

# Chiral Recognition and Resolution of the Enantiomers of Supramolecular Triangular Hosts: Synthesis, Circular Dichroism, NMR, and X-ray Molecular Structure of $[\text{Li}(\text{C}(\text{R},\text{R},\text{R})\text{-}\{\text{Cp}^*\text{Rh}(\text{5-chloro-2,3-dioxopyridine})\}_3)[\Delta\text{-Trisphat}]$

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Received May 17, 2004

The racemic triangular supramolecular host  $[\text{Cp}^*\text{Rh}(\text{5-chloro-2,3-dioxopyridine})_3]$  (**1**) was prepared in high yield. Treatment with LiCl followed by addition of silver salt AgOTf gave the triflate salt species  $[\text{Li}(\text{C}(\text{R},\text{R},\text{R})\text{-}\{\text{Cp}^*\text{Rh}(\text{5-chloro-2,3-dioxopyridine})\}_3)[\text{OTf}]$  (**2**). Subsequent anion metathesis using the optically pure chiral shift reagent [Cinchonidinium][ $\Delta$ -Trisphat] produced a pair of diastereomers  $[\text{Li}(\text{C}(\text{R},\text{R},\text{R})\text{-}\{\text{Cp}^*\text{Rh}(\text{5-chloro-2,3-dioxopyridine})\}_3)[\Delta\text{-Trisphat}]$  (**3a**) and  $[\text{Li}(\text{C}(\text{S},\text{S},\text{S})\text{-}\{\text{Cp}^*\text{Rh}(\text{5-chloro-2,3-dioxopyridine})\}_3)[\Delta\text{-Trisphat}]$  (**3b**). The resolution of these diastereomers was achieved by fractional crystallization, and their stereochemistry relationship was established by circular dichroism studies. The X-ray molecular structure of **3a** is reported and shows as an outstanding feature a chiral recognition between the  $\Delta$ -Trisphat anion and a single enantiomer cation  $[\text{Li}(\text{C}(\text{R},\text{R},\text{R})\text{-}\{\text{Cp}^*\text{Rh}(\text{5-chloro-2,3-dioxopyridine})\}_3)^+$  manifested through a  $\pi$ - $\pi$  interaction. <sup>1</sup>H NMR and circular dichroism studies in solution support the solid-state behavior.

## Introduction

Chirality is a very old and ever fascinating field. In the past decade, it has become an important feature of supramolecular chemistry.<sup>1</sup> Of particular interest is the chiral control at metal centers in the self-assembly of silver hexamers by von Zelewsky and co-workers using optically pure CHIRAGEN-type ligands.<sup>2ab</sup> Further, self-assembly of chiral metallomacrocycles and their use as hosts for metal catalysts have been recently considered as a hot challenging field.<sup>2c</sup>

Pursuing our research in the area of self-assembly of metallomacrocycles, metallocryptands, boxes, and coordina-

tion polymers,<sup>3</sup> we came across an interesting type of chiral triangular metallomacrocycle that was reported in the past decade by several groups.<sup>4</sup> These macrocycles were reported as racemates, and only Yamanari and co-workers have reported diastereomeric separations,<sup>5</sup> but no NMR studies have been made to differentiate these chiral macrocycles by the use of a chiral auxiliary. Hence we felt that the

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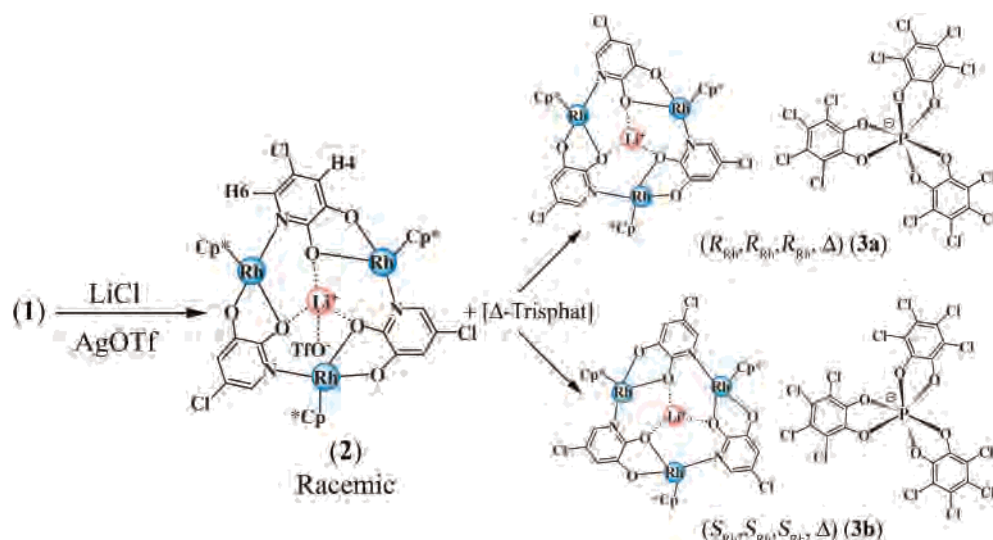
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## Scheme 1



differentiation and eventually the resolution of these chiral systems by the  $\Delta$ -Trisphat<sup>6</sup> anion would be a very intriguing and challenging subject.

