Stereoselective Synthesis of Hexacoordinated Mononuclear Cyclometalated Rhodium(III) Complexes − Transfer of Chirality from the Metal Center to the Ligand

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

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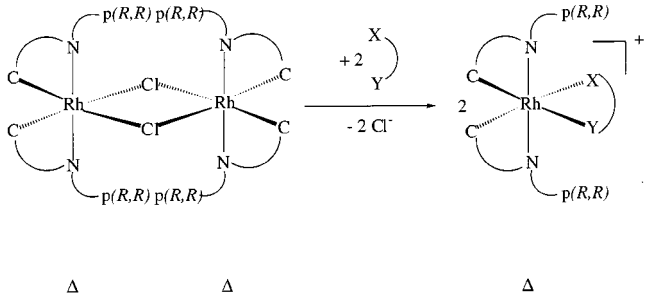
The cleavage of ΔΔ[Rh(th4,5ppy)$_2$(μ-Cl)]$_2$ [th4,5ppy is enantiomerically pure (8*R*,10*R*)-2-(2′-thienyl)-4,5-pinenopyridine(−)] by 5 different diimines and 11 diamines yields monomeric cations Δ[Rh(th4,5ppy)$_2$(*N*∩*N*)]$^+$. In all cases, the cleavage reaction preserves the original Δ configuration at the metal center. When *N*∩*N* is a chiral or a prochiral ligand, various degrees of stereoselectivity is observed, depending on where the stereogenic center is located in *N*∩*N*. The reported results open up a systematic method towards the synthesis of tris(bidentate)Rh^{III} complexes with a completely predetermined stereochemistry.

Introduction

The syntheses of coordination compounds in which the metal atom is a stereogenic center have not often been performed in a stereoselective manner.[1] This is in sharp contrast to the large number of examples known from organic chemistry in which stereoselectivity is the subject of intense study. Stereoselectivity in coordination compounds can be achieved through the use of enantiomerically pure chiral ligands in various ways. Here we describe the formation of mononuclear rhodium(III) complexes comprising of two cyclometalating bidentate ligands plus one bidentate diimine or diamine (Scheme 1).



Scheme 1

The reaction step that determines the configuration of the final product is the formation of a homochiral dimer.[2] The latter can be cleaved by achiral, prochiral or chiral bipyridine-type or diamine ligands (Table 1).[3]

This cleavage reaction takes place with the retention of the configuration at the metal centers in the dinuclear species.Thus, a generally applicable method is given for the stereoselective synthesis of compounds that are of high potential interest in various fields, such as enantioselective catalysis, and as intercalators in DNA.[4,5] Generally, the preparation of compounds that are isomerically pure is preferred over the often cumbersome and often inapplicable separation methods sometimes used in coordination chemistry.[6] This is certainly true for highly selective and efficient reactions such as those described in the present work.

[a] Institute of Inorganic Chemistry, University of Fribourg, Pérolles, 1700 Fribourg, Switzerland
Fax: (internat.) + 41-26/300-9738
E-mail: Alexander.vonzelewsky@unifr.ch
[b] Institute of Chemistry, University of Neuchâtel, Avenue de Bellevaux 51, 2000 Neuchâtel, Switzerland

Results and Discussion

The formation of the homochiral dinuclear precursor of the monomers, ΔΔ[Rh(th4,5ppy)$_2$(μ-Cl)]$_2$ (**I**) has been described before.[2] The configuration Δ at the two metal centers is induced by the natural product (−)-myrtenal, used for the synthesis of the thienyl-4,5-pinenepyridine ligand. Complex **I** can be prepared in high isomeric purity. It can be cleaved in a smooth reaction (CH_2Cl_2, 40 °C, ca. 60 min) producing the mononuclear species **I**−**XVII** in high yields (60−80%) as shown in Scheme 2, Scheme 3 and Scheme 4. We discuss the complexes according to the type of bidentate ligand used in the cleavage reaction.

Diimine Ligands

Three different types of diimine ligands can be distinguished: *Achiral* (bpy) → **II** (Scheme 2), *chiral with one pinene group* (4,5-pbpy, 5,6-pbpy) → **V**, **VI**, and *chiral with two pinene groups* (bis-4,5-pbpy, bis-5,6-pbpy) → **III** and **IV**. Complexes **II** and **III** were prepared as PF_6 salts.

The simplest of these species, **II**, has C_2 symmetry. The ^{1}H NMR spectrum clearly shows the equivalence of the corresponding protons in the two 2,2′-thienyl-4,5-pinenepyridine ligands and of those in the coordinated bpy in the complex. It also suggests the retention of configuration at the metal centers after the cleavage reaction, since two dia-

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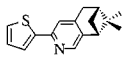
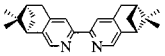
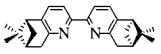
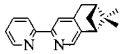
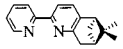
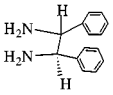
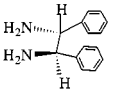
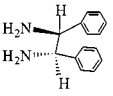
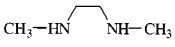
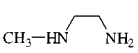
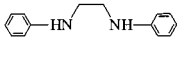
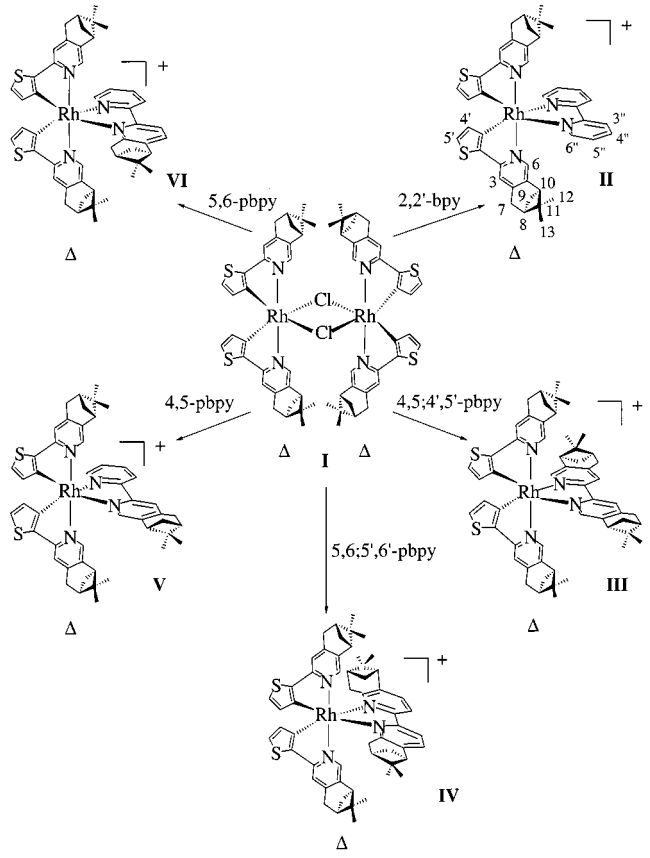
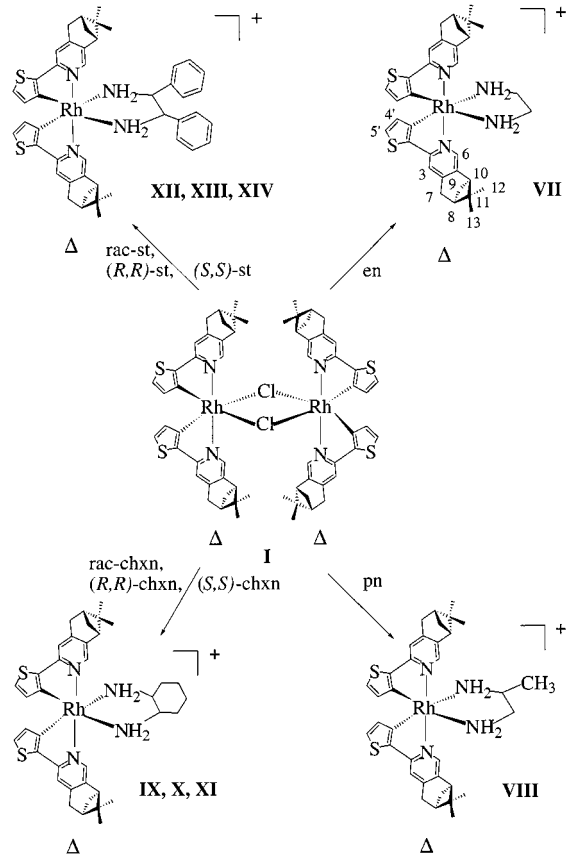
Table 1. Ligands and their abbreviations

Ligand name	Formula	Abbreviation
(8*R*,10*R*)-2-(2'-Thienyl)-4,5-pinenopyridine[(-)]		th4,5ppy
2,2'-bipyridine		2,2'-bpy
4,5;4',5'-pinenobipyridine		4,5;4',5'pbpy
5,6;5',6'-pinenobipyridine		5,6;5',6'pbpy
4,5-pinenobipyridine		4,5-pbpy
5,6-pinenobipyridine		5,6-pbpy
cis-1,2 -Diamino-cyclohexane		rac-chxn
(1*R*,2*R*)-(-)-1,2-diaminocyclohexane		*(R,R)*-chxn
(1*S*,2*S*)-(-)-1,2-diaminocyclohexane		*(S,S)*-chxn
ethylenediamine		en
propylenediamine		rac-pn
1,2-diphenyl-ethylenediamine		rac-st
(R,R)-diphenyl-ethylenediamine		*(R,R)*-st
(S,S)-diphenyl-ethylenediamine		*(S,S)*-st
N,N'-dimethyl-ehylenediamine		dmen
N-methyl-ehylenediamine		men
N,N'-diphenyl-ehylenediamine		dpen

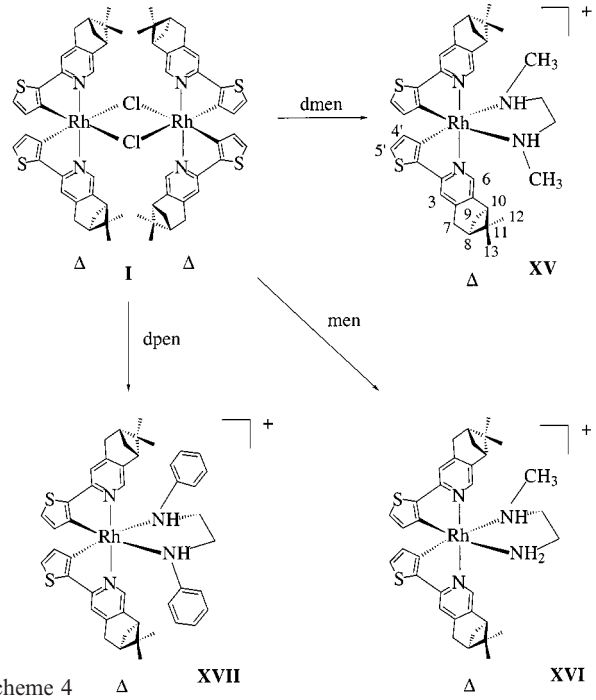


Scheme 2



Scheme 3

stereomeric products [(*R*,*R*)Δ and (*R*,*R*)Λ, both C_2-symmetric] would result in two sets of protons. The Δ configuration follows from the CD spectrum (Figure 1), that gives clear indications for this isomer.[7] The strong peak of mass



Scheme 4

767 (**II**-PF_6) confirms the mononuclear nature of this complex.

