Optically active Pt-terpyridyl coordination assemblies derived from planar chiral metallothioligands

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Optically Active Pt-terpyridyl Coordination Assemblies Derived from Planar Chiral Metallothioligands

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Dedicated to Professor Maurizio Peruzzini on the occasion of his 65th birthday

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Abstract: Optically active halogenated arenes containing stereogenic benzylic alcohol reacts with $[CpRu(CH_3CN)_3][PF_6]$ to give the major diastereomer with 90% de, in which the metal center is preferentially placed on one face of the arene ring. Thus starting with (*S*)-1-(2-chlorophenyl)ethanol the metal complex (*pS*, *S*)-$[CpRu(HO(CH_3)CH\text{-}C_6H_4\text{-}Cl)][PF_6]$ (*pS*, *S*)-**1** was obtained in good yield, while the (*R*)-alcohol provided (*pR*, *R*)-$[CpRu(HO(CH_3)CH\text{-}C_6H_4\text{-}Cl)][PF_6]$ (*pR*, *R*)-**1** metal complex. These compounds display planar and central chiralities. For comparison purposes the analogous racemic compound (*rac*)-$[CpRu(HO(CH_3)CH\text{-}C_6H_4\text{-}Cl)][PF_6]$ (*rac*)-**1** was also prepared in good yield as well. Subsequent treatment of enantiopure and racemic complexes **1** with NaSH in THF allows halogen displacement to occur at room temperature and generates the related enantiopure neutral metallothioligands of the type (*pS*, *S*)-$[CpRu(HO(CH_3)CH\text{-}C_6H_4\text{-}\mathbf{S})]$, (*pS*, *S*)-**2**, (*pR*, *R*)-$[CpRu(HO(CH_3)CH\text{-}C_6H_4\text{-}\mathbf{S})]$ (*pR*, *R*)-**2**, and (*rac*)-$[CpRu(HO(CH_3)CH\text{-}C_6H_4\text{-}\mathbf{S})]$ (*rac*)-**2 (S** = sulfur**)** . These metallothioligands react rapidly with $[(MeCN)Pt(terpy)][OTf]_2$ building blocks to give the chiral coordination assemblies $[Pt(terpy)\text{-}(pS,S)\text{-}\mathbf{2}][OTf]_2$ (*pS*,*S*)-**3,** $[Pt(terpy)\text{-}(pR,R)\text{-}\mathbf{3}][OTf]_2$ (*pR*,*R*)-**3** and the related racemic complex (*rac*)-**3** in which the metal-chromophore is now placed in a chiral environment. The molecular structures of (*rac*)-**3** and the enantiopure heterobimetallic complex (*pR*,*R*)-**3** were determined and show different arrangements at the supramolecular level depending on whether a homochiral or heterochiral assembly is obtained. The induced circular dichroism curves for the right-handed (*pR*,*R*)-**3** and left-handed (*pS*,*S*)-**3** bimetallic complexes displayed mirror image

Cotton bands, confirming the enantiomeric relationship between both compounds. Our method provides an entry to the preparation of a wide range of optically pure coordination compounds with potentially important properties

Introduction

The design and the construction of optically active discrete supramolecular architectures have attracted intense interest due to their wide range of potential applications.[1-4] The challenge is to be able to control the stereochemistry of the final assembly.[5-9] For instance it is well known that octahedral metal complexes containing at least two achiral bidentate ligands display helicoïdal chirality (Δ or Λ).[10-13] A convenient approach consists in the preparation of racemic molecules followed by separation using chiral auxiliaries[14, 15] or *via* chiral column chromatography[16] to obtain the target optically active building blocks, subsequent treatment with achiral assembling ligands provides the targets enantiopure coordination assemblies. However it is more challenging when the building block is deprived from a stereogenic center such as compounds displaying linear or square planar geometries. In this case, the use of an optically active organometallic ligand to assure chiral transfer or at least placement of the metal in a chiral environment is the most appropriate approach. Moreover the optically active assembling ligand should impose or control the homochiral assemblies of individual building block at the supramolecular level. The use of organometallic linkers to construct coordination assemblies has been done with some success,[17-19] however the use of optically active metalloligands as a tool to construct chiral assemblies is less known.[20, 21]

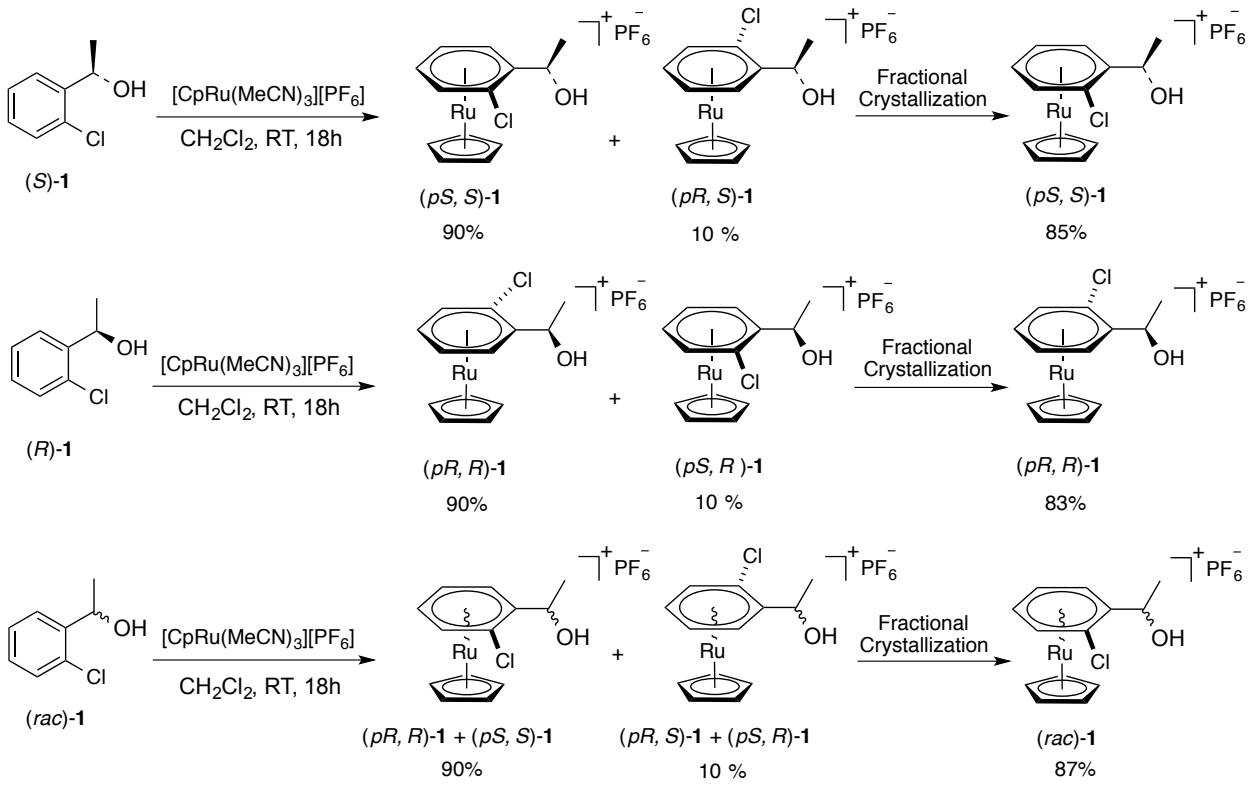
Our group has demonstrated that transition metal complexes and in particular the CpM moiety (M = Ru, Ir) have profound stabilizing properties towards reactive intermediates.[22-24] Indeed, *ortho*-quinone methides as well as *ortho*- and *para*-dithiobenzoquinones were isolated as π-complexes of ruthenium and iridium and their molecular structures were determined.[22, 25, 26] Moreover, the first molecular structures of a diselenoquinone π-complex stabilized by Cp*Ir and (*p*-cymene)-Ru moeities were confirmed by a single-crystal X-ray diffraction study.[27, 28]

In this work we report stable chiral metallothioligands comprising a CpRu moiety and a π-bonded arene containing a stereogenic benzylic alcohol and a sulfur donor atom available for coordination purposes. These metallothioligands display planar and central chirality (vide infra). We also demonstrate that our optically active metallothioligands can easily bind to

Pt(terpy) building blocks and generate the related enantiopure coordination assemblies. The molecular structures of these compounds were determined and confirmed the success of our approach. Our method provides an entry to the preparation of a wide range of optically pure coordination compounds with potentially important properties.