In this paper, we report the self-assembly of the novel triangular rhodium macrocycle [Cp\**Rh*(5-chloro-2,3-dioxypyridine)]<sub>3</sub> (**1**) obtained as a racemate. Conversion of this racemic material to a mixture of diastereomeric salts began by encapsulation of a lithium cation. Subsequent anion metathesis using the optically pure chiral shift reagent [Cinchonidinium][ $\Delta$ -Trisphat] provided a pair of diastereomers [LiC(*R,R,R*)-{Cp\**Rh*(5-chloro-2,3-dioxypyridine)}<sub>3</sub>]-[ $\Delta$ -Trisphat] (**3a**) and [LiC(*S,S,S*)-{Cp\**Rh*(5-chloro-2,3-dioxypyridine)}<sub>3</sub>]-[ $\Delta$ -Trisphat] (**3b**). The latter were separated by fractional crystallization. The X-ray molecular structure of one of the diastereomers (**3a**) is also reported and provided valuable information about the mean of chiral recognition between the optically pure anion and the cationic complex. Circular dichroism spectra and NMR studies in solution support the solid-state behavior and show an enhancement of the configurational stability at the metal centers in **3a,b** compared to the starting material **1**.

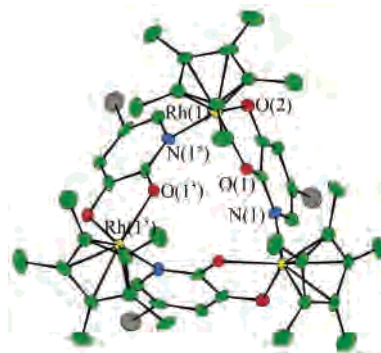
## Results

The model system we chose to study is neutral triangular metallomacrocycles recently described in the literature. These metallomacrocycles are obtained diastereoselectively by self-assembly (all metal centers have the same configuration) producing a racemate  $R_M R_M R_M$  and  $S_M S_M S_M$  (Scheme 1). Their binding properties toward alkali-halides A-X {A = Li, Na, K; X = Cl, Br, I} were also reported.<sup>7</sup> Thus treatment of [Cp\**Rh*( $\mu$ -Cl)Cl]<sub>2</sub>, with commercially available 5-chloro-2,3-dihydroxypyridine (**LH**<sub>2</sub>) in the presence of Cs<sub>2</sub>CO<sub>3</sub> in MeOH affords the novel trimetallic macrocycle [Cp\**RhL*]<sub>3</sub>

**Table 1.** Crystal and Structure Refinement Data for **1** and **3a**

	<b>1</b>	<b>3a</b>
empirical formula	C <sub>48</sub> H <sub>54</sub> Cl <sub>12</sub> N <sub>3</sub> O <sub>6</sub> Rh <sub>3</sub>	C <sub>85</sub> H <sub>82</sub> Cl <sub>17</sub> N <sub>3</sub> O <sub>14.50</sub> PLiRh <sub>3</sub>
unit cell	trigonal	orthorhombic
fw	1503.12	2326.92
space group	<i>P</i> $\bar{3}$ <i>c</i>	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
<i>a</i> (Å)	19.132(2)	18.816(5)
<i>b</i> (Å)	19.132(2)	22.695(6)
<i>c</i> (Å)	20.407(3)	23.105(8)
$\alpha$ (deg)	90	90
<i>V</i> (Å <sup>3</sup> )	6469(1)	9867(0)
<i>Z</i>	4	4
<i>D</i> <sub>calcd</sub> (g·cm <sup>-3</sup> )	1.54	1.57
temp (K)	295	180
$\lambda$ (Mo K $\alpha$ ) (Å)	0.710 730	0.710 730
$\mu$ (mm <sup>-1</sup> )	1.295	1.032
<i>R</i> ( <i>F</i> <sub>o</sub> ) <sup>a</sup>	0.0630	0.0809
<i>R</i> <sub>w</sub> ( <i>F</i> <sub>o</sub> ) <sup>b</sup>	0.0570	0.0850

$$^a R = \frac{\sum(|F_o| - |F_c|)}{\sum|F_o|}, \quad ^b R_w = \frac{[\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2}}$$



**Figure 1.** ORTEP view of **1** at 50% probability level showing the atom numbering system. Selected bond distances (Å) and angles (deg): O(1)–O(1') 3.09(1), Rh(1)–N(1') 2.139(7), Rh(1)–O(1) 2.086(6), Rh(1)–O(2) 2.075(6); N(1')–Rh(1)–O(1) 87.2(3), N(1')–Rh(1)–O(2) 84.8(2), O(1)–Rh(1)–O(2) 79.3(2).

