl(CH_3 CN)]} (6). − Data Collection: Suitable orange block-like crystals of compounds **1** and **2**, and red block-like crystals of compound **3** were grown by slow diffusion of diethyl ether into CH_2Cl_2 solutions of the respective compounds. Suitable crystals of **6** were grown from a solution of CH_2Cl_2/CH_3CN as yellow plates. − Intensity data for compounds **1**, **2** and **6** were collected at 223 K with a Stoe Image Plate Diffraction System using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) and equipped with a φ circle. The image plate distance was 70 mm, φ scans of 0−200°, step Δφ = 1°, 2θ range 3.27−52.1°, resolution limits $d_{min} - d_{max}$ = 12.45−0.81 Å. − Intensity data for compound **3** was collected at room temperature with a Stoe AED2 4-circle diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) with ω.2θ scans in the 2θ range 5−51°. Further crystallographic data are summarized in Tables 1 and 2.

Structure Solution and Refinement: The structure of compounds **1**, **2**, **3** and **6** were solved by direct methods with the program SHELXS-97.[15] The refinements and all further calculations were carried out with the program SHELXL-97.[16] For all four compounds the H atoms were included in calculated positions and treated as riding atoms with SHELXL-97[16] default parameters. The non-H atoms in all four compounds were refined anisotropically, using weighted full-matrix least squares on F^2. No corrections for extinction or absorption were applied. For all four compounds the coordinates correspond to the absolute structure of the molecules in the crystals. This is confirmed by reference to the absolute structure of the ligand used and the absolute structure factor parameters,[17] 0.13(9) for **1**, −0.16(7) for **2** and 0.03(5) for **3**. Compound **1** possesses crystallographic twofold symmetry and is associated with one whole molecule of diethyl ether, which is disordered over two sites related by a 2-fold axis (occupancy 0.5). Atoms C(9) and C(10) of one of the pinene ligands undergo considerable thermal motion. An attempt to split these atoms was unsuccessful leading to poor bond lengths and bond angles. Complex **2** crystallized with one molecule of dichloromethane per molecule of **2**. For compound **6** there are two independent molecules and two complete molecules of CH_3CN, one of which is disordered over two sites with occupancies of 0.5 each. The molecular structures and crystallographic numbering schemes are illustrated in the PLATON[18] drawings, Figures 1a, 3a, 4 and 5. − The CIF files, including complete tables of bond lengths, bond angles and torsion angles, have been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ (UK). Deposition numbers are CCDC-114591 (**1**), -114592 (**2**), -114593 (**3**), -114594 (**6**).

Synthesis and Characterization

[Rh(L_2)$_2$(μ-Cl)]$_2$: With a modified literature procedure,[3] a mixture of $RhCl_3 \cdot 3H_2O$ (264 mg, 1 mmol) and th4,5ppy (766 mg, 3 mmol) was suspended in 20 mL of 2-methoxyethanol and dispersed during 10 min in an ultrasonic bath. The resulting solution, refluxed for 4 h, was concentrated and after addition of Et_2O, the brownish-orange precipitate was filtered off. Because the reaction was not complete, the unchanged ligand was recovered. The purification and separation of different diastereoisomers was done by preparative thin layer plate silica gel chromatography with CH_3CN/BuOH/H_2O/KNO_3 (4:1:1:0.1) as eluent. ΔΔ[Rh(L_2)$_2$(μ-Cl)]$_2$/Δ[Rh(L_2)$_2$(NO_3)]/Λ[Rh(L_2)$_2$(NO_3)] = 61.27:28.17:10.56. If KNO_3 is replaced by NaCl, a ratio ΔΔ[Rh(L_2)$_2$(μ-Cl)]$_2$/ΛΛ[Rh(L_2)$_2$(μ-Cl)]$_2$ of 9:1 is observed.