The complexes **III** and **IV** also have C_2 symmetry, as demonstrated by ^{1}H NMR spectroscopy. The aromatic region of the ^{1}H NMR spectra is even more simple than that of **II** owing to the use of "dipineno"-fused 2,2′-bipyridines (bis-4,5-pbpy, bis-5,6-pbpy) ligands. Those spectra show one set of protons, which proves the isomeric purity of the complexes. The CD spectra are similar to those of **II**, again indicating the retention of the Δ configuration. The peaks (100%) at 955 (**III** − PF_6) and 956 (**IV** − Cl) correspond to mononuclear species.The complexes **V** and **VI** with the unsymmetrical ligands 4,5-pbpy and 5,6-pbpy are not C_2-symmetric. The ^{1}H NMR spectra are therefore more complicated. Nevertheless, only one complete set of signals is observed, again showing that the configuration of the metal center is retained. The assignment of the peaks was carried out using a combination of COSY and NOE techniques for **VI**, while **V** was characterised by COSY spectra. The CD spectra (Figure 1) are in agreement with the Δ configuration at the metal center and have the same shape as the spectra of the dinuclear ΔΔ precursor, and as the spectra of the complexes **II**, **III** and **IV**. The MS spectra show mass peaks 861 (**V**, **VI** − Cl), indicating that the complexes are mononuclear.

Diamine Ligands

Several 1,2-diamine-type ligands have been used: *Achiral diamines* (en) → **VII** (Scheme 3 and Scheme 4), *chiral and prochiral diamines with one stereogenic center* (pn and men) → **VIII**, **XVI** and *chiral and prochiral diamines with two stereogenic centers* (chxn, st, dmen, dpen) → **IX** → **XI**, **XII** → **XIV**, **XV**, **XVII**.

Δ[Rh(th4,5ppy)$_2$(en)]Cl

The cation **VII** shows all characteristic peaks of the th-4,5-pinenopyridine as well as the signals of the NH_2 and CH_2 groups of ethylenediamine in the ^{1}H NMR spectrum. No splitting of these peaks occurs, clearly indicating that only one configuration at the metal center is present. The CD spectrum of **VII** (Figure 2.) shows that the Δ configura-

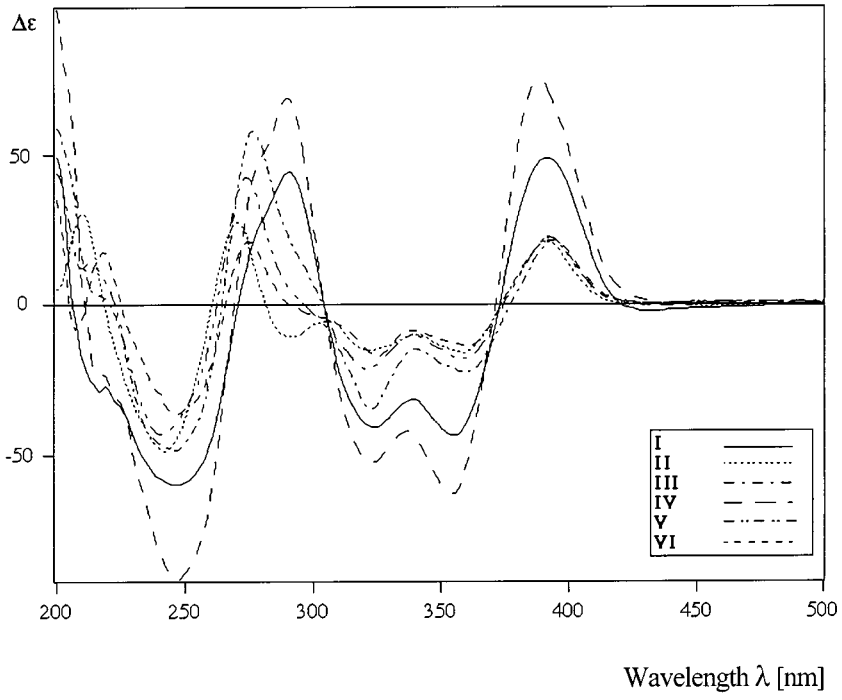


Figure 1. CD spectra of the complexes **I**, **II**, **III**, **IV**, **V** and **VI**

tion of the homochiral dinuclear precursor is preserved in the cleavage reaction.

Δ[Rh(th4,5ppy)$_2$(*rac*-pn)]Cl

The cation **VIII** occurs in two diastereomeric forms. The ^{1}H NMR spectrum shows a splitting of each signal of the th-4,5-pinenopyridine ligands in the aromatic region into four peaks (most easily seen e.g. in the signal of the 6′ proton at δ = 8.33 in the corresponding en complex). The small splitting (Δδ = 0.040 and 0.056, respectively, for 1:1 intensity lines for the 6′ proton) is due to the loss of the C_2 symmetry of the complex, whereas the larger splitting (Δδ = 0.27) is caused by the presence of two diastereoisomers Δ[Rh(th4,5ppy)$_2${(*R*)-pn}]Cl and Δ[Rh(th4,5ppy)$_2${(*S*)-pn}]Cl, respectively. These two diastereoisomers are formed in a ratio of 1:0.85, i.e. with a very low stereoselectivity. The CD spectra (Figure 2), which are mainly due to the disymmetry of the metal center and not to the ligands themselves, again clearly show the retention of the Δ configuration at the metal center.

Δ[Rh(th4,5ppy)$_2$(*rac*-chxn)]Cl (IX), Δ[Rh(th4,5ppy)$_2${(*R,R*)-chxn}]Cl (X), Δ[Rh(th4,5ppy)$_2${(*S,S*)-chxn}]Cl (XI)

Cleavage of the dinuclear complex **I** by *rac*-chxn (*rac*-trans-1,2-diaminocyclohexane) yields a product that shows a doubling of all peaks in the ^{1}H NMR spectrum (Figure 3, **IX**). The splitting is largest for proton 6 (Δδ = 0.32) and becomes smaller for proton 4 (Δδ = 0.038) and proton 3 (Δδ = 0.02), while the signals of protons 5 are superposed. The intensity ratio is nearly 1:1, indicating almost no stereoselectivity for this diamine ligand. An assignment of the two diastereomers is possible by using enantiomerically pure (*R*,*R*)-chxn and (*S*,*S*)-chxn. The two spectra in Figure 3 are obtained for **X** and **XI**.

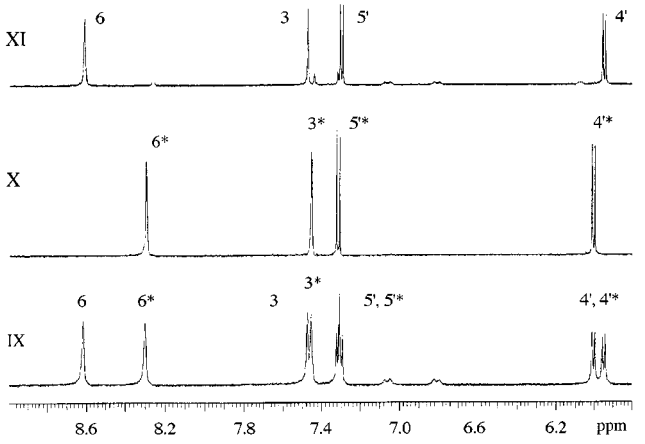


Figure 3. The aromatic region of the ^{1}H NMR spectra of complexes **IX**, **X** and **XI**

The CD spectra of all three complexes again show a retention of the Δ configuration upon cleavage of the dichloro bridge. Despite the fact that the ^{1}H NMR spectra show a relatively large splitting of the corresponding nuclei in the diastereomers, indicating an influence of the relative config-

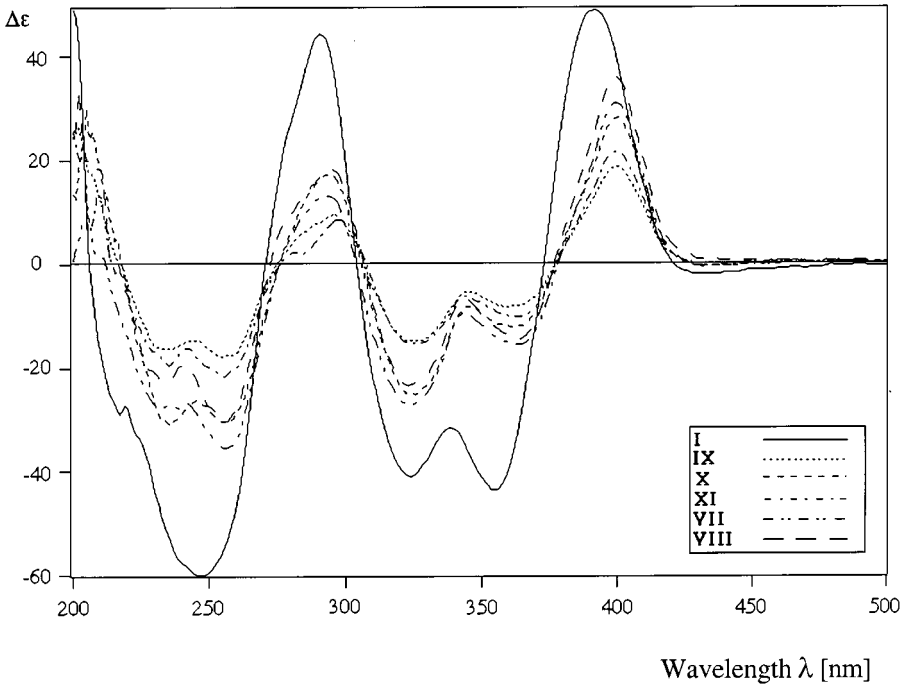


Figure 2. CD spectra of the complexes **I**, **VII**, **VIII**, **IX**, **X** and **XI**

urations of the chirality elements within the complex on the electronic structure, almost no chiral discrimination occurs in the cleavage reaction. Evidently, the differences in thermodynamic stability of the resulting diastereomers are too small to allow for significant stereoselectivity.