(**1**), where **L** stands for the dianionic tridentate ligand “5-chloro-2,3-dioxypyridine”. This compound was fully characterized, including its X-ray structure (Tables 1 and 2). A view of the molecule and selected bond distances and angles are given in Figure 1. The structure of **1** shows trirhodium macrocycle, where the tridentate ligand **L** is chelating one metal center by two oxygen atoms and acts as a monodentate

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**Table 2.** Selected Atomic Distances (Å) and Angles (deg) for **1** and **3a**

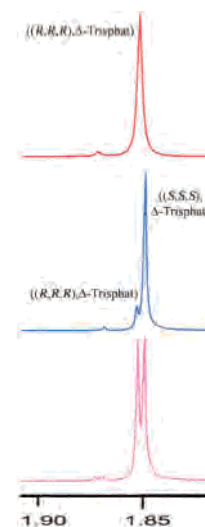
Compound <b>1</b>			
Rh(1)–Rh(1')	5.3	Rh(1)–O(1)	2.086(6)
O(1)–O(1')	3.09(1)	Rh(1)–O(2)	2.075(6)
Rh(1)–N(1')	2.139(7)		
N(1')–Rh(1)–O(1)	87.2(3)	O(1)–Rh(1)–O(2)	79.3(2)
N(1')–Rh(1)–O(2)	84.8(2)		
Compound <b>3a</b>			
Li–O(1)	1.76	O(1)–O(3)	3.04(1)
Li–O(3)	1.90	O(1)–O(5)	3.06(1)
Li–O(5)	1.91	O(3)–O(5)	3.07(1)
Rh(1)–Rh(2)	5.4	Rh(1)–N(3)	2.1062(1)
Rh(1)–Rh(3)	5.5	Rh(1)–O(1)	2.145(1)
Rh(2)–Rh(3)	5.4	Rh(1)–O(2)	2.087(1)
N(3)–Rh(1)–O(1)	86.4(4)	O(1)–Rh(1)–O(2)	80.0(4)
N(3)–Rh(1)–O(2)	85.5(5)		

ligand to the adjacent metal through the nitrogen atom. All over the three “Cp\*<sup>+</sup>Rh<sup>2+</sup>” dicationic moieties and the three dianionic ligands are disposed in an alternate fashion, thus providing a neutral metallomacrocyclic.

We then examined the solution behavior of this chiral metallomacrocyclic **1** in the presence of [n-Bu<sub>4</sub>N][Δ-Trisphat] by <sup>1</sup>H NMR. Surprisingly, neither a high concentration of Δ-Trisphat salt (1:15) in CD<sub>2</sub>Cl<sub>2</sub> nor cooling led to differentiation of enantiomers. We and others have shown that the Δ-Trisphat anion is an efficient chiral shift reagent for a variety of transition metal complexes of different shapes,<sup>8</sup> and most of these research investigations were recently reviewed.<sup>9</sup> While the previous studies concerned exclusively the differentiation of the enantiomers by NMR, we note that only in the case of Ru(bpy)<sub>3</sub> complexes separation of the diastereomers with Δ-Trisphat was achieved.<sup>10</sup>

To enhance the recognition process between the chiral metallomacrocyclics and Δ-Trisphat, we decided to obtain these metallomacrocyclics as a Δ-Trisphat salt with lithium cations inside the cavities. We anticipated that having cationic trinuclear species would enable ion-pairing process and, therefore, promote differentiation by NMR. Thus, treatment of **1** with LiCl and subsequent addition of AgOTf gave the triflate salt [Li⊂(Cp\*<sup>+</sup>RhL<sub>3</sub>)]<sup>+</sup>[OTf]<sup>-</sup> (**2**). Elemental analysis and NMR data (<sup>1</sup>H, <sup>13</sup>C, <sup>7</sup>Li, <sup>19</sup>F) were consistent with the proposed formula. Most remarkably the <sup>7</sup>Li NMR showed a singlet at δ -0.1 ppm, diagnostic of lithium bound by the neutral host.<sup>7</sup> The latter was chromatographed by CH<sub>2</sub>Cl<sub>2</sub> on neutral alumina with [Cinchonidinium][Δ-Trisphat] and gave the target triangular metallomacrocyclics as Δ-Trisphat diastereomers **3a,b** (Scheme 1).