***Synthesis of the optically active Metallothio-ligands (Sp, S)-2 , (Rp, R)-2 and* (*rac*)-2.**

In order to make these optically metallothioligands **2**, we first prepared the π-complexes of the optically active halogenated arenes containing stereogenic benzylic alcohol. Thus (*S*)-1-(2-chlorophenyl)ethanol (*S*)-**1** was treated with one equivalent of $[CpRu(CH_3CN)_3][PF_6]$ in CH_2Cl_2 for 18 hours, providing an off-white compound after reaction work-up. The ^{1}H-NMR of the mixture suggested the presence of two diastereomers in 9: 1 ratio. All attempts to purify the compound on column chromatography were unsuccessful. Gratifyingly we discovered that fractional crystallization in CH_2Cl_2/Et_2O, provided the major isomer as white crystals in 85%. The major isomer was identified as (*pS*, *S*)-$[CpRu(HO(CH_3)CH\text{-}C_6H_4\text{-}Cl)][PF_6]$ (*pS*, *S*)-**1**.

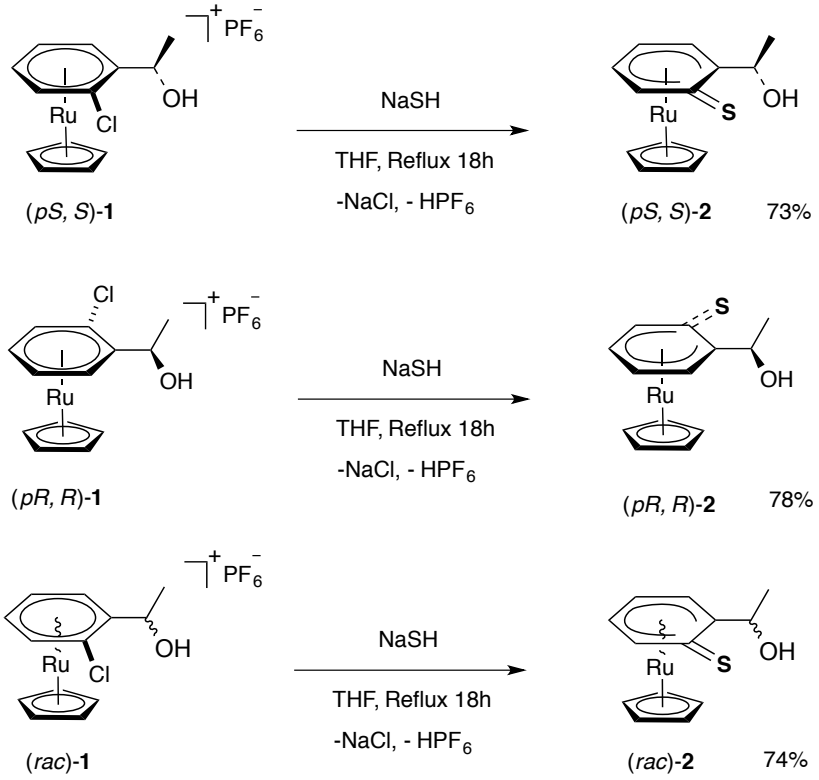


Scheme1. Synthesis of the optically active π-bonded halogenated arenes (*pS*, *S*)-**1,** (*pR*, *R*)-**1** and (*rac*)-**1**.

Repeating the above reaction but using (*R*)-1-(2-chlorophenyl)ethanol (*R*)-**1**, we obtained the enantiopure compound identified as (*pR*, *R*)-[CpRu(HO(CH_3)CH-C_6H_4-Cl)][PF_6] (*pR*, *R*)-**1** in 83% yield. The racemic compound (*rac*)-[CpRu(HO(CH_3)CH-C_6H_4-Cl)][PF_6] (*rac*)-**1** was also obtained in 87% yield and characterized (Scheme 1).

It should be borne in mind that electron-poor halogenated arenes, are resistant to metal π-coordination[29, 30], however in a previous work we demonstrated that (*S*)-1-(2-chlorophenyl)ethanol (*S*)-**1** reacts with the more lipophilic ruthenium solvated species [Cp*Ru($CH_3CN)_3$][OTf] and gives one single diastereomer identified as (*pS*, *S*)-[Cp*Ru(HO(CH_3)CH-C_6H_4-Cl)][OTf] with a preferential coordination on one face of the arene ring.[20] We feel the difference with the current work, may be originated to the steric hindrance displayed by Cp*Ru moiety (Cp* = C_5Me_5) when compared to the CpRu, (Cp = C_5H_5) and hence the minor diastereomer is formed as well but in small quantity (Scheme 1).

The second step consisted in reacting the optically active π-bonded halogenated arenes (*pS*, *S*)-**1,** (*pR*, *R*)-**1** and (*rac*)-**1** with a sulfur source to displace the halogen group.



Scheme 2. Preparation of the optically active metallothioligands (*pS*, *S*)-**2**, (*pR*, *R*)-**2** and (*rac*)-**2**.

The enantiopure and racemic π-bonded complexes of **1** were treated with excess NaSH in THF under reflux for 18h. Reaction work-up provided the metallated thioligands (*pS*, *S*)-**2**,

(*pR*, *R*)-**2** and (*rac*)-**2** as white microcrystalline products in 73%, 78% and 74% yields respectively (Scheme 2). The compounds were stable in the solid state, and in solution under argon. It is well known, that thioquinones (C=S) are less stable than their quinone (C=O) congeners, however for complexes **2** the presence of CpRu moiety allow us to stabilize this kind of compounds. In general the ^{1}H-NMR of complexes **2** show similar pattern for instance the *rac*-**2** recorded in CD_2Cl_2 displayed two sets of multiplets at δ 6.35-5.70 ppm and δ 5.6-5.4 ppm, which correspond to the four aromatic protons. The CpRu appears as a singlet at δ 5.06 ppm while the stereogenic methylcarbinol functional group displayed a doublet at δ 1.45 ppm assigned to the CH_3 group and a multiplet at δ 4.89 ppm attributed to the methine proton –H, while the –OH alcohol function appears downfield at δ 6.49 ppm. Gratifyingly after several attempts convenient crystals of (*pS*, *S*)-**2**, were obtained for an X-ray structural determination.