Δ[Rh(th4,5ppy)$_2$(*rac*-st)]Cl (XII), Δ[Rh(th4,5ppy)$_2${(*R*,*R*)-st}]Cl (XIII), Δ[Rh(th4,5ppy)$_2${(*S*,*S*)-st}]Cl (XIV)

The enantiomerically pure (*R*,*R*)- and (*S*,*S*)-stilbenediamines cleave the dinuclear complex **I** in a clean reaction, yielding isomerically pure mononuclear species (Figure 4). When the racemate of the ligand is used, both diastereomers, Δ[Rh(th4,5ppy)$_2${(*S*,*S*)-st}]Cl and Δ[Rh(th4,5ppy)$_2$-{(*R*,*R*)-st}]Cl, are observed in a 1:5.5 ratio by the ^{1}H NMR spectroscopy (Figure 4). The diastereomeric ratio was calculated from the signals for the protons at the 6 position in the ^{1}H NMR spectra. Since no separation step was applied to the reaction mixture after the cleavage reaction, this ratio represents the ''true'' stereoselectivity of this step.

In the case of Δ[Rh(th4,5ppy)$_2$[(*S*,*S*)-st}]Cl, crystals suitable for X-ray structure determination could be obtained.

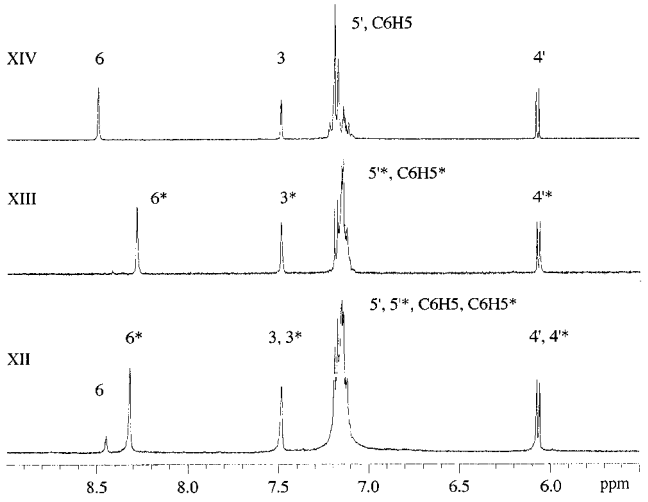


Figure 4. The aromatic region of the ^{1}H NMR spectra of complexes **XII**, **XIII** and **XIV**

Table 2. Crystallographic data

	XIV
Empirical formula	$C_{46}H_{48}ClN_4RhS_2 \cdot 3/4H_2O$
Molecular mass	872.88
Temperature [K]	223(2)
Crystal system	hexagonal
Space group	$P6_522$ (no. 179)
Color of crystal	orange
a [Å]	18.7322(10)
b [Å]	18.7322(10)
c [Å]	48.900(4)
V [Å^3]	14859.9(17)
Z	12
Density (calculated) [g/cm^{-3}]	1.170
Absorption coeff. [mm^{-1}]	0.516
F(000)	5442
Crystal size [mm]	0.45 × 0.25 × 0.15
Independent refls.	7849
Observed refls. [$I < 2\sigma(I)$]	4354
Final *R* indices [$I > 2\sigma(I)$][a]	$R1 = 0.0511$, $R2 = 0.1217$
R indices of all data[a]	$R1 = 0.0908$, $R2 = 0.1364$
Goodness-of-fit (obsd. data)	0.828
Residual density [e/Å^3]	0.529/−0.338

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

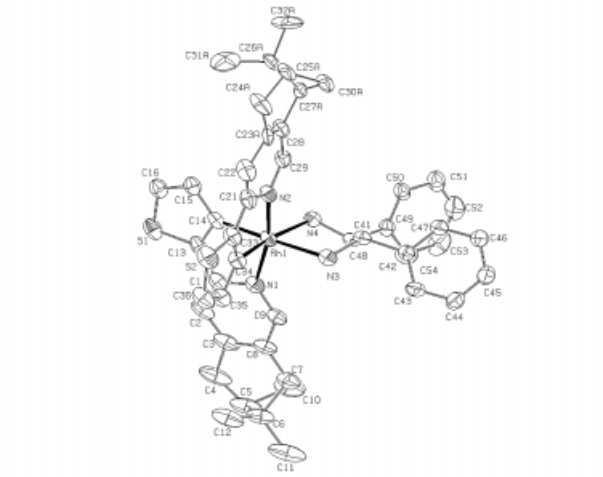


Figure 5. Numbered ORTEP[20] plot, with thermal ellipsoids drawn at the 30% probability level of the molecular structure of the cation Δ[Rh(th4,5ppy)$_2${(*S*,*S*)-st}]$^+$; the hydrogen atoms have been omitted for clarity

Structural Discussion

The X-ray structure (Table 2) of the Δ[Rh(th4,5ppy)$_2${(*S*,*S*)-st}]$^+$ cation (Figure 5) clearly reveals its absolute configuration. It is in agreement with all the other observations in this series of reactions, in which retention of the configuration at the metal center has always been observed. The enantiomerically pure diamine ligand with two (*S*)-configured stereogenic carbon centers adopts a δ conformation (ob) for the 5-membered chelate ring, putting the phenyl groups in equatorial positions.

This is to be expected from a consideration of interligand interactions, which would result in relatively large steric constraints in the axial orientation. The ^{1}H NMR spectrum reveals that this conformation is also strongly preferred in solution, since no broadening of the corresponding signals occur. The other features of the X-ray structure, such as bond lengths and angles, correspond to the expected values.

Δ[Rh{th4,5(*R*,*R*)ppy}$_2$(*N*,*N*′-dmen)]Cl (XV)

This compound is obtained from a smooth cleavage reaction of the dimer with *N*,*N*′-dimethylethylenediamine. Four diastereomers could be obtained, in principle, since the ligating nitrogen centers of the diamine are stereogenic after complexation. They can be designated as Δ[Rh-(th4,5(*R*,*R*)ppy)$_2$(*N*,*N*′-dm(*R*,*R*)en)]Cl (**A**), Δ[Rh{th4,5-(*R*,*R*)ppy}$_2${*N*,*N*′-dm(*S*,*S*)en}]Cl (**B**), Δ[Rh{th4,5-(*R*,*R*)ppy}$_2${*N*,*N*′-dm(*R*,*S*)en}]Cl (**C**), Δ[Rh{th4,5-

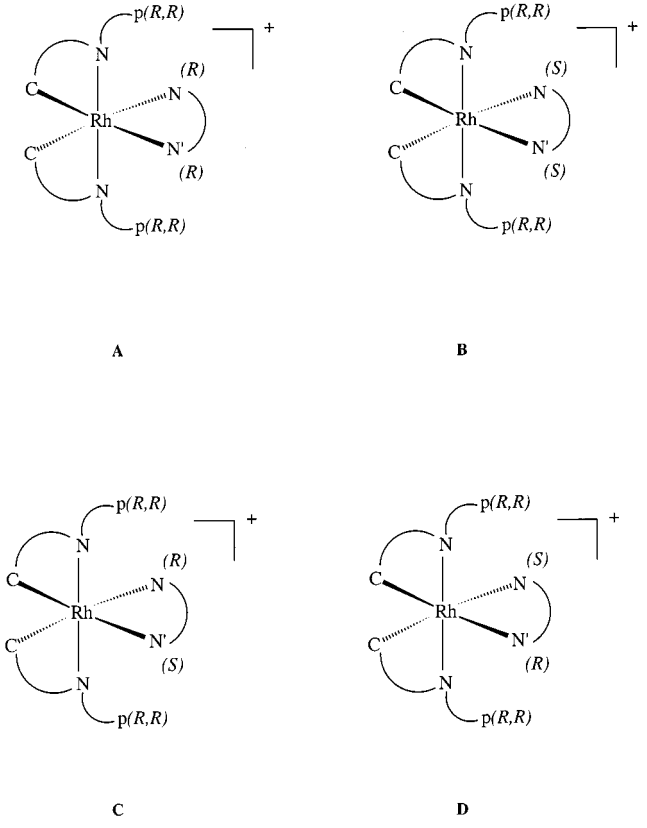


Figure 6. Isomers A, B, C, D

(*R*,*R*)ppy}$_2${*N*,*N*′-dm(*S*,*R*)en}] Cl (**D**). Compounds **A** and **B** are C_2-symmetric species, whereas **C** and **D** show no symmetry (Figure 6).

The ^{1}H NMR spectrum clearly indicates that only one C_2-symmetric complex is formed. Model considerations indicate that the species with a Δ,δ-(*R*,*R*) configuration should have the lowest energy. This corresponds to an axial configuration of the two methyl groups of the diamines.

Δ[Rh{th4,5(*R*,*R*)ppy}$_2$(*N*-men)]Cl (XVI), Δ[Rh{th4,5(*R*,*R*)ppy}$_2$(*N*,*N*′-dpen)]Cl (XVII)

Cleavage of the dinuclear precursor **I** with *N*-men and *N*,*N*′-dpen afforded the expected mononuclear species. These two ligands are prochiral in the sense that one or two ligating nitrogen centers are rendered stereogenic upon coordination to the metal center, as in the case of *N*,*N*′-dmen, described above. The unsymmetrical *N*-men ligand clearly forms one single isomer, within ^{1}H NMR detection limits. In analogy to the Δ[Rh{th4,5(*R*,*R*)ppy}$_2$(*N*,*N*′-dmen)]Cl, this isomer was assigned the configuration Δ-(*R*). The symmetrical *N*,*N*′-dpen again yields one single isomer, as in the case of *N*,*N*′-dmen.