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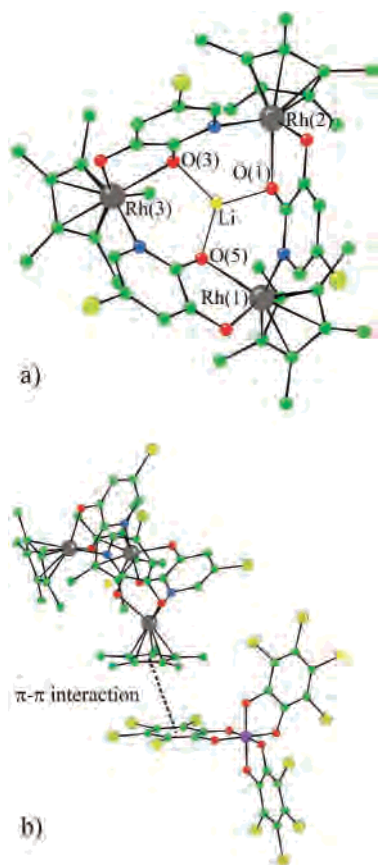


**Figure 2.** <sup>1</sup>H NMR (400 MHz) spectra of “Cp\*<sup>+</sup>Rh<sup>2+</sup>” region of sample 2 (enriched **3a**, top), sample 1 (enriched **3b**, middle), and 1:1 mixture (bottom) recorded in a (75/25) CD<sub>2</sub>Cl<sub>2</sub>/toluene-*d*<sub>8</sub> solution (1.8 mM).

The formation of **3a,b** was secured by full NMR studies (<sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P, <sup>7</sup>Li), IR, and elemental analysis. For instance the <sup>1</sup>H NMR spectra recorded in CD<sub>2</sub>Cl<sub>2</sub> were very informative and showed that the signals attributed to the protons (H4, H6) of the tridentate bridging ligand move closer to each other relative to the neutral host whereby H4 is markedly shifted downfield (Δδ ~ 0.3 ppm). The <sup>31</sup>P NMR showed a singlet at δ -79.9 ppm attributed to the Δ-Trisphat anion. Finally the <sup>7</sup>Li NMR gave a singlet at δ 0.2 ppm diagnostic of coordinated Li<sup>+</sup> cation. We note that this is the first Δ-Trisphat complex of such chiral metallomacrocyclics reported in the literature. Interestingly when the <sup>1</sup>H NMR spectrum of 1:1 mixture of the two diastereomers in a CD<sub>2</sub>Cl<sub>2</sub>/toluene-*d*<sub>8</sub> solution (75/25) was recorded at room temperature while monitoring the signals attributed to H4, H6, and Cp\*, significant changes occurred. For instance the doublet attributed to H6 split into a pair of doublets while the signal for H4 remains unchanged.

Remarkably the singlet corresponding to the methyl protons of the Cp\* split into two distinct lines supporting the formation of two diastereomers (Figure 2, bottom). We then examined the possibility of separating the 1:1 mixture of diastereomeric complexes by fractional crystallization. We found that the mixture can be separated in CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O. During the crystallization process, an orange microcrystalline material was formed and separated from the solution to give sample 1. The filtrate was left to crystallize again giving orange square crystals of sample 2. <sup>1</sup>H NMR (Figure 2, middle) of sample 1 recorded in a CD<sub>2</sub>Cl<sub>2</sub>/toluene-*d*<sub>8</sub> solution (75/25) showed by deconvolution of the two signals an enrichment in **3b** with ee of 74% (since Δ-Trisphat is optically pure, the diastereomeric excess observed reflects the enantiomeric excess of the cations **3a** and **3b**). Sample 2 showed an enrichment in **3a** with ee of 90% on the basis of the <sup>1</sup>H NMR spectrum (Figure 2), since the signal of the other isomer **3b** is not seen.

The structure of the major diastereomer **3a**, in sample 2, was determined. The crystals of the latter were grown from



**Figure 3.** (a) Frontal projection of the cationic part of **3a** showing  $\text{Li}^+$  encapsulation with atom numbering system and (b) sidewise projection of **3a** showing the  $\pi$ - $\pi$  interaction between  $\Delta$ -Trisphat and the triangular host. Selected bond distances (Å) and angles (deg): O(1)–O(3) 3.04(1), O(1)–O(5) 3.06(1), O(3)–O(5) 3.07(1), Rh(1)–N(3) 2.106(2), Rh(1)–O(1) 2.145(1), Rh(1)–O(2) 2.087(1); N(3)–Rh(1)–O(1) 86.4(4), N(3)–Rh(1)–O(2) 85.8(5), O(1)–Rh(1)–O(2) 80.0(4).