ΔΔ[Rh(L_2)$_2$(μ-Cl)]$_2$ (1): Yield (separation): 87 mg (27%). − ^{1}H NMR (CD_3CN, 300 MHz): δ = 8.76 (s, 4 H, 6-H), 7.37 (s, 4 H, 3-H), 7.13 (d, 4 H, ^3J = 4.8 Hz, 5′-H), 5.98 (d, 4 H, ^3J = 4.73 Hz, 4′-H), 3.14 (d, 8 H, ^3J = 2.48 Hz, 7-H), 2.97 (d×d, 4 H, ^4J = 5.5 Hz, ^3J = 5.5 Hz, 10-H), 2.78 (d×d×d, 4 H, ^2J = 9.7 Hz, ^3J = 5.8 Hz, ^3J = 5.9 Hz, 9-H^{exo}), 2.35 (t×d×d, 4 H, ^4J = 5.6 Hz, ^3J = 5.7 Hz, ^3J = 2.8 Hz, 8-H), 1.44 (s, 12 H, 13-H), 1.31 (d, 4 H, ^2J = 9.7 Hz, 9-H^{endo}), 0.78 (s, 12 H, 12-H). − ^{13}C NMR (CD_3CN, 75 MHz): δ = 165.59, 165.12 (quat), 160.3 (quat), 148.7 (tert), 147.4 (tert), 140.4 (quat), 135.5 (quat), 131.4 (tert), 127 (quat), 126.7 (tert), 45.4 (tert), 40.9 (tert), 40.1 (quat), 33.6 (sec), 32.3 (sec),

Table 1. Experimental crystallographic data for ΔΔ[Rh(L$_2$)$_2$(μ-Cl)]$_2$ (**1**), Δ[Rh(L$_2$)$_2$(NO$_3$)] (**2**) and Λ[Rh(L$_2$)$_2$(NO$_3$)] (**3**)

	1	**2**	**3**
Empirical formula	$C_{64}H_{64}Cl_2N_4Rh_2S_4\cdot(CH_3CH_2OCH_2CH_3)$	$C_{32}H_{32}N_3O_3RhS_2$	$C_{32}H_{32}N_3O_3RhS_2\cdot(CH_2Cl_2)$
Molecular mass	1368.27	673.64	758.56
Temperature [K]	223(2)	293(2)	223(2)
Crystal system	monoclinic	tetragonal	orthorhombic
Space group	*I*2 (no. 5)	$P4_32_12$ (no. 96)	$P2_12_12_1$ (no. 19)
Crystal color	orange	red	orange
Unit cell dimensions: *a* [Å]	14.2978(13)	10.4991(10)	10.6163(7)
b [Å]	16.3132(12)	10.4991(10)	14.9196(12)
c [Å]	14.3462(13)	27.740(3)	20.932(2)
β [°]	95.025(11)°	90°	90°
α°= γ [°]	90°	90°	90°
V [Å^3]	3333.3(5)	3057.8(5)	3315.4(5)
Z	2	4	4
Calculated density [g/cm^{-3}]	1.363	1.463	1.520
Absorption coeff. [mm^{-1}]	0.744	0.732	0.841
F [000]	1412	1384	1552
Crystal size [mm]	0.50 × 0.40 × 0.30	0.49 × 0.42 × 0.38	0.50 × 0.10 × 0.10
Independent reflns.	5172	2848	5173
Observed refls. [$I < 2\sigma(I)$]	4357	2350	2627
Final *R* indices [$I > 2\sigma(I)$]	*R*1 = 0.0838 *wR*2 = 0.2189	*R*1 = 0.0346 *wR*2 = 0.0720	*R*1 = 0.0567 *wR*2 = 0.1218
R indices (all data)	*R*1 = 0.0942 *wR*2 = 0.2260	*R1* = 0.0484 *wR*2 = 0.0898	*R*1 = 0.1132 *wR*2 = 0.1372
Goodness-of-fit (obsd. data)	1.045	1.091	0.801
Residual density [e/Å^3]	1.126/−0.794	0.362/−0.312	0.355/−0.576

[a] $R1 = \Sigma(F_o - F_c)/\Sigma(F_o)$; $wR2 = [\Sigma(w(F_o^2 - F_c^2)^2\}/\Sigma\{w(F_o^4)\}]^{1/2}$.

Table 2. Experimental crystallographic data for the artificial racemate {Δ[Rh(L$_2$)$_2$Cl(CH$_3$CN)] Λ[Rh(L$_2$′)$_2$Cl(CH$_3$CN)]} (**6**)