Stereoselectivity

A stereoselective synthesis of coordination compounds has been known since the time of A. Werner.[8] However, it was not developed until recently in a systematic manner.[1] The contents of the present article are a contribution to the field of stereoselective synthesis of Rh^{III} complexes. The first point concerns the regioselectivity in the synthesis of the dinuclear complex from which the mononuclear species are obtained through cleavage reactions. It was shown earlier[9,10] that the cyclometalation is completely regioselective, yielding the *C*,*C*-*cis* isomer.

Owing to the chiral induction by the pinene groups p(*R*,*R*), the Δ diastereomer is strongly preferred over the corresponding Λ form.[2] The cleavage of the dimer always occurs with *complete retention* of configuration at the Rh^{III} centers. Of the 8 possible diastereomers Δ/Λ,A, Δ/Λ,B, Δ/Λ,C, Δ/Λ,D, one single compound, namely Δ,A is obtained from the Δ/Δ dimer, when an unsymmetrical diimine ligand *N*,*N*′ is used in the cleavage reaction. The same is observed for symmetric diimine ligands *N*,*N*′, in which a total of 6 diastereomers (C = D in this case) are possible (see Scheme 2). In cases where several isomers can be obtained by using racemic mixtures of chiral bidentate ligands (pn, chxn, and stilbenediamine), or where stereogenic centers are created at nitrogen donor atoms (*N*,*N*′-dmen, *N*-men, *N*,*N*′-dpen), various degrees of stereoselectivity have been ob-

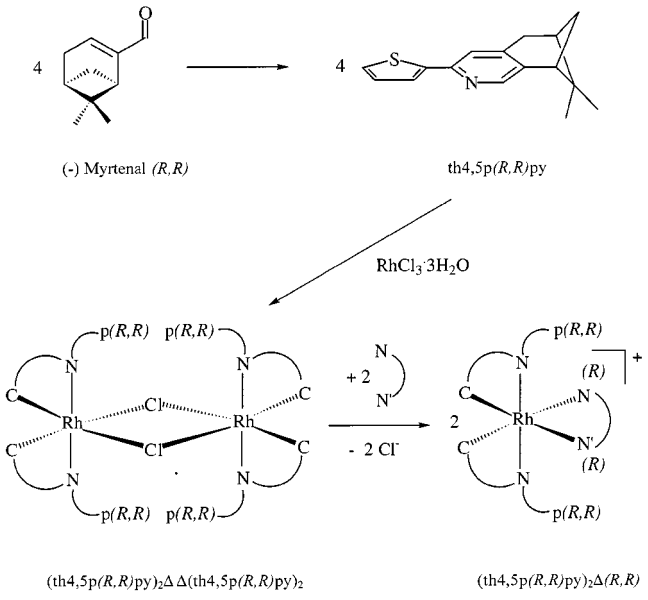
Table 3. Diastereomeric ratios of complexes obtained by cleavage with racemic (**1**−**3**) or prochiral (**4**−**6**) diamines

Entry	Diastereomers	*de* (%)[a]
1	Δ[Rh(th4,5ppy)$_2${(*R*,*R*)-chxn}]Cl/Δ[Rh(th4,5ppy)$_2${(*S*,*S*)-chxn}]Cl	0
2	Δ[Rh(th4,5ppy)$_2${(*R*,*R*)-pn}]Cl/Δ[Rh(th4,5ppy)$_2${(*S*,*S*)-pn}]Cl	8
3	Δ[Rh(th4,5ppy)$_2${(*R*,*R*)-st}]Cl/Δ[Rh(th4,5ppy)$_2${(*S*,*S*)-st}]Cl	70
4	Δ[Rh(th4,5ppy)$_2${(*R*,*R*)-dmen}]Cl/Δ[Rh(th4,5ppy)$_2${(*S*,*S*)-dmen}]Cl	100
5	Δ[Rh(th4,5ppy)$_2${(*R*,*R*)-men}]Cl/Δ[Rh(th4,5ppy)$_2${(*S*,*S*)-men}]Cl	100
6	Δ[Rh(th4,5ppy)$_2${(*R*,*R*)-dpen}]Cl/Δ[Rh(th4,5ppy)$_2${(*S*,*S*)-dpen}]Cl	100

[a] Determined by ^{1}H NMR spectroscopy from the solution after completion of the reaction. This *de* value did not change appreciably during the course of the reaction.

served. The values of the diastereomeric excess (*de*) are given in Table 3.

In the three cases of chiral bidentate ligands pn, chxn, and stilbenediamine, the stereoselectivity is either absent (chxn), very low (pn) or relatively low (stilbenediamine). This is due to the fact that the stereogenic centers in these ligands are situated relatively far from the stereogenic centers located at the 4,5 positions of the pinene on the pyridine rings. In contrast, in all complexes in which the stereogenic center is created at a ligating nitrogen atom of the incoming diamine in the cleavage reaction, *complete* (within analytical accuracy) stereoselectivity is observed. The coordinating stereogenic nitrogen centers are formed with only one of two possible absolute configurations. Model studies show a strong preference for a Δ-(*R*,*R*) configuration, where (*R*,*R*) designates the absolute configuration of the coordinating nitrogen centers. We can safely assume that for *N*-men, and *N*,*N*′-dpen, the same configurations are present. This result shows that with these cyclometalated Rh^{III} complexes, a cascade of chirality can be realized (Scheme 5).



Scheme 5

The origin of the isomeric purity of the final mononuclear complexes, e.g. Δ[Rh{th4,5(*R*,*R*)ppy}$_2$(*N*,*N*′-dmen)]Cl, lies in the natural product (−)-myrtenal, which was synthesised biochemically in the plant myrtle (held sacred to Venus in ancient times).[11] All steps in the reaction scheme leading to the final product are stereoselective. Chirality is thus transferred from a relatively simple organic molecule to the bidentate ligand th4,5p(*R*,*R*)py, From there it is transferred to the metal center Rh^{III}, and then further to another ligand (*N*,*N*′-dmen, *N*-men, *N*,*N*′-dpen), in which two new stereogenic centers are created upon complexation.

Conclusions

The incorporation of a chiral natural compound, which is available in enantiomerically pure form, into a ligand by highly efficient synthetic procedures opens up new possibilities in coordination chemistry. In this contribution we showed that in this way, a family of chiral mononuclear Rh^{III} complexes with a predetermined absolute configuration is easily accessible. Starting with a cyclometalation reaction, the reaction sequence yields isomerically pure mononuclear products that consist of four stereogenic centers located on the ligands, and one on the metal ion. Chirality can be further transferred to prochiral ligands that form stereogenic centers upon complexation, increasing the number of chirality elements in the whole complex by one or two. The stereoselectivity of this last step strongly depends on the distance between the newly created stereogenic centers and the metal ion.

Experimental Section

Measurements and Materials: NMR spectra were obtained with a Varian Gemini-300 spectrometer (300 MHz for ^{1}H and 75.46 MHz for ^{13}C) using the solvent as internal standard relative to TMS; J values are reported in Hz, and δ in ppm. Definitive assignments of NMR spectra was achieved with a combination of NOE and COSY experiments, and APT techniques; qr = quaternary, te = tertiary, se = secondary, pr = primary carbon. − UV/Vis spectral data were recorded with Perkin−Elmer Lambda 5 and Perkin−Elmer Lambda 40 spectrometers; λ_{max} in nm, ε in M^{-1} cm^{-1}. − CD spectra were recorded with Jobin-Yvon and JASCO J-715 spectropolarimeters; λ_{max} (Δε) in nm. − IR spectral data were obtained with Perkin−Elmer 683 and Perkin−Elmer 16 PC FT-IR spectrometers; using samples (1%) in compressed KBr pellets; $\tilde{\nu}$ in cm^{-1}. − MS: VG-Instruments 7070E mass spectrometer equipped with an FAB inlet system. − Elemental analyses were carried out by CIBA Specialty Chemicals, Marly, Switzerland and in Ecole D'Ingineurs de Fribourg, Switzerland. − Unless otherwise stated, all chemicals and reagent-grade products were obtained from Fluka, Aldrich or Merck and used without further purification. (1*R*)-(−)-Myrtenal was obtained from Fluka, > 97%, [α] = 14.6. − The ligands (8*R*,10*R*)-2-(2′-thienyl)-4,5-pinenopyridine,[12] 4,5-pinenobipyridine,[3,13] 5,6-pinenobipyridine,[14] 4,5;4′,5′-pinenobipyridine,[15] 5,6;5′,6′-pinenobipyridine,[16] and 1,2-diphenylethylendiamine[17] were prepared according to literature methods.

X-ray Structure Determination of Δ[Rh(th4,5ppy)$_2${(*S*,*S*)-st}]Cl: Suitable crystals (yellow/orange cubes) of **XIV** were grown by the slow diffusion of diethyl ether into a solution of CH_2Cl_2. Intensity data were collected at 223 K with a Stoe Image Plate Diffraction system using Mo-K_α graphite-monochromated radiation. Image plate distance 70 mm, φ scans 0−200°, step Δφ = 1°, θ range 2.01−25.86°, $d_{max.}-d_{min.}$ = 12.45−0.81 Å. The structure was solved by direct methods using the program SHELXS-97.[18] The refinement and all further calculations were carried out using SHELXL-97.[19] The H atoms were included in calculated positions and treated as riding atoms using SHELXL-97 default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least squares on F^2. The Cl anion was disordered over two sites, one being situated on a twofold axis. The second was located at a general position and given an occupancy of 0.5. The coordinates correspond to the correct absolute structure of the molecule in the crystal. For one of the ligands, the pinene group was disordered over two sites (A, B); they were each given occupancies of 0.5. A region of electron density observed in a final difference map