a toluene/ $\text{CH}_2\text{Cl}_2$  solution and formed in the orthorhombic crystal system, space group  $P2_12_12_1$  (Tables 1 and 2). The absolute configuration of the molecules in the structure was confirmed by refining Flack's  $x$  parameter and was equal to 0.01(7), attesting at the enantiopure character of the crystal.<sup>11</sup> In this diastereomer, the absolute configuration of each metal center is *R*. Further the CD curve of the analyzed crystal **3a** (Figure 4) was recorded in  $\text{CH}_2\text{Cl}_2$  in a microcell (1 mm) allowing us to establish without ambiguity the identity of the major isomer in sample 2. Comparison between the intensity of the Cotton effects of the enantiopure crystal **3a** and that of sample 2 suggests that this sample is highly enriched (>90%) and in agreement with the  $^1\text{H}$  NMR analysis (Figure 2).

The structure shows the formation of the expected cationic triangular macrocycle with  $\Delta$ -Trisphat as counteranion (Figure 3). The trinuclear complex has a pseudo- $C_3$  symmetry axis passing through the encapsulated lithium cation and consists of alternating " $\text{Cp}^*\text{Rh}^{2+}$ " vertexes and 5-chloro-2,3-dioxopyridine dianion edges. The Li–O distances lie between 1.76 and 1.91 Å. This is shorter than the values reported for [12]-crown-3 and the metallomacrocycles previously described

(1.83–1.99 Å).<sup>7,12</sup> In these systems, the encapsulated lithium cation featured a bond with an anion (Li–Cl for example). To the best of our knowledge, **3a** is the first triangular metallomacrocyclic host where a lithium cation is only coordinated to three oxygen atoms of the metallocrown-ether.

Further, the structure displays as an outstanding feature an interaction between the  $\Delta$ -Trisphat anion and the cationic metal complex (Figure 3b). Indeed, there is a  $\pi$ - $\pi$  interaction between one of the tetrachlorocatecholate ring of the  $\Delta$ -Trisphat and a " $\text{Cp}^*\text{Rh}^{2+}$ " unit with a plane to plane distance of 3.6 Å ( $\alpha = 20^\circ$ ). In this interaction the ring acts as a  $\pi$ -acceptor and the " $\text{Cp}^*\text{Rh}^{2+}$ " as a  $\pi$ -donor.

It is noteworthy that such type of interaction has been suggested to occur in supramolecular chemistry by Stoddart and co-workers for the synthesis of pseudorotaxanes. These are formed through  $\pi$ - $\pi$  interaction between  $\pi$ -deficient tetracationic cyclophane and  $\pi$ -excessive hydroquinone ring.<sup>13</sup>

The novelty in our work is that the chiral recognition between the  $D_3$   $\Delta$ -Trisphat anion and the cationic  $C_3$  chiral supramolecular host is manifested through this kind of  $\pi$ - $\pi$  interaction and strengthened by the favorable Coulombic interactions.

The stereochemical relationships between **3a** (*(R,R,R)*,  $\Delta$ ) and **3b** (*(S,S,S)*,  $\Delta$ ) were assigned by circular dichroism (Figure 4), in which we note that in both diastereomers the  $\Delta$ -Trisphat shows a characteristic negative Cotton effect centered at 240 nm.

At this stage a comment on the configurational stability at metal centers of these novel species is required. Preliminary studies in  $^1\text{H}$  NMR carried out at room temperature on samples 1 and 2 to study their evolution as function of time showed no interconversion or exchange in the ratio of the two diastereomers even after several days. This was also confirmed by circular dichroism studies. These results contrast completely with the behavior of the parent molecular host (**1**). For instance several authors have demonstrated that such metallomacrocycles are configurationally unstable and that the enantiomers epimerize at metal centers.<sup>4e</sup> We also note that Brunner and co-workers have studied the half-sandwich  $\text{Cp}^*\text{M}$  (M = Rh, Ir) complexes of the " $\text{Cp}^*\text{M}(\text{NN}^*)\text{Cl}$ " and " $\text{Cp}^*\text{M}(\text{ON}^*)\text{Cl}$ " types, where  $\text{NN}^*$  is the anion of (+)-2-*N*-[(*S*)-1-phenylethylpyrrolcarbaldimine] and  $\text{ON}^*$  is the anion of (+)-2-*N*-[(*S*)-1-phenylethylsalicylaldimine], and showed that such compounds are configurationally unstable at metal centers.<sup>14</sup>