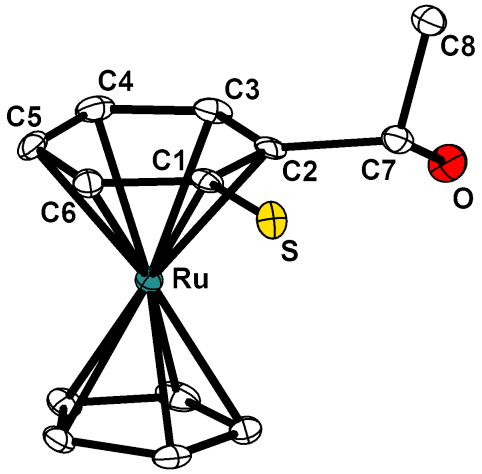


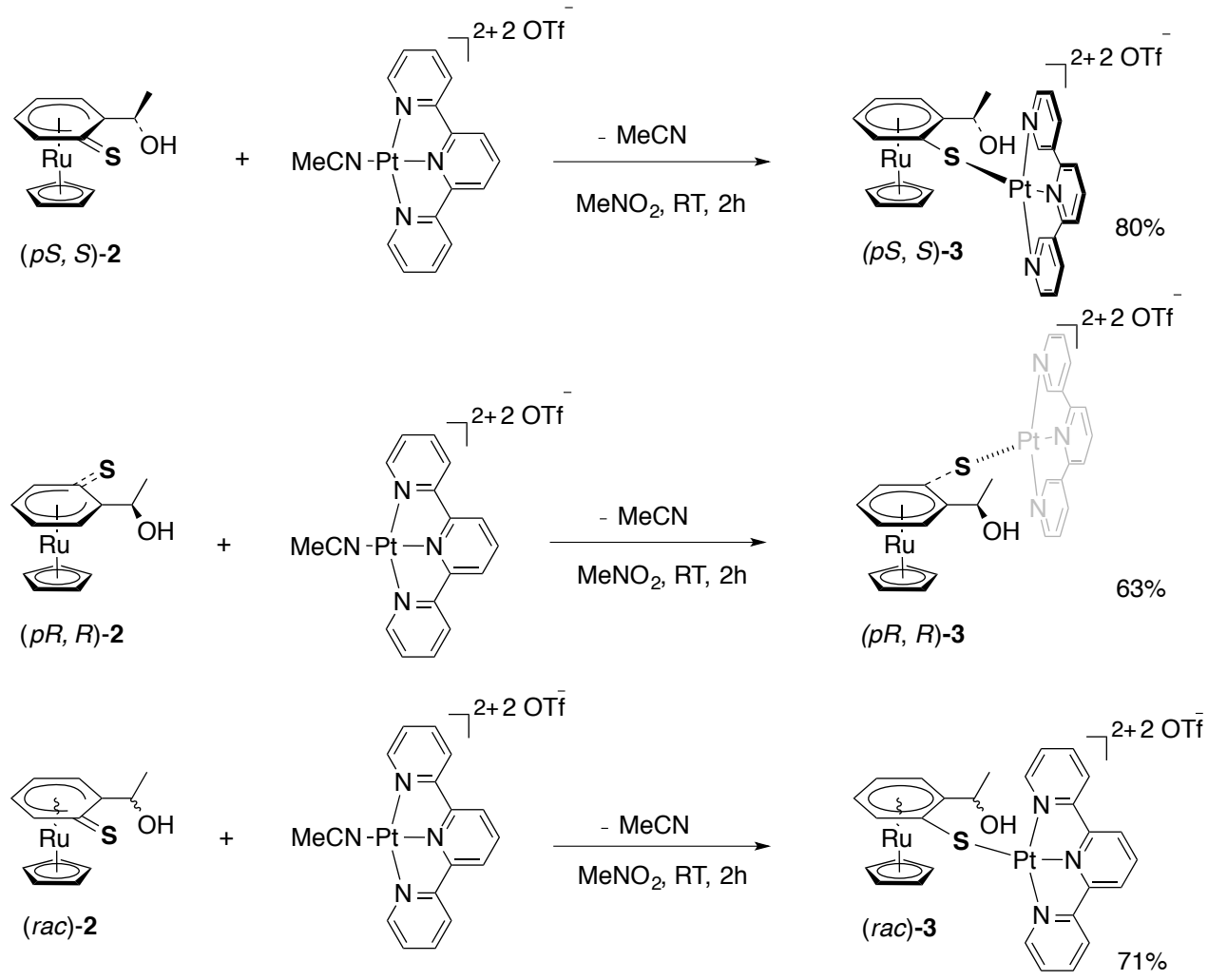
Figure 1. Molecular structure of (*pS*, *S*)-[CpRu(HO(CH_3)C-C_6H_4-**S**)], (*pS*, *S*)-**2** with partial atom numbering system.

Complex (*pS*, *S*)-**2**, crystallizes in the Sohncke space group $P2_1$, a view of the complex is shown in (Figure 1). The structure of (*pS*, *S*)-[CpRu(HO(CH_3)CH-C_6H_4-**S**)], (*pS*, *S*)-**2** confirmed the formation of the target molecule and shows that the aromatic ring is unsymmetrically bound to the CpRu moiety with an average Ru---C (C1-C6) bond distance of 2.23(5) Å, while Ru----C1 (carbon atom attached to the sulfur atom) bond distance is 2.307 (3) Å suggesting perhaps a weaker interaction. The C=S bond distance is 1.748 (4) Å, which is shorter than those of general arene-thiolato ligands (ca. 1.80 A°)[29, 31] and hence is in favor of a partial double bond character between the sulfur and the carbon atom. The solid-state structure also shows that the CH_3- group of the alcohol function points upward, distal from the CpRu center perhaps to minimize steric hindrance, while the –OH group

leans towards the metal center. The absolute structure was determined by refinement of the Flack x parameter, which is equal to -0.018(8) and confirms the absolute configuration of the complex. While X-ray molecular structures of π-bonded quinones are well documented,[32, 33] those with thioquinones are rare,[26, 34, 35] to our knowledge this is the first X-ray molecule structure of a stable enantiopure π-bonded thioquinone complex to be reported.

Having successfully obtained the target chiral metallothioligands we then focused our efforts to construct the related chiral Pt(terpy) assemblies and to study the effect of the chiral organometallic ligand on their aggregation at the supramolecular level (vide infra).

Synthesis of the enantiopure coordination assemblies [Pt(terpy)-(pS,S)-2][OTf]$_2$ (pS,S)-3, [Pt(terpy)-(pR,R)-2][OTf]$_2$ (pR,R)-3 and the related racemic complex [Pt(terpy)-(rac)-2][OTf]$_2$ (rac)-3



Scheme 3. Synthesis of the enantiopure *(pS,S)-**3***, ***(**pR,R)-**3*** and the racemic *rac*-**3** coordination assemblies.

Upon treatment of (*pS, S*)-**2** with [Pt(terpy)(CH_3CN)][OTf]$_2$ in nitromethane/CH_2Cl_2 (1:1) solution, instantaneously provided a red solution. Reaction work-up allowed the isolation of [Pt(terpy)-(*pS, S*)-**2**][OTf]$_2$ (*pS, S*)-**3** in 80% yield. The (*pR, R*)-**3** and the *rac*-3 compound were also obtained in good yields following a similar synthetic procedure and also exhibited red color.