was modeled satisfactorily as three partially occupied water molecules and the SWAT[19] parameter was also refined. The molecular structure and crystallographic numbering scheme are illustrated in the PLATON[20] drawing (Figure 5). The CIF files, including complete tables of bond lengths, bond angles and torsion angles have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 150465 {Δ[Rh(th4,5ppy)$_2$[(S,S)-st)]Cl}. Copies of the data can be obtained free of charge on applicaton to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Δ[Rh(th4,5ppy)$_2$(bpy)]PF$_6$ (II): A solution of ΔΔ[Rh(th4,5ppy)$_2$(μ-Cl)]$_2$ (64.73 mg, 0.05 mmol) and 2,2′-bipyridine (15.62 mg, 0.10 mmol) in CH_2Cl_2 (20 mL) was heated at reflux for 90 min under N_2 and protected from light. After cooling, addition of NH_4PF_6 (10% solution in MeOH, 3 mL) gave a white precipitate which was filtered off. Addition of a large excess of Et_2O to the filtrate yielded a yellow-orange precipitate of Δ[Rh(th4,5ppy)$_2$-(bpy)]PF$_6$, which was filtered off. The filtrate {still containing Δ[Rh(th4,5ppy)$_2$(bpy)]PF$_6$} was concentrated and diluted with CH_3CN (1 mL). Addition of H_2O (5 mL) gave the yellow-orange precipitate Δ[Rh(th4,5ppy)$_2$(bpy)]PF$_6$. The solid was filtered, added to the rest of the Δ[Rh(th4,5ppy)$_2$(bpy)]PF$_6$ powder and dried in vacuo. Yield: 57 mg (67%). − ^{1}H NMR (CD_3CN, 300 MHz): δ = 8.47 (d, 2 H, ^3J = 8.2 Hz, H−C(3′′)], 8.13 (dd, 2 H, ^3J = 8.12 Hz, ^3J = 7.69 Hz, ^4J = 1.65 Hz H−C(4′′)], 7.97 (ddd, 2 H, ^3J = 5.3 Hz, ^3J = 0.72 Hz H−C(6′′)], 7.54 (tdd, 2 H, ^3J = 7.6 Hz, ^3J = 5.38 Hz, ^4J = 1.15 Hz, H−C(5′′)], 7.45 (s, 2 H, H−C(6)] 7.43 (d, 2 H, ^3J = 4.8 Hz, H−C(5′)], 6.97 (s, 2 H, H−C(3)], 6.23 (d, 2 H, ^3J = 4.73 Hz, H−C(4′)], 3.04 (d, 4 H, ^3J = 3.02 Hz, H−C(7)], 2.567−2.63 (m, 4 H, H−C(10), H−C(9$_{exo}$)], 2.232 (tdd, 2 H, ^4J = 5.52 Hz, ^3J = 5.68 Hz, ^3J = 2.7 Hz, H−C(8)], 1.3 (s, 6 H, H−C(13)], 0.96 (d, 2 H, ^2J = 9.6 Hz, H−C(9$_{endo}$)], 0.68 (s, 6 H, H−C(12)]. − MS (FAB); *m/z* (%): 767 (100) [M − PF_6^-], 611 (43) [Rh(th4,5ppy)$_2$], 356 (5) [Rh(th4,5ppy]. − UV/Vis (CH_3CN): λ (ε) = 378 (10057), 307 (sh), 286 (34913), 270 (sh). − IR (KBr): ṽ = 3450 (w), 3055 (w), 2937 (m), 1619 (m), 1489 (s), 1469 (m), 1444 (m), 1427 (m), 1385 (w), 1242 (w), 1027 (w), 948 (w), 840 (s), 764 (m), 738 (w), 709 (w), 557 (m). − CD (CH_3CN): λ (Δε) = 391 (21), 358 (−16.1), 321 (−15.2), 270 (27.7), 242 (−49.5), 210 (30.5). − $C_{42}H_{40}F_6N_4PRhS_2\cdot 2H_2O$: calcd. C 53.16, H 4.67, N 5.90; found C 53.45, H 4.63, N 5.99.

Δ[Rh(th4,5ppy)$_2$(4,5;4′,5′pbpy)]PF$_6$ (III): III was prepared as described for II, using ΔΔ[Rh(th4,5ppy)$_2$(μ-Cl)]$_2$ (64.73 mg, 0.05 mmol) and 4,5;4′,5′-pinenobipyridine (34.45 mg, 0.10 mmol) in CH_2Cl_2 (15 mL). Yield: 94 mg (85%) of orange Δ[Rh(th4,5ppy)$_2$-(4,5;4′,5′pbpy)]PF$_6$. − ^{1}H NMR (CD_3CN, 300 MHz): δ = 8.22 (s, 2 H, H−C(3′′)], 7.49 (s, 2 H, H−C(6′′)], 7.41 (s, 2 H, H−C(3)], 7.39 (d, 2 H, ^3J = 4.8 Hz, H−C(5′)], 6.73 (s, 2 H, H−C(6)], 6.22 (d, 2 H, ^3J = 4.8 Hz, H−C(4′)], 3.16 (d, 4 H, ^3J = 2.5 Hz, H−C(7′′)], 3.03 (d, 4 H, ^3J = 3.1 Hz, H−C(7)], 2.687−2.54 (m, 6 H, H−C(10′′), H−C(9′′$_{exo}$), H−C(8′′)], 2.345−2.14 (m, 6 H, H−C(10), H−C(9$_{exo}$), H−C(8)], 1.4 (s, 6 H, H−C(13′′)], 1.3 (s, 6 H, H−C(13)], 1.07 (d, 2 H, ^2J = 9.62 Hz, H−C(9′′$_{endo}$)], 0.97 (d, 2 H, ^2J = 9.83 Hz, H−C(9$_{endo}$)], 0.68 (s, 12 H, H−C(12′′, 12)]. − ^{13}C NMR (CD_3CN, 75 MHz): δ = 168.1 (qr), 160.4 (qr), 154.5 (qr), 150.3 (qr), 149.6 (qr), 148 (qr), 146.9 (te), 144.9 (te), 141.1 (qr), 136.6 (qr), 131.5 (te), 128.9 (te), 124 (te), 119.2 (te), 45.6 (te), 45.5 (te), 40.6 (te), 40.5 (te), 39.9 (qr), 39.8 (qr), 33.9 (se), 33.5 (se), 31.9 (se), 31.6 (se), 25.9 (pr), 25.8 (pr), 21.65 (pr), 21.6 (pr). − MS (FAB); *m/z* (%): 955 (100) [M −PF_6^-], 611 (16) [Rh(th4,5ppy)$_2$], 356 (9) [Rh(th4,5ppy)]. − UV/Vis (CH_3CN): λ (ε) = 378 (10523), 316 (sh), 275 (52754). − IR (KBr): ṽ = 2926 (m), 2364 (w), 2344 (w), 1711 (m), 1619 (m), 1488 (m), 1422 (w), 1407 (w), 1365 (w), 1263 (w), 1220 (w), 1032 (w), 948 (w), 913 (w), 875 (m), 840 (s), 711 (w), 557 (m). − CD (CH_3CN): λ (Δε) = 392 (21.3), 359 (−22.1), 322 (−35), 276 (57.3), 245 (−48.). − $C_{56}H_{60}F_6N_4PRhS_2\cdot 2H_2O$: calcd. C 59.14, H 5.67, N 4.93; found C 59.49, H 6.06, N 4.42.

Δ[Rh(th4,5ppy)$_2$(5,6;5′,6′pbpy)]Cl (IV): A solution of ΔΔ[Rh(th4,5ppy)$_2$(μ-Cl)]$_2$ (64.73 mg, 0.05 mmol) and 5,6;5′,6′-pinenobipyridine (34.45 mg, 0.10 mmol) in CH_2Cl_2 (15 mL) was heated at reflux for 90 min under N_2 and protected from light. The solution was concentrated and the addition of Et_2O yielded Δ[Rh(th4,5ppy)$_2$(5,6;5′,6′pbpy)]Cl as a yellow precipitate (65 mg, 65%). − ^{1}H NMR (CD_3CN, 300 MHz): δ = 8.76 (s, 2 H, H−C(6)], 8.03 (d, 2 H, ^3J = 7.75 Hz, H−C(3′′)], 7.36−7.34 (m, 4 H, H−C(3), H−C(4′′)], 7.13 (d, 2 H, ^3J = 4.8 Hz, H−C(5′)], 5.99 (d, 2 H, ^3J = 4.7 Hz, H−C(4′)], 3.14 (d, 4 H, ^3J = 2.5 Hz, H−C(7′′)], 3.09 (d, 4 H, ^3J = 2.75 Hz, H−C(7)], 2.97 (dd, 2 H, ^3J = 5.42 Hz, H−C(10′′)], 2.84−2.69 (m, 6 H, H−C(10), H−C(9′′$_{exo}$, 9$_{exo}$)], 2.4−2.33 (m, 4 H, H−C(8′′), H−C(8)], 1.44 (s, 6 H, H−C(13′′)], 1.41 (s, 6 H, H−C(13)], 1.32−1.24 (m, 4 H, H−C(9′′, 9$_{endo}$)], 0.78 (s, 6 H, H−C(12′′)], 0.64 (s, 6 H, H−C(12)]. − MS (FAB); *m/z* (%): 956 (100) [M − Cl^-], 611 (62) [Rh(th4,5ppy)$_2$]. − UV/Vis (CH_3CN): λ (ε) = 376 (30171), 282 (90478). − IR (KBr): ṽ = 3436 (m), 2926 (m), 2361 (w), 1618 (s), 1489 (s), 1428 (w), 1261 (w), 1238 (w), 1134 (w), 1012 (w), 946 (w), 873 (m), 705 (w). − CD (CH_3CN): λ (Δε) = 388 (76.6), 354 (−63.3), 323 (−52.9), 289 (69.1), 247 (−97.6.). − $C_{56}H_{60}ClN_4RhS_2\cdot 2CH_2Cl_2\cdot H_2O$: calcd. C 59.06, H 5.64, N 4.75; found C 58.83, H 5.13, N 4.14.