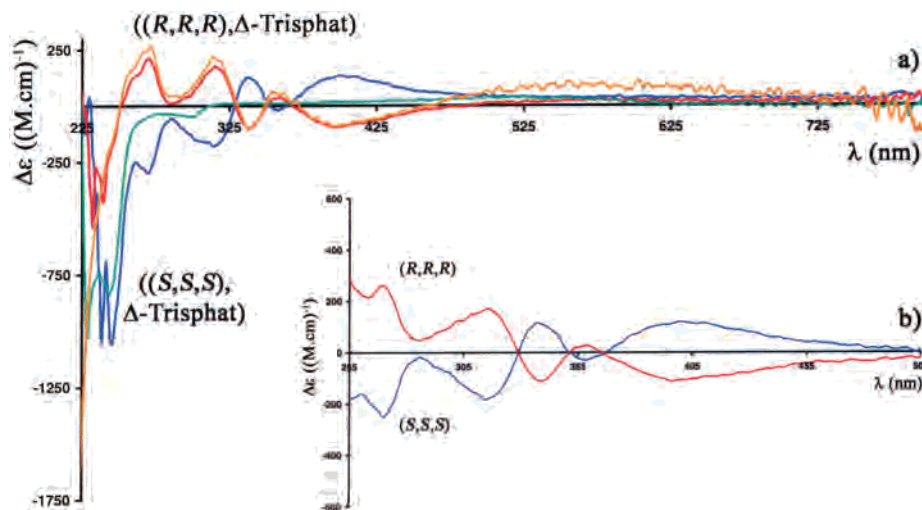
## Conclusion

In this paper, we reported the self-assembly of the racemic neutral metallomacrocyclic [Cp\*Rh(5-chloro-2,3-dioxopyridine)]<sub>3</sub> (**1**). Conversion to the related 1:1 mixture of the two diastereomers salt [LiC(*R,R,R*)-(Cp\*RhL)<sub>3</sub>][ $\Delta$ -Trisphat] (**3a**) and [LiC(*S,S,S*)-(Cp\*RhL)<sub>3</sub>][ $\Delta$ -Trisphat] (**3b**) was achieved through only three steps. Our results showed that enantiomer discrimination of supramolecular triangular hosts **3a,b** by

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**Figure 4.** (a) CD curves for analyzed crystal **3a** ((*R,R,R*),  $\Delta$ -Trisphat) (orange line), for sample 2, enriched **3a** ((*R,R,R*),  $\Delta$ -Trisphat) (red line), for sample 1 enriched **3b** ((*S,S,S*),  $\Delta$ -Trisphat) (blue line), and for [*n*-Bu<sub>4</sub>N][ $\Delta$ -Trisphat] (green line) recorded in CH<sub>2</sub>Cl<sub>2</sub> solution and at the same concentration (0.03 mM). (b) CD curves of only the two enantiomers (*R,R,R*) and (*S,S,S*) after subtraction of the curve due to the  $\Delta$ -Trisphat anion.

<sup>1</sup>H NMR using  $\Delta$ -Trisphat as a chiral shift reagent is possible. Furthermore, separation of these supramolecular rhodium trimers was successfully achieved. To the best of our knowledge this is the first demonstration in the area of supramolecular chemistry using  $\Delta$ -Trisphat as chiral auxiliary. We also reported the first X-ray molecular structure of one of the diastereomer **3a** displaying a direct observation of chiral recognition between the  $\Delta$ -Trisphat anion and the single enantiomer cation (*R*<sub>Rh</sub>,*R*<sub>Rh</sub>,*R*<sub>Rh</sub>) manifested by  $\pi$ - $\pi$  interaction between the  $\pi$ -deficient tetrachlorocatecholate ring and  $\pi$ -donor “Cp\**Rh*<sup>2+</sup>” moiety. We are currently pursuing our investigations on the configurational stability at metal centers of these trimeric salts and other related compounds. The results will be published in due course.

## Experimental Section

**Materials and Methods.** Unless otherwise stated, all reactions were performed under an argon atmosphere using standard Schlenk techniques but products were handled in air. [Cp\**Rh*( $\mu$ -Cl)Cl]<sub>2</sub>,<sup>15</sup> [*n*-Bu<sub>4</sub>N][ $\Delta$ -Trisphat],<sup>8h</sup> and [Cinchonidinium][ $\Delta$ -Trisphat]<sup>6b</sup> were prepared by literature procedures. Solvents were purified and dried prior to use by conventional distillation techniques. All reagents obtained from commercial sources were used without further purification. NMR spectra were recorded using a Bruker Avance 400 instrument. NMR chemical shifts are reported in parts per million referenced to the residual solvent proton/carbon resonance [<sup>1</sup>H] CD<sub>2</sub>Cl<sub>2</sub>, 5.32, CDCl<sub>3</sub>, 7.26; [<sup>13</sup>C] CD<sub>2</sub>Cl<sub>2</sub>, 53.1, CDCl<sub>3</sub>, 77.1]. The numbering system used for protons and carbons is shown on Scheme 1. Infrared spectra were obtained on a Bio-Rad IR-FT spectrophotometer from samples prepared on KBr disks. Specific rotations were measured at 20 °C, in a 1 dm cell using the sodium D-line of an America AA5 polarimeter. Circular dichroism spectra were recorded using a Jasco model J-710 spectropolarimeter. Elemental analyses were performed by the Microanalytical Laboratory of the Université Paris VI.