For instance, the ^{1}H-NMR spectrum of the complex (*pS, S*)-**3** recorded in nitromethane-d_3 showed the presence of six multiplets in the region δ 7.8-9.2 ppm assigned to the Pt(terpy) protons, and two doublets and two triplets in the region of δ 5.7-7.1 ppm attributed to the four protons of π-bonded arene, while a singlet at δ 5.17 ppm is visible and assigned to the protons of the CpRu moiety. Finally a multiplet centered at δ 5.50 ppm and a doublet at δ 1.65 ppm are also seen and assigned to the -CH methine and –CH_3 groups of the chiral carbinol substituent. The other enantiomer and the *rac* complexes showed similar spectroscopic features.

The electronic absorption spectra of the (*pS*, *S*)-**3** and (*pR*, *R*)-**3** compounds were recorded in MeOH and displayed similar features (Figure S19). A strong band is visible at 280 nm which is ascribed to allowed π-π transitions of admixtures of intraligand (IL) transitions of terpyridine and the organometalic Cp*Ru(thioligand) system. While the low-energy absorption at 470 and tails to 550 nm can be tentatively assigned as admixtures of [dp(Pt) $\rightarrow$ π*(terpy)] metal-to-ligand charge transfer (MLCT) and metal-perturbed [$\pi \rightarrow \pi$*] IL transitions of the the organometalic Cp*Ru(thioligand) system.[34, 36]

The enantiomeric relationship between (*pS*, *S*)-**3** and (*pR*, *R*)-**3** was assigned by circular dichroism (Figure 2). The induced CD curves recorded in methanol show a mirror-image relationship for the two enantiomers of **3**. In both cases, a strong Cotton band (with opposite signs for the two enantiomers) are visible at 280 nm, associated with the polarized π-π* transition of the Pt(terpy) unit. Moreover, induced circular dichroism bands of weaker intensity attributed to Pt(terpy) electronic transitions are also visible at 335, 350, 370 and 400 nm. These data suggest that the Pt(terpy) chromophore is indeed placed in a chiral environment.

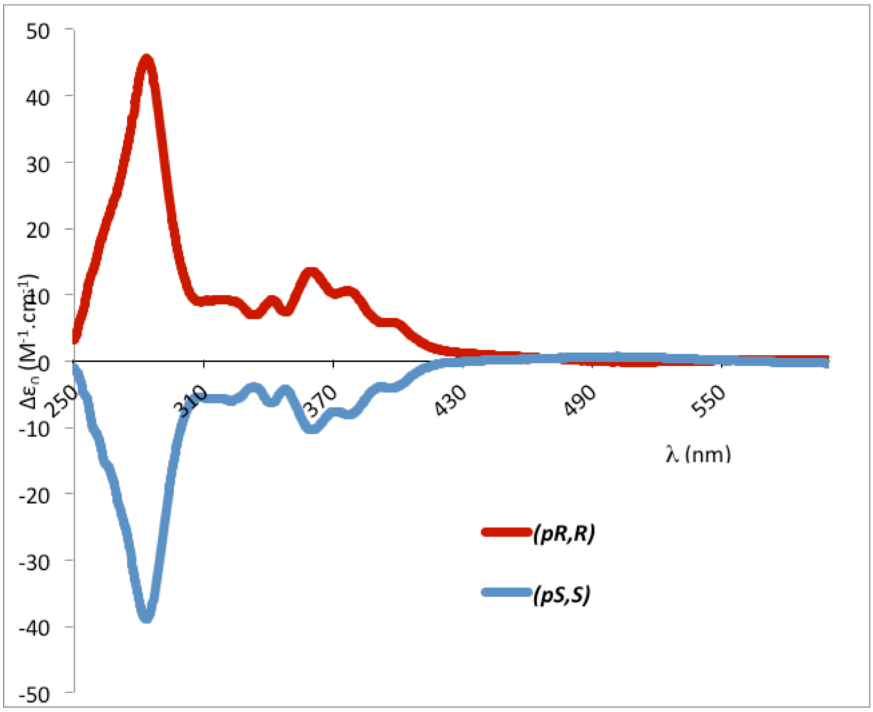


Figure 2. CD curves of (*pR, R*)**-3** (red line), and (*pS, S*)**-3** (blue line), showing the mirror-image relationship in methanol solution and at the same concentration (5.10^{-4}M).

Gratifyingly after many attempts we were able to obtain convenient crystals of the chiral coordination assemblies notably the racemic (*rac*)-**3** and the related enantiopure (*pR, R*)**-3** to investigate the role of the metalloligand on the control of the assembly whether homochiral or heterochiral at the supramolecular level.

Crystals of (*rac*)-**3** and (*pR, R*)-**3** were obtained by slow diffusion of ether into a saturated nitromethane solution of either complex. The structures of *rac*-**3** and the enantiopure compound (*pR*, *R*)-**3** confirm the spectroscopic assignment and show that the chiral metallothioligand binds to the Pt(terpy) unit through the sulfur center (Figure 4). The Pt atom exhibits nearly square-planar coordination geometry. The CpRu moiety is π-bonded to the arene ring in a symmetric fashion. Details for crystal structure determination are given in the supplementary information.

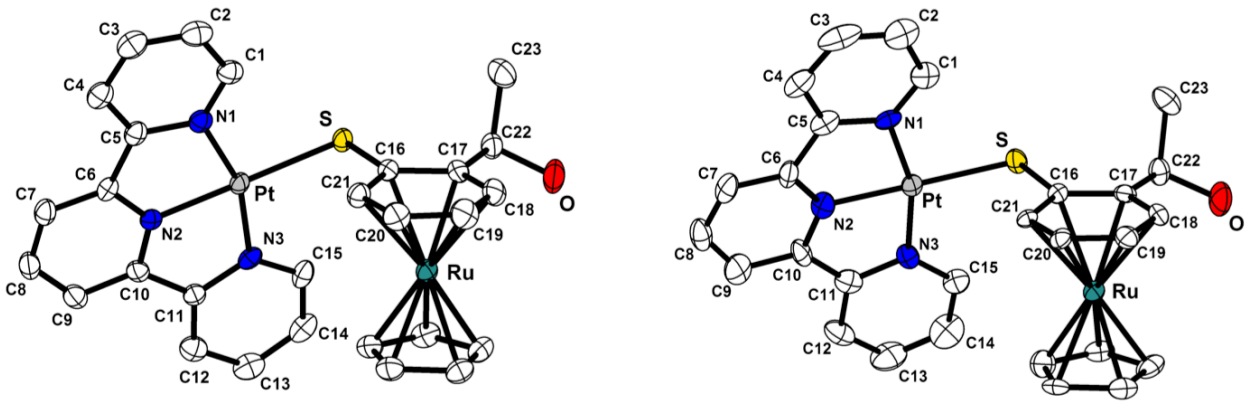


Figure 3. Molecular structures of *rac*-**3** and (*pR, R*)-**3**. Selected bond distances (Å) and angles (°) Pt-N1 : 2.023(5) / 2.022(11), Pt-N2 : 1.971(4) / 1.947(11), Pt-N3 : 2.032(5) / 2.015(12), Pt-S : 2.310(2) / 2.299(3), N1-Pt-N2 : 80.9(2) 80.8(5), N2-Pt-N3 : 80.8(2) / 81.7(5), N3-Pt-S : 98.3(2) / 97.7(3), S-Pt-N1 : 100.0(2) / 99.7(4)

Careful analysis of the packing in the crystals of *rac*-**3** provided us with valuable information (Figure 4). For instance, a dimer is formed between two individual units with opposite configurations (*pR*, *R*)-**3** and (*pS*, *S*)-**3**, displaying a Pt---Pt separation of 3,434(4) Å. Moreover we note that in this heterochiral arrangement the Pt(terpy) chromophore is disposed in a head-to-tail fashion with an angle θ = 180°. For the crystals of the enantiopure complex (*pR*, *R*)-**3**, a different arrangement is observed. This dimer made of two monomers with identical configurations (*pR*, *R*)-**3** and (*pR*, *R*)-**3**, has a Pt---Pt contact distance of 3,567 (4) Å, which is longer by 0,133 Å from that observed for the racemic complex **3**. More interestingly, in this homochiral arrangement, the two Pt(terpy) chromophores are forced to endorse a different orientation, adopting a crossed geometry with angle θ = 85,35° (15)°.