Δ[Rh(th4,5ppy)$_2$(4,5pbpy)]Cl (V): V was prepared as described for IV, using ΔΔ[Rh(th4,5ppy)$_2$(μ-Cl)]$_2$ (64.73 mg, 0.05 mmol) and 4,5-pinenobipyridine (25.04 mg, 0.10 mmol) in CH_2Cl_2 (15 mL). Yield: 87 mg (96%) of yellow Δ[Rh(th4,5ppy)$_2$(4,5pbpy)]Cl. − ^{1}H NMR (CD_3CN, 300 MHz): δ = 8.48 (d, 1 H, ^3J = 8.21 Hz, H−C(3′′′)], 8.37 (s, 1 H, H−C(3′′)], 8.11 (ddd, 1 H, ^3J = 7.94 Hz, ^3J = 7.86 Hz, ^4J = 1.67 Hz, H−C(4′′′)], 7.97 (ddd, 1 H, ^3J = 5.3 Hz, ^4J = 1.6 Hz, H−C(6′′′)], 7.53−7.37 (m, 6 H, H−C(5′′′), H−C(6′′), H−C(3), H−C(3°), H−C(5°), H−C(5′)], 6.99 (s, 1 H, H−C(6°)], 6.71 (s, 1 H, H−C(6)], 6.25 (d, 1 H, ^3J = 4.6 Hz, H−C(4°)], 6.18 (d, 1 H, ^3J = 4.7 Hz, H−C(4′)], 3.17 (d, 2 H, ^3J = 2.5 Hz, H−C(7′′)], 3.05−3.01 (m, 4 H, H−C(7°), H−C(7)], 2.67−2.2 (m, 9 H, H−C(10′′), H−C(10°), H−C(10), H−C(9′′$_{exo}$), H−C(9°$_{exo}$), H−C(9$_{exo}$), H−C(8′′), H−C(8°), H−C(8)], 1.38 (s, 3 H, H−C(13′′)], 1.31 (s, 3 H, H−C(13°)], 1.28 (s, 3 H, H−C(13)], 1.07 (d, 1 H, ^2J = 9.55 Hz, H−C(9′′$_{endo}$)], 0.96 (d, 1 H, ^2J = 9.34 Hz, H−C(9°$_{endo}$)], 0.95 (d, 1 H, ^2J = 9.83 Hz, H−C(9$_{endo}$)], 0.68 (s, 3 H, H−C(12′′)], 0.67(s, 3 H, H−C(12°)], 0.66(s, 3 H, H−C(12)]. − MS (FAB); *m/z* (%): 861 (100) [M − Cl^-], 611 (36) [Rh(th4,5ppy)$_2$]. − UV/Vis (CH_3CN): λ (ε) = 378 (9729), 313 (sh), 301(sh), 287 (sh), 273 (43182), 236 (sh). − IR (KBr): ṽ = 3384 (m), 2923 (m), 1618 (s), 1488 (s), 1473 (m), 1421 (m), 1261 (m), 1240 (w), 1098 (w), 1032 (w), 947 (w), 874 (m), 797 (m), 756 (m), 708 (m). − CD (CH_3CN): λ (Δε) = 391 (23.2), 358 (−18.3), 320 (−21.2), 273 (43.5), 240 (−44.4.), 212 (14.5). − $C_{49}H_{50}ClN_4RhS_2\cdot CH_2Cl_2$: calcd. C 61.13, H 5.33, N 5.70; found C 60.80, H 5.71, N 5.66.

Δ[Rh(th4,5ppy)$_2$(5,6pbpy)]Cl (VI): ΔΔ[Rh(th4,5ppy)$_2$(μ-Cl)]$_2$ (64.73 mg, 0.05 mmol) and 5,6-pinenobipyridine (25.04 mg, 0.10 mmol) in CH_2Cl_2 (15 mL) were heated at reflux for 90 min and treated as described for **IV** to give Δ[Rh(th4,5ppy)$_2$(5,6pbpy)]Cl (70 mg, 78%). − ^{1}H NMR (CD_3CN, 300 MHz): δ = 8.42 (d, 1 H, ^3J = 8.24 Hz, H−C(3′′′)], 8.25 (d, 1 H, ^3J = 8.03 Hz, H−C(3′′)], 8.07 (ddd, 1 H, ^3J = 7.9 Hz, ^3J = 7.89 Hz, ^4J = 1.65 Hz, H−C(4′′′)]:

7.74 (ddd, 1 H, ^3J = 5.5 Hz, ^4J = 1.65 Hz, ^5J = 0.94 Hz, H−C(6′′′)], 7.64 (d, 1 H, J = 8.03 Hz, H−C(4′′)], 7.46 (s, 1 H, H−C(3°)], 7.43−7.38 (m, 4 H, H−C(3), H−C(6°), H−C(5′′′), H−C(5°)], 7.3 (d, 1 H, J = 4.8 Hz, H−C(5′)], 6.89 (s, 1 H, H−C(6)], 6.16 (d, 2 H, ^3J = 4.89 Hz, H−C(4′), H−C(4°)], 3.07−3.03 (m, 4 H, H−C(7′′), H−C(7°)], 2.99 (d, 2 H, ^3J = 2.47 Hz, H−C(7)], 2.89−2.16 (m, 9 H, H−C(10′′), H−C(10°), H−C(10), H−C(9′′), H−C(9°), H−C(9), H−C(8′′), H−C(8°), H−C(8)], 1.33 (s, 3 H, H−C(13′′)], 1.28 (s, 3 H, H−C(13°)], 1.25 (s, 3 H, H−C(13)], 1.2 (d, 1 H, ^2J = 9.73 Hz, H−C(9′′$_{endo}$)], 0.98 (d, 1 H, ^2J = 9.4 Hz, H−C(9°$_{endo}$)], 0.83 (d, 1 H, ^2J = 9.6 Hz, H−C(9$_{endo}$)], 0.7 (s, 3 H, H−C(12′′)], 0.64 (s, 3 H, H−C(12°)], 0.07 (s, 3 H, H−C(12)]. − MS (FAB); *m/z* (%): 861 (100) [M − Cl$^-$], 611 (30) [Rh(th4,5ppy)$_2$]. − UV/Vis (CH_3CN): λ (ε) = 374 (8694), 317 (sh), 305 (sh), 289 (sh), 273 (36225). − IR (KBr): ṽ = 3406 (m), 2929 (m), 2362 (m), 2342 (m), 1706 (m), 1619 (m), 1488 (s), 1433 (m), 1364 (w), 1221 (w), 1035 (w), 873 (w), 793 (w), 710 (w). − CD (CH_3CN): λ (Δε) = 393 (22.1), 360 (−13.7), 324 (−16.7), 274 (21.4), 246 (−37.3), 218 (18.3). − $C_{49}H_{50}ClN_4RhS_2·3H_2O$: calcd. C 61.85, H 5.93, N 5.89; found C 61.65, H 5.69, N 5.53.

Δ[Rh(th4,5ppy)$_2$(en)]Cl (VII): ΔΔ[Rh(th4,5ppy)$_2$(μ-Cl)]$_2$ (48.00 mg, 0.04 mmol) and ethylenediamine (7.00 mg, 0.12 mmol) in CH_2Cl_2 (15 mL) were heated at reflux for 90 min under N_2 and protected from light. The solvent was evaporated and the pale yellow powder was dried in vacuo. Yield: 45 mg (86%) of Δ[Rh(th4,5ppy)$_2$(en)]Cl. − ^{1}H NMR (CD_3CN, 300 MHz): δ = 8.24 (s, 2 H, H−C(6)], 7.42 (s, 2 H, H−C(3)], 7.1 (d, 2 H, ^3J = 4.52 Hz, H−C(5′)], 6.06 (d, 2 H, ^3J = 4.53 Hz, H−C(4′)], 3.748−3.71 (m, NH_2), 3.15 (d, 4 H, ^3J = 2.26 Hz, H−C(7)], 3.01−2.98 (m, 2 H, H−C(10), CH_2), 2.836−2.667 (m, 2 H, H−C(9′$_{exo}$)], 2.36 (tdd, 2 H, ^3J = 2.81 Hz, ^3J = 5.66 Hz, ^3J = 5.63 Hz, H−C(8)], 1.45 (s, 6 H, H−C(13)], 1.26 (d, 2 H, ^2J = 9.67 Hz, H−C(9$_{endo}$)], 0.78 (s, 6 H, H−C(12)]. − MS (FAB); *m/z* (%): 671 (62) [M − Cl$^-$], 611 (95) [Rh(th4,5ppy)$_2$], 356 (12) [Rh(th4,5ppy) − H$^+$]. − UV/Vis (CH_3CN): λ (ε) = 391 (11456), 333 (sh), 302 (sh), 278 (30975). − IR (KBr): ṽ = 3282 (w), 3110 (w), 2928 (m), 1709 (m), 1619 (m), 1485 (s), 1428 (w), 1361 (w), 1219 (w), 1038 (w), 871 (w), 709 (w), 528 (w). − CD (CH_3CN): λ (Δε) = 399 (31), 363 (−15.4), 324 (−27.2), 293 (13.7), 255 (−35.4), 234 (−28). − $C_{34}H_{40}ClN_4RhS_2·2H_2O$: calcd. C 54.94, H 5.97, N 7.54, S 8.63; found C 55.24, H 5.89, N 7.66, S 8.46.

Δ[Rh(th4,5ppy)$_2$(*rac*-pn)]Cl (VIII): As described for **VII**, using ΔΔ[Rh(th4,5ppy)$_2$(μ-Cl)]$_2$ (48.00 mg, 0.04 mmol) and propylenediamine (1,2-diaminopropane) (8.25 mg, 0.09 mmol) in CH_2Cl_2 (15 mL) afforded Δ[Rh(th4,5ppy)$_2$(*rac*-pn)]Cl (49 mg, 91%). − ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 8.64 (s, 1 H, H−C(6*S*)], 8.60 (s, 1 H, H−C(6′′*S*)], 8.33 (s, 1 H, H−C(6*R*)], 8.29 (s, 1 H, H−C(6′′*R*)], 7.48−7.47 (m, 4 H, H−C(3*S*), H−C(3′′*S*), H−C(3*R*), H−C(3′′*R*)], 7.335−7.292 (m, 4 H, H−C(5′*S*), H−C(5′′′*S*), H−C(5′*R*), H−C(5′′′*R*)], 6.035−5.93 (m, 4 H, H−C(4′*R*), H−C(4′′′*R*), H−C(4′*S*), H−C(4′′′*S*)], 4.49−4.23 (NH_2), 3.85−3.79 (CH), 3.625−3.566 (CH_2), 3.349 (s, 3 H, CH_3), 3.194−3.101 (m, 8 H, H−C(7)], 3.01−2.737 (m, 8 H, H−C(10), H−C(9$_{exo}$)], 2.4−2.33 (m, 4 H, H−C(8)], 1.44 (s, 12 H, H−C(13)], 1.27−1.13 (m, 4 H, H−C(9$_{endo}$)], 0.75 (s, 12 H, H−C(12)]. − MS (FAB); *m/z* (%): 685 (65) [M − Cl$^-$], 611 (100) [Rh(th4,5ppy)$_2$], 356 (10) [Rh(th4,5ppy) − H$^+$]. − UV/Vis (CH_3CN): λ (ε) = 391 (11386), 334 (sh), 302 (sh), 278 (30552). − IR (KBr): ṽ = 3292 (w), 3081 (w), 3052 (w), 2918 (m), 1619 (s), 1485 (s), 1366 (w), 1266 (w), 1071 (w), 1041 (w), 871 (m), 709 (m). − CD (CH_3CN): λ (Δε) = 399 (36.6), 363 (−14), 324 (−23.4), 294 (17.8), 256 (−29.9), 233 (−21.5). − $C_{35}H_{42}ClN_4RhS_2·H_2O$: calcd. C 56.86, H 5.99, N 7.58, S 8.67; found C 56.31, H 6.11, N 7.90, S 8.16.