**Synthesis of [Cp\**RhL*]<sub>3</sub> (1).** [Cp\**Rh*( $\mu$ -Cl)Cl]<sub>2</sub> (0.203 g, 0.33 mmol), 5-chloro-2,3-dihydropyridine (**LH**<sub>2</sub>) (0.103 g, 0.70 mmol), and Cs<sub>2</sub>CO<sub>3</sub> (0.568 g, 1.74 mmol) were put in suspension in 25

mL of methanol. The mixture was stirred at room temperature for 4 h. Evaporation of methanol under reduced pressure gave a dark red solid. This solid was dissolved in CH<sub>2</sub>Cl<sub>2</sub>, and the suspension was filtered off. After evaporation under reduced pressure of CH<sub>2</sub>Cl<sub>2</sub> and drying in vacuo, a red product was obtained (quantitative yield). Anal. Calcd for C<sub>45</sub>H<sub>51</sub>N<sub>3</sub>O<sub>6</sub>Rh<sub>3</sub>Cl<sub>3</sub>·CH<sub>2</sub>Cl<sub>2</sub> (*M*<sub>r</sub> = 1229.9): C, 44.92; H, 4.43; N, 3.42. Found: C, 44.34; H, 4.44; N, 3.00. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 6.66 (1H, d, *J* = 2.4 Hz, H6), 6.15 (1H, d, *J* = 2.4 Hz, H4), 1.71 (s, 15H, Cp\*). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  = 169.7 (C2), 158.8 (C3), 127.8 (C6), 116.5 (C5), 114.8 (C4), 90.4 (d, *J*<sub>C-Rh</sub> = 8.6 Hz, C, Cp\*), 9.3 (CH<sub>3</sub>, Cp\*).

**Synthesis of [LiC(Cp\**RhL*)<sub>3</sub>][Cl].** [Cp\**RhL*]<sub>3</sub> (0.569 g, 0.497 mmol) and LiCl (0.421 g, 9.93 mmol) were put in suspension in 20 mL of CH<sub>2</sub>Cl<sub>2</sub> and stirred at room temperature for 4 h. A red solution was obtained by filtration. After evaporation under reduced pressure of CH<sub>2</sub>Cl<sub>2</sub> and drying in vacuo, a red product was obtained (0.458 g, yield 77%). Anal. Calcd for C<sub>45</sub>H<sub>51</sub>N<sub>3</sub>O<sub>6</sub>Rh<sub>3</sub>Cl<sub>4</sub>Li·2CH<sub>2</sub>Cl<sub>2</sub> (*M*<sub>r</sub> = 1357.2): C, 41.59; H, 4.08; N, 3.10. Found: C, 42.02; H, 4.47; N, 2.64. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz):  $\delta$  6.60 (1H, d, *J* = 2.0 Hz, H6), 6.29 (1H, d, *J* = 2.0 Hz, H4), 1.73 (s, 15H, Cp\*). <sup>7</sup>Li NMR (CD<sub>2</sub>Cl<sub>2</sub>, 155 MHz, reference  $\delta$  (LiOH/D<sub>2</sub>O) = 0 ppm):  $\delta$  -0.04 (s, Li<sup>+</sup>).

**Synthesis of [LiC(Cp\**RhL*)<sub>3</sub>][CF<sub>3</sub>SO<sub>3</sub>] (2).** [LiC(Cp\**RhL*)<sub>3</sub>][Cl] (0.400 g, 0.34 mmol) and AgCF<sub>3</sub>SO<sub>3</sub> (0.087 g, 0.34 mmol) were put in suspension in 20 mL of CH<sub>2</sub>Cl<sub>2</sub>. The red mixture was stirred for 30 min and filtered off. After evaporation under reduced pressure of CH<sub>2</sub>Cl<sub>2</sub> and drying in vacuo, a dark red product was obtained (0.380 g, yield 87%). Anal. Calcd for C<sub>46</sub>H<sub>51</sub>N<sub>3</sub>O<sub>9</sub>Rh<sub>3</sub>Cl<sub>3</sub>LiF<sub>3</sub>S·2CH<sub>2</sub>Cl<sub>2</sub> (*M*<sub>r</sub> = 1470.9): C, 39.20; H, 3.77; N, 2.86. Found: C, 39.86; H, 4.33; N, 2.85. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz):  $\delta$  6.68 (1H, d, *J* = 2.3 Hz, H6), 6.42 (1H, d, *J* = 2.3 Hz, H4), 1.69 (s, 15H, Cp\*). <sup>7</sup>Li NMR (CD<sub>2</sub>Cl<sub>2</sub>, 155 MHz, reference  $\delta$  (LiOH/D<sub>2</sub>O) = 0 ppm):  $\delta$  -0.1 (s, Li<sup>+</sup>). <sup>19</sup>F NMR (CD<sub>2</sub>Cl<sub>2</sub>, 376 MHz, reference  $\delta$  (CFCl<sub>3</sub>/CDCl<sub>3</sub>) = 0 ppm):  $\delta$  -79.2 (s, CF<sub>3</sub>SO<sub>3</sub>). IR (KBr disk, cm<sup>-1</sup>): ( $\nu$ <sub>C-F</sub>) 1240.