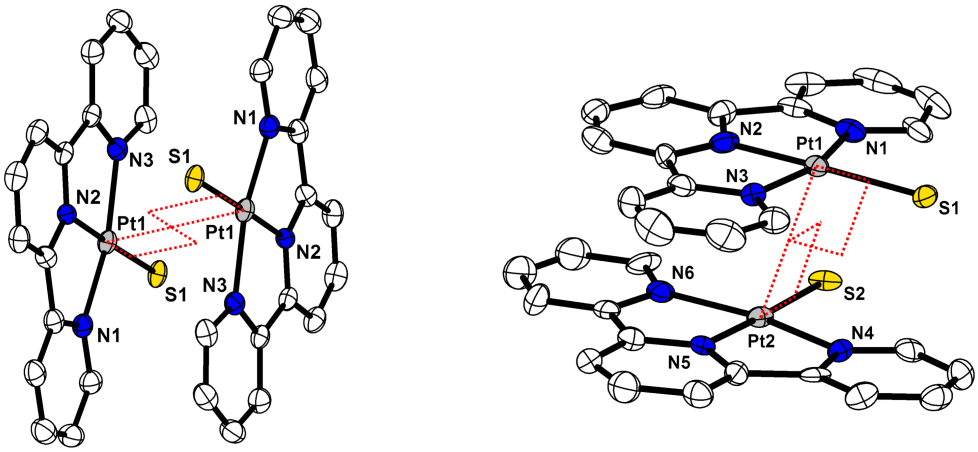


Figure 4. Packing of individual molecules in *rac*-**3** and (*pR*, *R*)-**3**. The organometallic π-complex, [CpRu(HO(CH_3)CH-C_6H_4-)] was removed for clarity.

These results highlight the role of the chiral metallothioligand as a tool to control the arrangement of the Pt(terpy) building blocks at the supramolecular level generating different assemblies whether homo- or hetero-chiral.

To conclude we have successfully described a novel approach to prepare chiral coordination assemblies from achiral square-planar platinum building blocks but using appropriate optically active metallothioligands as assembling ligands, which place the platinum chromophore in a chiral environment as demonstrated by CD technique. These results pave the way to the preparation of other chiral assemblies with useful properties from different building blocks displaying variety of geometrical shapes.

General experimental methods. All reactions were carried out under an argon atmosphere. Solvents were distilled under argon from calcium hydride (CH_3CN, CH_2Cl_2), potassium carbonate (acetone) or sodium/benzophenone (Et_2O, THF). Hexane and nitromethane were used as HPLC grade without further purification. The starting precursors $[Pt(terpy)(MeCN)][OTf]_2$, $[Pt(t\text{-}Bu_3terpy)(MeCN)][OTf]_2$ and halogenated metal arene compounds (*rac*)-$[CpRu(\eta^6\text{-}1\text{-}(2\text{-chlorophenyl})ethanol][PF_6]$, (*pS*)-$[CpRu(\eta^6\text{-}(S)\text{-}1\text{-}(2\text{-chlorophenyl})ethanol][PF_6]$ and (*pR*)-$[CpRu(\eta^6\text{-}(R)\text{-}1\text{-}(2\text{-chlorophenyl})ethanol][PF_6]$ were prepared according to published procedures.[1-2] Sodium hydrogen sulfide was dried under vacuum at 110°C overnight prior to use. All other reagents, for instance, the 1-(2-chlorophenyl)ethanol racemic and enantiopure (*R*) and (*S*) (ee 99%) were purchased from Acros. The $[CpRu(MeCN)_3]PF_6$ precursor complex was purchased from sigma Aldrich. ^1H- and ^{13}C-NMR spectra were recorded on a Bruker Avance 300 or 400 MHz or on a Bruker Neo 500 MHz spectrometers at ambient temperature. NMR chemical shifts are reported in parts per million referenced to the residual solvent as follows: $\delta_{CD_2Cl_2}$ = 5.32 ppm; $\delta_{CD_3NO_2}$ = 4.33 ppm, $\delta_{CD_3COCD_3}$ = 2.05 ppm for ^1H NMR and $\delta_{CD_2Cl_2}$ = 53.5 ppm, $\delta_{CD_3NO_2}$ = 62.5 ppm, $\delta_{CD_3COCD_3}$ = 29.7 ppm for ^{13}C NMR. CD spectra were recorded on a Jasco J-815 CD spectrometer with a 1mm path-length quartz cell. The elementary analysis measurements were performed on a Perkin-Elmer 2400 device.

Synthesis of racemic and optically active halogenated arenes (*rac*)-$[CpRu(HO(CH_3)CH\text{-}C_6H_4\text{-}Cl)][PF_6]$ (*rac*)-**1**, (*pS*, *S*)-$[CpRu(\eta^6\text{-}HO(CH_3)CH\text{-}C_6H_4\text{-}Cl)][PF_6]$ (*pS*, *S*)-**1** and (*pR*, *R*)-$[CpRu(HO(CH_3)CH\text{-}C_6H_4\text{-}Cl)][PF_6]$ (*pR*, *R*)-**1**

General procedure:

(*rac*)-$[CpRu(\eta^6\text{-}HO(CH_3)CH\text{-}C_6H_4\text{-}Cl)][PF_6]$ (*rac*)**-1**: To a pale yellow solution of $[CpRu(MeCN)_3][PF_6]$ (100mg ; 0,23 mmol) in dichloromethane (20 mL), was added 1-(2-chlorophenyl)ethanol (0,153 mL ; 1,15 mmol). The mixture was stirred at room temperature during 18h. The solvent was removed under vacuum until 4ml then l'Et_2O (20mL) was added to allow the precipitation of a brown solid. After filtration with a cannula, the product is taken into 5 mL of dichloromethane and allowed to crystallize by diffusion of Et_2O. After 24h the colorless needles were filtrated from a brown solution. (93,6 mg, 0,20 mmol, 87%)

^1H-NMR (500 MHz, acetone-d_6) δ (ppm): 6.77 (dd; *J*=5.8; 0.8 Hz ; 1H ; H_6), 6.70 (d ; *J*=5.8 Hz; 1H ; H_3), 6.44 (td; *J*=5.8; 1.0 Hz; 1H; H_5), 6.39 (t; *J*=5,8 Hz; 1H; H_4), 5.62 (s; 5H ; Cp),

5.16 (qd; *J*=6.5; 4.9 Hz; 1H, H_7), 5.08 (d; *J*=4.9 Hz; 1H; OH), 1.54 (d; *J*=6.5 Hz; 3H; H_8). ^{13}C-NMR (125 MHz, acetone-d_6): δ = 110.8 (C_2), 104.9 (C_1), 88.2 (C_6), 86.3 (C_5), 86.2 (C_4), 83.3 (Cp), 83.1 (C_3), 65.7 (C_7), 24.2 (C_8). ES-HRMS in MeOH: m/z : $[M-PF_6)]^+$ = 322.98 Found 322.97.