Δ[Rh(th4,5ppy)$_2$(*rac*-chxn)]Cl (IX): A solution of ΔΔ[Rh(th4,5ppy)$_2$(μ-Cl)]$_2$ (64.73 mg, 0.05 mmol) and *rac*-chxn (17.00 mg, 0.15 mmol) in CH_2Cl_2 (15 mL) was heated at reflux for 90 min. The solvent was evaporated and the pale yellow powder was dried in vacuo. Yield: 78 mg (73%) of Δ[Rh(th4,5ppy)$_2$(*rac*-chxn)]Cl. − ^{1}H NMR ([D$_6$]DMSO, aromatic region, 300 MHz): δ = 8.62 (s, 2 H, H−C(6*S,S*)], 8.3 (s, 2 H, H−C(6*R,R*)], 7.47 (s, 2 H, H−C(3*S,S*)], 7.45 (s, 2 H, H−C(3*R,R*)], 7.33−7.29 (m, 4 H, H−C(5′*R,R*), H−C(5′*S,S*)], 6.00 (d, 2 H, ^3J = 4.7 Hz, H−C(4′ *R,R*)], 5.95 (d, 2 H, ^3J = 4.7 Hz, H−C(4′*S,S*)]. − MS (FAB); *m/z* (%): 725 (100) [M − Cl$^-$], 611 (77) [Rh(th4,5ppy)$_2$], 356 (6) [Rh(th4,5ppy) − H$^+$]. − UV/Vis (CH_3CN): λ (ε) = 391 (7785), 336 (sh), 302 (sh), 278 (20021). − IR (KBr): ṽ = 3290 (w), 3275 (w), 3111 (w), 2930 (m), 2861 (w), 2360 (w), 2343 (w), 1709 (w), 1622 (m), 1579 (w), 1546 (w), 1489 (s), 1359 (w), 1293 (m), 1239 (w), 1176 (w), 1132 (w), 1103 (w), 1043 (w), 875 (m), 709 (w). − CD (CH_3CN): λ (Δε) = 399 (18.9), 360 (− 8.43), 325 (−15), 295 (9.47), 256 (−17.9), 234 (−16). − $C_{38}H_{46}ClN_4RhS_2·3H_2O·NH_4OH$: calcd. C 53.66, H 6.75, N 8.23; found C 53.53, H 6.29, N 8.89.

Δ[Rh(th4,5ppy)$_2${(*R,R*)-chxn}]Cl (X): As described for **IV**, using ΔΔ[Rh(th4,5ppy)$_2$(μ-Cl)]$_2$ (129.45 mg, 0.10 mmol) and (*R,R*)-chxn (34.25 mg, 0.29 mmol) in CH_2Cl_2 (20 mL) afforded Δ[Rh(th4,5ppy)$_2${(*R,R*)-chxn}]Cl (125 mg, 82%). − ^{1}H NMR ([D$_6$]DMSO, aromatic region, 300 MHz): δ = 8.29 (s, 2 H, H−C(6)], 7.45 (s, 2 H, H−C(3)], 7.32 (d, 2 H, ^3J = 4.76 Hz, H−C(5′)], 6.00 (d, 2 H, ^3J = 4.76 Hz, H−C(4′)]. − MS (FAB); *m/z* (%): 725 (98) [M − Cl$^-$], 611 (64) [Rh(th4,5ppy)$_2$], 356 (7) [Rh(th4,5ppy) − H$^+$]. − UV/Vis (CH_3CN): λ (ε) = 391 (11237), 334 (sh), 301 (sh), 280 (37247). − IR (KBr): ṽ = 3272 (m), 3205 (w), 3100 (m), 2928 (m), 1709 (m), 1619 (s), 1485 (s), 1366 (w), 1293 (w), 1128 (w), 1047 (w), 1028 (w), 876 (m), 704 (m). − CD (CH_3CN): λ (Δε) = 399.8 (28.2), 360 (−11.6), 324 (−25), 293 (17.5), 256 (−30), 235 (−31). − $C_{38}H_{46}ClN_4RhS_2·H_2O$: calcd. C 58.56, H 6.2, N 7.19; found C 58.91, H 6.2, N 7.84.

Δ[Rh(th4,5ppy)$_2${(*S,S*)-chxn}]Cl (XI): As described for IV, using ΔΔ[Rh(th4,5ppy)$_2$(μ-Cl)]$_2$ (64.73 mg, 0.05 mmol) and (*S,S*)-chxn (17.00 mg, 0.15 mmol) in CH_2Cl_2 (15 mL) afforded Δ[Rh(th4,5ppy)$_2${(*S,S*)-chxn}]Cl (61 mg, 80%). − ^{1}H NMR ([D$_6$]DMSO, aromatic region, 300 MHz): δ = 8.61 (s, 2 H, H−C(6)], 7.47 (s, 2 H, H−C(3)], 7.29 (d, 2 H, ^3J = 4.73 Hz, H−C(5′)], 6.00 (d, 2 H, ^3J = 4.73 Hz, H−C(4′)]. − MS (FAB), *m/z*: 725 (97) [M − Cl$^-$], 611 (85) [Rh(th4,5ppy)$_2$], 356 (7) [Rh(th4,5ppy) − H$^+$]. − UV/Vis (CH_3CN): λ (ε) = 391 (10721), 329 (sh), 279 (33678). − IR (KBr): ṽ = 3282 (w), 3110 (w), 2928 (m), 1700 (w), 1619 (m), 1485 (s), 1238 (w), 1133 (w), 1033 (w), 871 (w), 704 (w). − CD (CH_3CN): λ (Δε) = 399 (21.8), 362 (−10.4), 326 (−15), 296 (8.56), 254 (−21.7), 234 (−19.8). − $C_{38}H_{46}ClN_4RhS_2·2H_2O$: calcd. C 57.24, H 6.32, N 7.03; found C 57.29, H 6.08, N 7.06.

Δ[Rh(th4,5ppy)$_2$(*rac*-st)]Cl (XII): A mixture of ΔΔ[Rh(th4,5ppy)$_2$(μ-Cl)]$_2$ (16.00 mg, 0.012 mmol) and 1,2-diphenylethylendiamine (15.75 mg, 0.075 mmol) in CH_2Cl_2 (15 mL) was stirred for 1 h at room temperature. The yellow-orange solution was heated at reflux for 90 min. After the removal of the solvent, orange Δ[Rh(th4,5ppy)$_2$(*rac*-st)]Cl was obtained (20 mg, 94%). The excess ligand was removed by crystallisation after redissolving the powder obtained after the reaction. − ^{1}H NMR (CD_3CN, 300 MHz): δ = 8.43 (s, 2 H, H−C(6*S,S*)], 8.32 (s, 2 H, H−C(6*R,R*)], 7.48 (s, 4 H, H−C(3*S,S*), H−C(3*R,R*)], 7.28−7.11 (m, 24 H, C_6H_5, H−C(5′*S,S*), H−C(5′*R,R*)], 6.07 (m, 4 H, H−C(4′*S,S*), H−C(5′*R,R*)], 4.25−3.9 (m, 6 H, NH_2, CH), 3.32 (m, 12 H, H−C(7*S,S*), H−C(7*R,R*), H−C(10*S,S*), H−C(10*R,R*)],

2.95−2.87 (m, 4 H, H−C(9_{exo} *S,S*), H−C(9_{exo}*R,R*)], 2.48−2.4 (m, 4 H, H−C(8*S,S*), H−C(8*R,R*)], 1.58−1.502 (m, 12 H, H−C(13*S,S*), H−C(13*R,R*)], 1.44−1.411 (m, 4 H, H−C(9_{endo}*S,S*), H−C(9_{endo}*R,R*)], 0.83 (s, 12 H, H−C(12*S,S*), H−C(12*R,R*)]. − MS (FAB), *m/z*: 823 (90) [M − Cl^-], 611 (95) [Rh(th4,5ppy)$_2$], 356 (9) [Rh(th4,5ppy) − H^+]. − UV/Vis (CH_3CN): λ (ε) = 388 (9894), 331 (sh), 278 (29011). − IR (KBr): ṽ = 3397 (w), 3311 (w), 3052 (w), 2928 (m), 1705 (m), 1619 (s), 1485 (s), 1429 (w), 1367 (w), 1224 (w), 1133 (w), 1019 (w), 871 (w), 762 (w), 700 (m), 562(w). − CD (CH_3CN): λ (Δε) = 400 (29.2), 361 (−11.3), 326 (−16.8), 289 (23), 254 (−21.6 sh), 237 (−28.8). − $C_{46}H_{48}ClN_4RhS_2\cdot H_2O$: calcd. C 62.96, H 5.74, N 6.39; found C 63.05, H 5.99, N 6.72.