Empirical formula	**6** $C_{36}H_{38}ClN_4RhS_2\cdot C_{36}H_{35}ClN_3RhS_2CH_3CN$
Molecular mass	729.18
Temperature [K]	223(2)
Crystal system	triclinic
Space group	*P*1bar (no. 2)
Crystal color	yellow
Unit cell dimensions: *a* [Å]	15.4610(13)
b [Å]	15.6988(13)
c [Å]	16.2503(15)
α [°]	99.914(10)
β [°]	106.810(10)
γ [°]	92.586(10)
V [Å^3]	3700.4(6)
Z	4
Calculated density [g/cm^{-3}]	1.306
Absorption coeff. [mm^{-1}]	0.675
F(000)	1500
Crystal size [mm]	0.3 × 0.18 × 0.05
Independent reflns.	13296
Observed refls. [$I < 2\sigma(I)$]	7482
Final *R* indices [$I > 2\sigma(I)$]	*R*1 = 0.0432, *wR*2 = 0.0991
R indices (all data)	*R*1 = 0.0890, *wR*2 = 0.1089
Goodness-of-fit (obsd. data)	0.833
Residual density [e/Å^3]	0.920/−0.600

[a] $R1 = \Sigma(F_o - F_c)/\Sigma(F_o)$; $wR2 = [\Sigma(w(F_o^2 - F_c^2)^2\}/\Sigma\{w(F_o^4)\}]^{1/2}$.

26.1 (prim), 21.68 (prim). − MS (FAB); *m*/*z* (%): 1259 (13) [M$^+$ − Cl$^-$], 646 (100) [Rh(th4,5ppy)$_2$Cl − H$^+$], 612 (100) [Rh(th4,5ppy)$_2$], 356 (50) [Rh(th4,5ppy) − H$^+$], 256 (32) [Hth4,5ppy]. − UV/Vis (CH$_3$CN): λ (ε) = 376 (18582), 282 (56137). − IR (KBr): ṽ = 3423 (w), 2926 (m), 2362 (w), 2342 (w), 1619 (m), 1490 (s), 1428 (m), 1384 (w), 1260 (w),1239 (w), 1134 (w), 874 (m), 757 (w), 703 (m) cm^{-1}. − CD (CH$_3$CN): λ (Δε) = 389 (49.9), 355 (−43.5), 323 (−40.8), 290 (44.5), 247 (−59.8). − $C_{64}H_{64}Cl_2N_4Rh_2S_4$ (1294.39): calcd. C 59.38, H 4.98, N 4.33; found C 59.08, H 5.34, N 4.16.

Δ[Rh(L$_2$)$_2$(NO$_3$)] (2): Yield (separation): 40 mg (12%). − ^{1}H NMR (CD$_3$CN, 300 MHz): δ = 8.35 (s, 2 H, 6-H), 7.46 (s, 2 H, 3-H), 7.2 (d, 2 H, ^3J = 4.9 Hz, 5′-H), 5.97 (d, 2H, ^3J = 4. 9 Hz, 4′-H), 3.17 (d, 4 H, ^3J = 2.75 Hz, 7-H), 3.02 (d×d, 2 H, ^4J = 5.5 Hz, ^3J = 5.5 Hz, 10-H), 2.8 (d×d×d, 2 H, ^2J = 9.8 Hz, ^3J = 5.74 Hz, ^3J = 5.9 Hz, 9-H^{exo}), 2.37 (txdxd, 2H, ^4J = 5.65 Hz, ^3J = 5.8 Hz, ^3J = 2.9 Hz, 8-H); 1.46 (s, 6H, 13-H); 1.29 (d, 2H, ^2J = 9.8 Hz, H−C(9 endo)); 0.78 (s, 6 H, 12-H). − MS (FAB); *m*/*z* (%): 612 (100) [Rh(th4,5ppy)$_2$], 356 (43) [Rh(th4,5ppy)-H$^+$], 256 (25) [Hth4,5ppy]. − UV/Vis (CH$_3$CN): λ (ε) = 375 (7457), 282 (21842). − IR (KBr): ṽ = 3424 (m), 2933 (m), 2362 (m), 2342 (m), 1619 (m), 1491 (s), 1433 (w), 1384 (m), 1249 (w), 1131 (w), 873 (w), 729 (w) cm^{-1}. − CD (CH$_3$CN): λ (Δε) = 386 (42.4), 353 (−36.5), 320 (−26.9), 289 (30.9), 246 (−54). − $C_{32}H_{32}N_3O_3RhS_2\cdot Et_2O\cdot CH_2Cl_2$ (832.80): calcd. C 53.36, H 5.33, N 5.04; found C 53.38, H 4.62, N 5.40.