Following the above procedure, (*pS, S*)-[CpRu(η^6-HO(CH_3)CH-C_6H_4-Cl][PF_6] **(***pS*, *S*)-**1** was obtained as a white solid (91 mg, 0,195mmol, 85%) from [CpRu($MeCN)_3$][PF_6] (100mg ; 0,23 mmol) and (*S*)-1-(2-chlorophenyl)ethanol (0,153 mL ; 1,15 mmol) as starting materials followed by fractional crystallization from CH_2Cl_2/ Et_2O using slow diffusion technique (V_{CH2Cl2} = 7ml, V_{Et2O} = 20 mL). ^{1}H-NMR (300 MHz, acetone-d_6), δ (ppm): 6.77 (dd; *J*=5.8; 0.8 Hz ; 1H ; H_6), 6.70 (d ; *J*=5.8 Hz; 1H ; H_3), 6.44 (td; *J*=5.8; 1.0 Hz; 1H; H_5), 6.39 (t; *J*=5,8 Hz; 1H; H_4), 5.62 (s; 5H ; Cp), 5.16 (qd; *J*=6.5; 4.9 Hz; 1H, H_7), 5.08 (d; *J*=4.9 Hz; 1H; OH), 1.54 (d; *J*=6.5 Hz; 3H; H_8).^{13}C-NMR (125 MHz, acetone-d_6): δ = 110.8 (C_2), 104.9 (C_1), 88.2 (C_6), 86.3 (C_5), 86.2 (C_4), 83.3 (Cp), 83.1 (C_3), 65.7 (C_7), 24.2 (C_8). ES-HRMS in MeOH: m/z : $[M-PF_6)]^+$ = 322.98 Found 322.97.

In a similar way, (*pR*, *R*)-[CpRu(η^6- HO(CH_3)CH-C_6H_4-Cl][PF_6] (*pR*, *R*)-**1** was obtained as a white solid (89 mg, 0,191 mmol, 83%) from [CpRu($MeCN)_3$][PF_6] (100mg ; 0,23 mmol) and (*R*)-1-(2-chlorophenyl)ethanol (0,153 mL ; 1,15 mmol) as starting materials followed by fractional crystallization from CH_2Cl_2/ Et_2O using slow diffusion technique (V_{CH2Cl2} = 7ml, V_{Et2O} = 20 mL). ^{1}H-NMR (300 MHz, acetone-d_6), δ (ppm): 6.77 (dd; *J*=5.8; 0.8 Hz ; 1H ; H_6), 6.70 (d ; *J*=5.8 Hz; 1H ; H_3), 6.44 (td; *J*=5.8; 1.0 Hz; 1H; H_5), 6.39 (t; *J*=5,8 Hz; 1H; H_4), 5.62 (s; 5H ; Cp), 5.16 (qd; *J*=6.5; 4.9 Hz; 1H, H_7), 5.08 (d; *J*=4.9 Hz; 1H; OH), 1.54 (d; *J*=6.5 Hz; 3H; H_8). ^{13}C-NMR (125 MHz, acetone-d_6): δ = 110.8 (C_2), 104.9 (C_1), 88.2 (C_6), 86.3 (C_5), 86.2 (C_4), 83.3 (Cp), 83.1 (C_3), 65.7 (C_7), 24.2 (C_8). ES-HRMS in MeOH: m/z : $[M-PF_6)]^+$ = 322.98 Found 322.97.

Synthesis of the racemic and optically active metallothioligands (*rac*)-[CpRu(η^6-HO(CH_3)CH-C_6H_4-**S**)] (*rac*)-**2**, (*pS*, *S*)-[CpRu(η^6-HO(CH_3)CH-C_6H_4-**S**)], (*pS*, *S*)-**2**, (*pR*, *R*)-[CpRu(η^6-HO(CH_3)CH-C_6H_4-**S**)] (*pR*, *R*)-**2**.

General Procedure

(*rac*)-[CpRu(η^6-HO(CH_3)CH-C_6H_4-**S**)] (*rac*)-**2**: The halogenated precursor [CpRu(η^6- η^6-HO(CH_3)CH-C_6H_4-Cl][PF_6] (70 mg, 0.15 mmol) and sodium hydrogen sulfide (450 mg, 4.81 mmol) were introduced into a Schlenk tube containing a freshly dried THF (10 mL). The

suspension mixture was stirred at 70°C for 18 h. The solvent was removed under reduced pressure, and the residue was extracted with CH_2Cl_2 (10 mL, three times) and filtered through a plug of celite. The combined filtrates were then concentrated under vacuum (2 mL) and the addition of n-hexane (25 mL) allowed the formation of **2** as a white crystalline solid. Starting from *(rac)*-halogenated precursor. *(rac)*-**2** was isolated as a white solid (37mg; 0,12mmol; 78%). ^{1}H-NMR (400 MHz, CD_2Cl_2) δ (ppm): 6,50 (d ; J=1,8 Hz ; 1H ; -OH) ; 6,33 (d ; J=5,9; 1H; H_6) ; 5,79 (d; J=5,1 Hz ; 1H ; H_3) ; 5,58 (t; J=5,6 Hz ; 1H; H_5) ; 5,43 (m; 1H; H_4) ; 5,06 (s; 5H ; Cp) ; 4,89 (m; 1H ; H; H_7) ; 1,45 (d; 3H ; -CH_3; H_8). ^{13}C-NMR (125 MHz, CD_2Cl_2): δ= 136.3 (C_1), 110.3 (C_2), 89.4 (C_6), 82.5 (C_5), 82.3 (C_3), 79.2 (Cp), 77.9 (C_4), 65.3 (C_7), 19.3 (C_8). ES-HRMS: m/z: [M] = 319.98 Found 319.98. $[M+H]^+$ = 320.98. Found 320.98

In a similar fashion, (*pS, S*)-**2** was obtained as a white solid (35mg, 0,111mmol, 74%)

^{1}H-NMR (400 MHz, CD_2Cl_2) δ (ppm): 6,49 (d ; J=1,8 Hz ; 1H ; -OH) ; 6,32 (d ; J=5,9; 1H ; H; H_6) ; 5,79 (d; J=5,1 Hz ; 1H ; H_3) ; 5,56 (t; J=5,6 Hz ; 1H ; H_5) ; 5,41 (m; J=5,6 ; 1,0 Hz ; 1H ; H_4) ; 5,04 (s; 5H ; Cp) ; 4,89 (m; 1H ; H_7) ; 1,45 (d; J=6,6 Hz ; 3H ; -CH_3 ; H_8). ^{13}C-NMR (125 MHz, CD_2Cl_2): δ= 136.3 (C_1), 110.3 (C_2), 89.4 (C_6), 82.5 (C_5), 82.3 (C_3), 79.2 (Cp), 77.9 (C_4), 65.3 (C_7), 19.3 (C_8). ES-HRMS in CH_3CN: m/z : [M] = 319.98 Found 319.98. $[M+H]^+$ = 320.98. Found 320.98. The structure of this product was confirmed by single crystal x-ray diffraction study.

In a similar way, (*pR, R*)-**2** was obtained as a white solid (34mg, 0,109mmol, 73%).