Δ[Rh(th4,5ppy)$_2${(*R,R*)-st}]Cl (XIII): As described for **IV**, using ΔΔ[Rh(th4,5ppy)$_2$(μ-Cl)]$_2$ (7.00 mg, 0.005 mmol) and (*R,R*)-st (2.30 mg, 0.01 mmol) in CH_2Cl_2 (15 mL) yielded Δ[Rh(th4,5ppy)$_2${(*R,R*)-st}]Cl (9 mg, 97%). − ^{1}H NMR (CD_3CN, 300 MHz): δ = 8.29 (s, 2 H, H−C(6)], 7.49 (s, 2 H, H−C(3)], 7.2−7.110 (m, 12 H, C_6H_5, H−C(5′)], 6.07 (d, 2 H, ^3J = 4.85 Hz, H−C(4′)], 4.225−4.10 (m, 4 H, NH_2), 3.21 (d, 4 H, ^3J = 2.26 Hz, H−C(7)], 3.09 (dd, 2 H, ^4J = 5.43, ^3J = 5.5 Hz, H−C(10)], 2.9 (ddd, 2 H, ^3J = 5.8 Hz, ^3J = 5.9 Hz, ^2J = 9.73 Hz, H−C(9_{exo})], 2.42 (tdd, 2 H, ^4J = 4.94 Hz, ^3J = 5.8 Hz, ^3J = 2.5 Hz, H−C(8)] 1.501 (s, 6 H, H−C(13)], 1.42 (d, 2 H, ^2J = 9.61 Hz, H−C(9_{endo})], 0.83 (s, 6 H, H−C(12)]. − MS (FAB); *m/z* (%): 823 (85) [M − Cl^-], 611 (100) [Rh(th4,5ppy)$_2$], 356 (8) [Rh(th4,5ppy) − H^+]. − UV/Vis (CH_3CN): λ (ε) = 392 (10299), 331 (sh), 302 (sh), 278 (28651). − CD (CH_3CN): λ (Δε) = 399 (30.7), 362 (−11.33), 326 (−16.5), 290 (26.2), 252 (−23.53 sh), 236 (−31.5). − $C_{46}H_{48}ClN_4RhS_2\cdot CH_3CN\cdot CH_2Cl_2$: calcd. C 59.72, H 5.42, N 7.106, S 6.5; found C 60.155, H 5.45, N 7.13, S 6.31.

Δ[Rh(th4,5ppy)$_2${(*S,S*)-st}]Cl (XIV): As described for **IV**, using ΔΔ[Rh(th4,5ppy)$_2$(μ-Cl)]$_2$ (70.00 mg, 0.054 mmol) and (*S,S*)-st (22.96 mg, 0.11 mmol) in CH_2Cl_2 (15 mL) afforded Δ[Rh(th4,5ppy)$_2${(*S,S*)-st}]Cl (80.86 mg, 87%). − ^{1}H NMR (CD_3CN, 300 MHz): δ = 8.49 (s, 2 H, H−C(6)], 7.49 (s, 2 H, H−C(3)], 7.23−7.12 (m, 12 H, C_6H_5, H−C(5′)], 6.07 (d, 2 H, ^3J = 4.7 Hz, H−C(4′)], 4.15−4.12 (m, 4 H, NH_2), 3.21 (d, 4 H, ^3J = 2.32 Hz, H−C(7)], 3.16 (dd, 2 H, ^4J = 5.34, ^3J = 5.5 Hz, H−C(10)], 2.9 (ddd, 2 H, ^3J = 5.6 Hz, ^3J = 5.98 Hz, ^2J = 10.1 Hz, H−C(9_{exo})], 2.42 (tdd, 2 H, ^4J = 5.7 Hz, ^3J = 5.9 Hz, ^3J = 3.02 Hz, H−C(8)] 1.5 (s, 6 H, H−C(13)], 1.41 (d, 2 H, ^2J = 9.83 Hz, H−C(9_{endo})], 0.83 (s, 6 H, H−C(12)]. − MS (FAB); *m/z* (%): 823 (92) [M − Cl^-], 611 (90) [Rh(th4,5ppy)$_2$], 356 (10) [Rh(th4,5ppy) − H^+]. − UV/Vis (CH_3CN): λ (ε) = 391 (9532), 337 (sh), 278 (26434). − IR (KBr): ṽ = 3406 (w), 2924 (m), 1709 (s), 1621 (m), 1489 (s), 1432 (w), 1384 (m), 1364 (m), 1222 (m), 1013 (w), 874 (w), 842 (w), 758 (w), 700 (m), 564 (w), 530 (w). − CD (CH_3CN): λ (Δε) = 399 (30.2), 365 (−13), 325 (−15.2), 294 (16.6), 279 (sh), 249 (−22.8), 238 (−25.4), 206 (34). − $C_{46}H_{48}ClN_4RhS_2\cdot 3H_2O$: calcd. C 60.48, H 5.96, N 6.13, S 7.02; found C 60.74, H 5.705, N 6.33, S 6.655.

Δ[Rh(th4,5ppy)$_2$(dmen)]Cl (XV): A mixture of ΔΔ[Rh(th4,5ppy)$_2$(μ-Cl)]$_2$ (25 mg, 0.02 mmol) and *N,N′*-dimethylethylenediamine (3.40 mg, 0.04 mmol) in CH_2Cl_2 (15 mL) was heated at reflux for 90 min. The solvent was removed to afford orange Δ[Rh(th4,5ppy)$_2$(dmen)]Cl (26 mg, 92%). − ^{1}H NMR (CD_3CN, 500 MHz): δ = 8.58 (s, 2 H, H−C(6)], 7.432 (s, 2 H, H−C(3)], 7.21 (d, 2 H, ^3J = 4.76 Hz, H−C(5′)], 6.04 (d, 2 H, ^3J = 4.84 Hz, H−C(4′)], 4.71 (2 H, NH), 3.15−3.08 (m, 10 H, CH_2, H−C(7), H−C(10)], 2.81−2.76 (ddd, 2 H, ^3J = 5.76 Hz, ^3J = 5.81 Hz, ^2J = 9.74 Hz, H−C(9_{exo})], 2.43−2.35 (m, 2 H, 2H−C(8)], 1.59 (d, 6 H, ^3J = 5.76 Hz, CH_3), 1.46 (s, 6 H, H−C(13)], 1.30 (d, 2 H, ^2J = 9.7 Hz, H−C(9_{endo})], 0.7857 (s, 6 H, H−C(12)]. − MS (ESI); *m/z* (%): 699 (100) [M − Cl^-]. − UV/Vis (CH_3CN): λ (ε) = 392 (9139), 333 (sh), 278 (25327). − CD (CH_3CN): λ (Δε) = 400 (25.4), 365 (−12.8), 329 (−15.36), 297 (14.7), 279 (10.26), 254 (−23.07.), 234 (−22.8), 204 (13.79). − $C_{36}H_{44}ClS_2N_4Rh\cdot 5H_2O$: calcd. C 52.38, H 6.59, N 6.78; found C 52.04, H 6.56, N 6.28.

Δ[Rh(th4,5ppy)$_2$(men)]Cl (XVI): As described for **XV**, using ΔΔ[Rh(th4,5ppy)$_2$(μ-Cl)]$_2$ (20 mg, 0.015 mmol) and *N*-methylethylenediamine (2.30 mg, 0.03 mmol) in CH_2Cl_2 (5 mL) gave Δ[Rh(th4,5ppy)$_2$(men)]Cl (15 mg, 67%). − ^{1}H NMR (CD_3CN, 300 MHz): δ = 8.54 (s, 1 H, H−C(6)], 8.43 (s, 1 H, H−C(6)], 7.435 (s, 2 H, H−C(3)], 7.42 (s, 2 H, H−C(3)], 7.216−7.17 (m, 2 H, H−C(5′, 5′′′)], 6.1 (d, 1 H, ^3J = 4.74 Hz, H−C(4′)], 5.99 (d, 1 H, ^3J = 4.88 Hz, H−C(4′)], 4.655−4.49 (m, 1 H, NH), 4.014−3.87 (m, 1 H, NH), 3.145−2.93 (m, 8 H, CH_2, H−C(7), H−C(7′), H−C(10), H−C(10′)], 2.834−2.64 (m, 2 H, H−C(9_{exo}), H−C($9'_{exo}$)], 2.365−2.15 (m, 4 H, H−C(8), H−C(8′), CH_2), 1.63 (d, 3 H, ^3J = 5.98 Hz, CH_3), 1.45 (s, 6 H, H−C(13)], 1.322−1.234 (m, 2 H, H−C(9_{endo}), H−C($9'_{endo}$)], 0.78 (s, 6 H, H−C(12)]. − MS (ESI); *m/z* (%): 685 (100) [M − Cl^-]. − UV/Vis (CH_3CN): λ (ε) = 391 (12246), 333 (sh), 278 (33782). − CD (CH_3CN): λ (Δε) = 401 (33.1), 365 (−14.9), 326 (−22.37), 295 (17.6), 281 (10.56) 254 (−29.4.), 234 (−24.35), 207 (13.76). −: $C_{35}H_{42}ClN_4RhS_2\cdot H_2O$: calcd. C 56.86, H 5.99, N 7.58; found C 56.16, H 6.04, N 7.97.

Δ[Rh(th4,5ppy)$_2$(dpen)]Cl (XVII): As described for **XV**, using ΔΔ[Rh(th4,5ppy)$_2$(μ-Cl)]$_2$ (20 mg, 0.015 mmol) and *N,N′*-diphenylethylenediamine (6.56 mg, 0.03 mmol) in CH_2Cl_2 (15 mL) afforded Δ[Rh(th4,5ppy)$_2$(dpen)]Cl (22.4 mg, 84%). − ^{1}H NMR (CD_3CN, 300 MHz): δ = 8.76 (s, 2 H, H−C(6)], 7.36 (s, 2 H, H−C(3)], 7.105 (m, 6 H, C_6H_5), 6.60 (m, 6 H, H−C(5′), C_6H_5), 5.99 (d, 2 H, ^3J = 4.94 Hz, H−C(4′)], 4.51 (m, 2 H, NH), 3.26 (m, 4 H, CH_2), 3.14 (d, 4 H, ^3J = 2.41 Hz, H−C(7)], 2.97 (dd, 2 H, ^4J = 5.49, ^3J = 5.43 Hz, H−C(10)], 2.77 (ddd, 2 H, ^3J = 5.7 Hz, ^3J = 5.84 Hz, ^2J = 9.83 Hz, H−C(9_{exo})], 2.34 (tdd, 2 H, ^4J = 5.62 Hz, ^3J = 5.68 Hz, ^3J = 2.74 Hz, H−C(8)] 1.44 (s, 6 H, H−C(13)], 1.30 (d, 2 H, ^2J = 9.62 Hz, H−C(9_{endo})], 0.77 (s, 6 H, H−C(12)]. − MS (ESI); *m/z* (%): 823 (10) [M − Cl^-], 611 (100) [Rh(th4,5ppy)$_2$]. − UV/Vis (CH_3CN): λ (ε) = 373 (12076), 282 (31405), 254 (33407). − CD (CH_3CN): λ (Δε) = 384 (17.2), 352 (−12.5), 321 (−18. 6), 288 (16.77), 249 (−17.38) 242 (−17.3.), 204 (13.12). − $C_{46}H_{48}ClN_4RhS_2\cdot 3H_2O$: calcd. C 60.48, H 5.95, N 6.133 found C 60.46, H 5.86, N 5.55.

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