Λ[Rh(L$_2$)$_2$(NO$_3$)] (3): Yield (separation): 15 mg (4.58%). − ^{1}H NMR (CD$_3$CN, 300 MHz): δ = 8.33 (s, 2 H, 6-H), 7.46 (s, 2 H, 3-H), 7.2 (d, 2 H, ^3J = 4.9 Hz, 5′-H), 6.06 (d, 2 H, ^3J = 4.9 Hz, 4′-H), 3.16 (d, 4 H, ^3J = 2.75 Hz, 7-H), 3.02 (d×d, 2 H, ^4J = 5.5 Hz, ^3J = 5.8 Hz, 10-H), 2.8 (d×d×d, 2 H, ^2J = 9.9 Hz, ^3J = 5.9 Hz, ^3J = 5.7 Hz, 9-H^{exo}), 2.37 (t×d×d, 2 H, ^4J = 5.7 Hz, ^3J = 5.9 Hz, ^3J = 3.0 Hz, 8-H), 1.46 (s, 6 H, 13-H), 1.29 (d, 2 H, ^2J = 9.8 Hz,

9-H^{endo}), 0.74 (s, 6 H, 12-H). − MS (FAB); *m/z* (%): 612 (100) [Rh(th4,5ppy)$_2$], 356 (45) [Rh(th4,5ppy) − H$^+$], 256 (25) [Hth4,5ppy]. − UV/Vis (CH_3CN): λ (ε) = 375 (8853), 281 (26307). − IR (KBr): $\tilde{\nu}$ = 3440 (m), 2924 (w), 1619 (m), 1490 (m), 1431 (w), 1384 (s), 1243 (w), 1099 (m), 874 (w), 709 (w) cm^{-1}. − CD (CH_3CN): λ (Δε) = 386 (−55), 355 (45), 319 (28.5), 281 (−48.6), 246 (51.4). − $C_{32}H_{32}ClN_3O_3RhS_2$ (709.20): calcd. C 54.19, H 4.55, N 5.92; found: C 53.65, H 4.61, N 5.75.

(8*S*,10*S*)-2-(2′-Thienyl)-4,5-pinenopyridine (L_2') (4): A method analogous to that already described for $\mathbf{L}_2$[8] was applied. A mixture of (2-thienylacetyl)pyridinium bromide (1.65 g, 6 mmol) in 10 mL of formamide, ammonium acetate (0.897 g, 11.6 mmol) (added under vigorous stirring) and (0.87 g, 6 mmol) of (+)-myrtenal was refluxed at 60°C for 16 h. The reaction was quenched by addition of water (10 mL) and the brownish solution was extracted with hexane (8 × 50 mL). After the mixture was dried with $MgSO_4$, the solvent was removed and an orange oil that solidified at 4°C was obtained. Yield: 75% (1.11 g). − ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.07 (s, 1 H, 6-H), 7.50 (d×d, 1 H, ^3J = 3.7 Hz, ^4J = 1.2 Hz, 3′-H), 7.44 (s, 1 H, 3-H), 7.31 (d×d, 1 H, ^3J = 5.0 Hz, ^4J = 1.2 Hz, 5′-H), 7.07 (d×d, 1 H, ^3J = 5.0 Hz, ^3J = 3.7 Hz, 4′-H), 2.97 (d, 2 H, ^3J = 2.7 Hz, 7-H), 2.80 (d×d, 1 H, ^4J = 5.6 Hz, ^3J = 5.6 Hz, 10-H), 2.68 (d×d×d, 1 H, ^2J = 9.6 Hz, ^3J = 5.6 Hz, ^3J = 5.6 Hz, 9-H^{exo}), 2.28 (t×d×d, 1 H, ^4J = 5.6 Hz, ^3J = 5.6 Hz, ^3J = 2.7 Hz, 8-H), 1.38 (s, 3 H, 13-H), 1.20 (d, 2 H, ^2J = 9.6 Hz, 9-H^{endo}), 0.63 (s, 3 H, 12-H). − ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 150.8 (quat), 145.7 (quat), 145.5 (quat), 145.2 (tert), 141.2 (quat), 127.8 (tert), 126.6 (tert), 123.5 (tert), 118.3 (tert), 44.4 (tert), 40.0 (tert), 39.3 (quat), 32.8 (sec), 31.9 (sec), 26.0 (prim), 21.4 (prim). − MS (EI); *m/z* (%): 255 (20) [M$^+$], 240 (10) [M$^+$ − CH_3], 212 (100) [M$^+$ − C_3H_7]. − UV/Vis (CH_2Cl_2): λ (ε) = 307 (15545), 292 (sh), 229 (6281). − IR (KBr): $\tilde{\nu}$ = 2920 (s), 1596 (w), 1536 (w), 1474 (m), 1384 (m), 1262 (w), 1220 (w), 1128 (w), 1054 (w), 942 (w), 828 (w), 692 (s) cm^{-1}. − $C_{16}H_{17}NS$ (255.38): calcd. C 75.25, H 6.71, N 5.48, S 12.55; found C 74.98, H 6.72, N 5.63, S 12.63.