^{1}H-NMR (500 MHz, CD_2Cl_2) δ (ppm): 6,49 (s; 1H ; -OH); 6.32 (dd; *J*=6.0; 0.4 Hz ; 1H; H_6), 5.80 (d ; *J*=5.6 Hz; 1H; H_3), 5.57 (ddd; *J*=6.0; 5.6; 0.4 Hz; 1H; H_5), 5.42 (t; *J*=5,6 Hz; 1H; H_4), 5.05 (s; 5H ; Cp), 4.89 (q; *J*=6.5 Hz; 1H; H_7), 1.45 (d; *J*=6.5 Hz ; 3H; H_8). ^{13}C-NMR (125 MHz, CD_2Cl_2): δ = 136.3 (C_1), 110.3 (C_2), 89.4 (C_6), 82.5 (C_5), 82.3 (C_3), 79.2 (Cp), 77.9 (C_4), 65.3 (C_7), 19.3 (C_8). ES-HRMS in CH_3CN: m/z : [M] = 319.98. Found 319.98. $[M+H]^+$ = 320.98. Found 320.98.

Synthesis of racemic and optically active coordination assemblies [Pt(terpy)-(*rac*)-**2**][OTf]$_2$ (*rac*)-**3**, [Pt(terpy)-(*pS*,*S*)-**2**][OTf]$_2$ (*pS*,*S*)-**3**, and [Pt(terpy)-(*pR*,*R*)-**3**][OTf]$_2$ (*pR*,*R*)-**3**.

General procedure: To a solution of [Pt(terpy)(MeCN][OTf]$_2$ (45 mg; 0,586 mmol) in dry nitromethane (10 mL) was added a solution of compound **1** (20 mg ; 0,626mmol) in dichloromethane (10 mL). An intense red color appeared immediately. 2 mL of nitromethane

was added to solubilize the mixture. The reaction mixture was then allowed to stir at room temperature for 30 minutes. After concentrating the mixture to 2 mL by removing the solvent under vacuum, Et_2O (20 mL) was added to allow the precipitation of a microcrystalline red solid. The solid was filtered and washed three times with 1 mL of dichloromethane and three times with 5 mL of Et_2O, and dried. (*rac*)**-3** was obtained as a red microcrystalline solid (39 mg, 0,037 mmol, 71%).^{1}H-NMR (500 MHz, CD_3NO_2) δ (ppm) 9.16 (ddd; *J*=5.6; 1.4; 0.6 Hz; $^3J_{Pt\text{-}H}$ = 32,0 Hz; 2H; H_1, H_{15}); 8.63 (dd; *J*=8.5; 7.7 Hz; 1H; H_8), 8.49 (d; *J*=8,1 Hz; 2H; H_7, H_9), 8.41-8.49 (m; 4H; H_3, H_4, H_{12}, H_{13}); 7.86 (ddd; *J*=7.2; 5.6; 2.1 Hz, 2H; H_2, H_{14}), 7.10 (d; *J*=5.9 Hz; 1H; H_{21}) 6.37 (d; *J*=5.9 Hz; 1H; H_{18}), 5.88 (t; *J*=5.9 Hz; 1H; H_{19}), 5.78 (td; *J*= 5.9; 1.0 Hz; 1H; H_{20}), 5.54 (qd; *J*=6.5; 4.6 Hz; 1H; H_{22}), 5.19 (s; 5H; Cp), 3.46 (d; *J*=4.6 Hz; 1H ;OH), 1.67 (d; *J*=6.5 Hz; 3H; H_{23}). ^{13}C-NMR (125 MHz, CD_3NO_2): δ = 160.3 (C_5, C_{11}), 155.5 (C_6, C_{10}), 153.9 (C_1, C_{15}), 144.4 (C_8), 144.0 (C_3, C_{13}), 130.4 (C_2, C_{14}), 126.8 (C_4, C_{12}), 125.2 (C_7, C_9), 117.4 (C_{16}), 110.3 (C_{17}), 88.4 (C_{21}), 84.0 (C_{20}), 83.4 (C_{19}), 81.9 (C_{18}), 81.3 (Cp), 66.9 (C_{22}), 23.5 (C_{23}). ES-HRMS in MeOH: m/z : $[M\text{-}2OTf]^{2+}$ = 373.93. Found 373.52 Elemental analysis Calcd. for $C_{30}H_{25}N_3F_6O_7S_3RuPt.(CH_2Cl_2)_3$ C, 30.47; H, 2.40; N, 3.23; S, 7.39 Found C, 30.41; H, 2.17; N, 3.65; S, 7.79. The structure of this product was confirmed by the x-ray diffraction study.

(*pS, S*)**-3:** In a similar fashion, starting from (*pS, S*)**-2**, complex (*pS, S*)**-3** was obtained as a red crystalline solid (43 mg, 0.042 mmol, 80%). ^{1}H-NMR (400 MHz, CD_3NO_2) δ : ^{1}H-NMR (500 MHz, CD_3NO_2) 9.15 (ddd; *J*=5.6; 1.4; 0.6 Hz; $^3J_{Pt\text{-}H}$ = 32,0 Hz; 2H; H_1, H_{15}); 8.63 (dd; *J*=8.5; 7.7 Hz; 1H; H_8), 8.49 (d; *J*=8,1 Hz; 2H; H_7, H_9), 8.41-8.49 (m; 4H; H_3, H_4, H_{12}, H_{13}); 7.86 (ddd; *J*=7.2; 5.6; 2.1 Hz, 2H; H_2, H_{14}), 7.09 (d; *J*=5.9 Hz; 1H; H_{21}) 6.37 (d; *J*=5.9 Hz; 1H; H_{18}), 5.88 (t; *J*=5.9 Hz; 1H; H_{19}), 5.78 (td; *J*= 5.9; 1.0 Hz; 1H; H_{20}), 5.53 (qd; *J*=6.5; 4.6 Hz; 1H; H_{22}), 5.18 (s; 5H; Cp), 3.49 (d; *J*=4.6 Hz; 1H ;OH), 1.66 (d; *J*=6.5 Hz; 3H; H_{23}). ^{13}C-NMR (125 MHz, CD_3NO_2): δ = 160.3 (C_5, C_{11}), 155.5 (C_6, C_{10}), 153.9 (C_1, C_{15}), 144.5 (C_8), 144.0 (C_3, C_{13}), 130.5 (C_2, C_{14}), 126.9 (C_4, C_{12}), 125.2 (C_7, C_9), 117.4 (C_{16}). ES-HRMS in MeOH: m/z : $[M\text{-}2OTf]^{2+}$ = 373.93. Found 373.52.

(*pR, R*)**-3 :** In a similar way, starting from (*pR, R*)**-2,** complex (*pR, R*)**-3** was obtained as a red microcrystalline solid (34 mg, 0,033 mmol, 63%). ^{1}H-NMR (500 MHz, CD_3NO_2) 9.15 (ddd; *J*=5.6; 1.4; 0.6 Hz; $^3J_{Pt\text{-}H}$ = 32,0 Hz; 2H; H_1, H_{15}); 8.63 (dd; *J*=8.5; 7.7 Hz; 1H; H_8), 8.49 (d; *J*=8,1 Hz; 2H; H_7, H_9), 8.41-8.49 (m; 4H; H_3, H_4, H_{12}, H_{13}); 7.86 (ddd; *J*=7.2; 5.6; 2.1 Hz, 2H; H_2, H_{14}), 7.09 (d; *J*=5.9 Hz; 1H; H_{21}) 6.37 (d; *J*=5.9 Hz; 1H; H_{18}), 5.88 (t; *J*=5.9 Hz; 1H; H_{19}), 5.78 (td; *J*= 5.9; 1.0 Hz; 1H; H_{20}), 5.53 (qd; *J*=6.5; 4.6 Hz; 1H; H_{22}), 5.18 (s; 5H; Cp),

3.49 (d; *J*=4.6 Hz; 1H ;OH), 1.66 (d; *J*=6.5 Hz; 3H; H_{23}). ^{13}C-NMR (125 MHz, CD_3NO_2): δ = 160.3 (C_5, C_{11}), 155.5 (C_6, C_{10}), 153.9 (C_1, C_{15}), 144.5 (C_8), 144.0 (C_3, C_{13}), 130.5 (C_2, C_{14}), 126.9 (C_4, C_{12}), 125.2 (C_7, C_9), 117.4 (C_{16}) .ES-HRMS in MeOH: m/z : $[M\text{-}2OTf]^{2+}$ = 373.93. Found 373.52. Elemental analysis Calcd. for $C_{30}H_{25}N_3F_6O_7S_3RuPt.(CH_2Cl_2)_2$ C, 31.62; H, 2.40; N, 3.46; S, 7.91 Found C, 31.61; H, 2.31; N, 3.67; S, 8.10. The structure of this product was confirmed by the x-ray diffraction structure of his crystal.

X-Ray crystal structure determination. Single crystals were selected, mounted and transferred into a cold nitrogen gas stream. Intensity data was collected with Bruker Kappa-APEX2 systems using micro-source Cu-Kα radiation (*pS*,*S*)**-2** and (*pR*,*R*)-**3** or fine-focus sealed tube Mo-Kα radiation *rac*-**3**. Unit-cell parameters determination, data collection strategy, integration and absorption correction were carried out with the Bruker APEX2 suite of programs. The structure was solved with SHELXT[37] and refined anisotropically by full-matrix least-squares methods with SHELXL[37] within WinGX.[38] Absolute structure (*pS*,*S*)**-2** and (*pR*,*R*)-**3** was determined by anomalous scattering effects analysis and chemical absolute configuration was then deduced. The structures were deposited at the Cambridge Crystallographic Data Centre with numbers CCDC 2023666-2023668 and can be obtained free of charge via www.ccdc.cam.ac.uk.

Crystal data for (*pS*,*S*)**-2**. $C_{13}H_{14}ORuS$, monoclinic P 2_1, a = 7.9240(3) Å, b = 9.2999(4) Å, c = 8.4978(3) Å, α = γ = 90°, β = 112.755(3)°, V = 577.48(4) Å^3, Z = 2, pale yellow prism 0.08 × 0.06 × 0.02 mm^3, μ = 12.451 mm^{-1}, min / max transmission = 0.52 / 0.88, T= 200(1) K, λ = 1.54178 Å, θ range = 5.65° to 66.57°, 10505 reflections measured, 2000 independent, R_{int} = 0.0324, completeness = 0.999, 146 parameters, 1 restraint, Flack x = -0.018(8), final R indices R1 [I>2σ(I)] = 0.0181 and wR2 (all data) = 0.0438, GOF on F^2 = 1.097, largest difference peak / hole = 0.25 / -0.25 e·Å^{-3}.

Crystal data for *rac*-**3.** $C_{32}H_{31}F_6N_5O_{11}PtRuS_3$, triclinic P -1, a = 10.4755(3) Å, b = 12.3022(4) Å, c = 16.6583(5) Å, α = 93.376(2)°, β = 93.871(2)°, γ = 98.203(2)°, V = 2114.86(11) Å^3, Z = 2, yellow prism 0.34 × 0.08 × 0.02 mm^3, μ = 3.895 mm^{-1}, min / max transmission = 0.69 / 0.94, T= 200(1) K, λ = 0.71073 Å, θ range = 1.97° to 30.65°, 65167 reflections measured, 12860 independent, R_{int} = 0.0368, completeness = 0.983, 535 parameters, 48 restraints, final R indices R1 [I>2σ(I)] = 0.0464 and wR2 (all data) = 0.1370, GOF on F^2 = 1.063, largest difference peak / hole = 3.10 / -0.96 e·Å^{-3}.

Crystal data for (*pR*, *R*)-3. $C_{31.5}H_{30}F_6N_3O_{8.5}PtRuS_3$, orthorhombic P 2_1 2_1 2_1, a = 11.4155(3) Å, b = 22.9965(6) Å, c = 27.3165(9) Å, α = β = γ = 90°, V = 7171.0(4) Å^3, Z = 8, orange prism 0.13 × 0.03

× 0.02 mm^3, μ = 13.025 mm^{-1}, min / max transmission = 0.40 / 0.83, T= 200(1) K, λ = 1.54178 Å, θ range = 2.51° to 66.80°, 32286 reflections measured, 11885 independent, R_{int} = 0.0534, completeness = 0.992, 999 parameters, 214 restraints, Flack x = -0.032(7), final R indices R1 [I>2σ(I)] = 0.0486 and wR2 (all data) = 0.1161, GOF on F^2 = 1.018, largest difference peak / hole = 1.76 / -0.74 e·$Å^{-3}$.

Supplementary data

The Supplementary data contains ^{1}H- and ^{13}C-NMR and spectra of the prepared compounds. UV-vis spectra of complexes of (*pR, R*)-**3** and (*pS, S*)-**3**. CCDC reference numbers 2023666-2023668 contain crystallographic data for complexes (*pS*, *S*)-**2**, (*rac*)-**3** and (*pR, R*)-**3** presented in this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Conflict of interest

The authors declare no conflict of interest in relation to this work.

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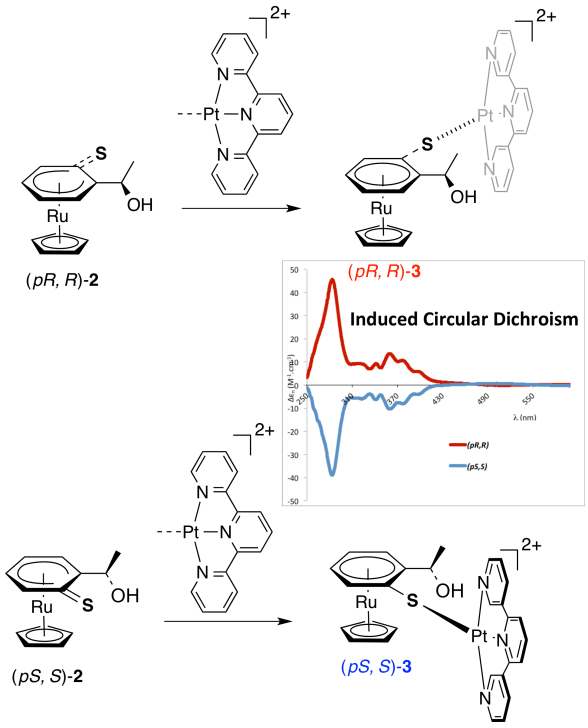

Summary: A novel enantioselective synthetic procedure to obtain chiral coordination compounds is described. The designed optically active organometallic thioligands (*pR*, *R*)-**2** and (*pS*, *S*)-**2** react with Pt(terpy) building blocks to give the related enantiopure

coordination assemblies (*pR*, *R*)-**3** and (*pS*, *S*)-**3** as confirmed by the induced circular dichroism traces.