ΛΛ[Rh(L_2')$_2$(μ-Cl)]$_2$ (5): This compound was synthesized as described for [Rh(L_2)$_2$m-Cl)]$_2$. Preparative thin layer plate silica gel chromatography with CH_3CN/BuOH/H_2O/KCl/NaCl (4:1:1:0.05:0.05) as eluent was used for the purification and separation of the different diastereoisomers. A ratio of ΛΛ[Rh(L_2')$_2$(μ-Cl)]$_2$/ΔΔ[Rh(L_2')$_2$(μ-Cl)]$_2$ = 9:1 was obtained. All data are identical with those of ΔΔ[Rh(L_2)$_2$(μ-Cl)]$_2$ except for the mirror-image CD spectra.

{Δ[Rh(L_2)$_2$Cl(CH_3CN)] Λ[Rh(L_2')$_2$Cl(CH_3CN)]} (6): This compound was obtained by "crystallization" of ΔΔ[Rh(L_2)$_2$(μ-Cl)]$_2$ and ΛΛ[Rh(L_2')$_2$(μ-Cl)]$_2$ from a CH_2Cl_2/CH_3CN mixture.

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[1] A. P. Smirnoff, *Helv. Chim. Acta* **1920**, *3*, 177−195.
[2] U. Knof, A. von Zelewsky, *Angew. Chem. Int. Ed.* **1999**, *38*, 302−322.
[3] U. Maeder, A. von Zelewsky, H. Stoeckli-Evans, *Helv. Chim. Acta* **1992**, *75*, 1320−1332.
[4] U. Maeder, T. Jenny, A. von Zelewsky, *Helv. Chim. Acta* **1986**, *69*, 1085−1087.
[5] S. Sprouse, K. A. King, P. J. Spellane, R. J. Watts, *J. Am. Chem. Soc.* **1984**, *106*, 6647−6653.
[6] P. J. Steel, *J. Organomet. Chem.* **1991**, *408*, 395−402.
[7] P. Hayoz, A. von Zelewsky, *Tetrahedron Lett.* **1992**, *33*, 5165−5168.
[8] M. Gianini, A. Forster, P. Haag, A. von Zelewsky, H. Stoeckli-Evans, *Inorg. Chem.* **1996**, *35*, 4889−4895.
[9] D. Sandrini, M. Maestri, V. Balzani, U. Maeder, A. von Zelewsky, *Inorg. Chem.* **1988**, *27*, 2640−2643.
[10] M. Maestri, D. Sandrini, V. Balzani, U. Maeder, A. von Zelewsky, *Inorg. Chem.* **1987**, *26*, 1323−1327.
[11] N. Y. Sardesai, K. Zimmermann, J. K. Barton, *J. Am. Chem. Soc.* **1994**, *116*, 7502−7508.
[12] M. R. Arkin, E. D. A. Stemp, C. Turro, N. J. Turro, J. K. Barton, *J. Am. Chem. Soc.* **1996**, *118*, 2267−2274.
[13] M. R. Arkin, E. D. A. Stemp, R. E. Holmlin, J. K. Barton, A. Hoerman, E. J. C. Olson, P. F. Barbara, *Science* **1996**, *273*, 475−480.
[14] R. K. de Richter, M. Bonato, M. Follet, J-M. Kamenka, *J. Org. Chem.* **1990**, *55*, 2855−2860
[15] G. M. Sheldrick, "SHELXS-97, Program for Crystal Structure Determination", *Acta Crystallogr.* **1990**, *A46*, 467.
[16] G. M. Sheldrick, *SHELXL-97, Program for Crystal Structure Refinement*, Universität Göttingen, Göttingen, Germany, **1997**.
[17] H. D. Flack, *Acta Crystallogr.* **1983**, *A39*, 876.
[18] A. L. Spek, "PLATON/PLUTON", *Acta Crystallogr.* **1990**, *A46*, C34.

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