**Synthesis of [LiC(*R,R,R*)-(Cp\**RhL*)<sub>3</sub>][ $\Delta$ -Trisphat] (3a) and [LiC(*S,S,S*)-(Cp\**RhL*)<sub>3</sub>][ $\Delta$ -Trisphat] (3b).** [LiC(Cp\**RhL*)<sub>3</sub>][CF<sub>3</sub>SO<sub>3</sub>] (0.430 g, 0.33 mmol) and [Cinchonidinium][ $\Delta$ -Trisphat] (1.07 g, 1 mmol) were deposited on a neutral alumina column and eluted with CH<sub>2</sub>Cl<sub>2</sub>. The first fraction was evaporated giving a red product (0.382 g, yield 60%). Anal. Calcd for C<sub>63</sub>H<sub>51</sub>N<sub>3</sub>O<sub>12</sub>Rh<sub>3</sub>Cl<sub>15</sub>LiP (*M*<sub>r</sub> = 1919.4): C, 39.40; H, 2.68; N, 2.19. Found: C, 39.66; H, 3.03;

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N, 2.03.  $^1\text{H}$  NMR (**3a**) ( $\text{CD}_2\text{Cl}_2/\text{toluene-}d_8$  (75/25), 400 MHz):  $\delta$  6.97 (1H, d,  $J = 2.4$  Hz, H6), 6.74 (1H, d,  $J = 2.3$  Hz, H4), 1.82 (s, 15H, Cp\*).  $^1\text{H}$  NMR (**3b**) ( $\text{CD}_2\text{Cl}_2/\text{toluene-}d_8$  (75/25), 400 MHz):  $\delta$  7.02 (1H, d,  $J = 2.4$  Hz, H6), 6.79 (1H, d,  $J = 2.4$  Hz, H4), 1.853 (s, 15H, Cp\*).  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 100 MHz):  $\delta$  164.6 (C2), 156.9 (C3), 141.4 (d,  $^2J_{\text{C}-\text{P}} = 6.4$  Hz, C10,  $\Delta$ -Trisphat), 127.5 (C6), 122.1 (C12,  $\Delta$ -Trisphat), 121.2 (C5), 119.0 (C4), 113.1 (d,  $^3J_{\text{C}-\text{P}} = 19.7$  Hz, C11,  $\Delta$ -Trisphat), 92.1 (d,  $J_{\text{C}-\text{Rh}} = 8.8$  Hz, C, Cp\*), 8.7 ( $\text{CH}_3$ , Cp\*).  $^7\text{Li}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 155 MHz, reference  $\delta$  (LiOH/D $_2$ O) = 0 ppm):  $\delta$  0.2 (s, Li $^+$ ).  $^{31}\text{P}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 162 MHz):  $\delta$  -79.9 (s, P,  $\Delta$ -Trisphat). IR (KBr disk,  $\text{cm}^{-1}$ ): ( $\nu_{\text{P}-\text{O}, \Delta\text{-Trisphat}}$ ) 992, ( $\nu_{\text{C}-\text{Cl}, \Delta\text{-Trisphat}}$ ) 825, ( $\nu_{\text{C}-\text{Cl}, \Delta\text{-Trisphat}}$ ) 668.

**Separation of 3a,b by Fractional Crystallization.** A 100 mg amount of **3a,b** was dissolved in  $\text{CH}_2\text{Cl}_2$  (10 mL), and the system was left to crystallize with  $\text{Et}_2\text{O}$  through the slow evaporation method. After 2 weeks, an orange precipitate (sample 1) was formed and filtered off (ee 74% in **3b**,  $m = 36$  mg). The  $[\alpha]_{\text{D}}^{293}$  value for this sample is +61 ( $c = 0.0164$ ,  $\text{CH}_2\text{Cl}_2$ ). The filtrate was left to crystallize again. After 2 days, orange crystals were obtained and separated from the solution to give sample 2 (ee 90% in **3a**,  $m = 33$  mg). The  $[\alpha]_{\text{D}}^{293}$  value for this sample is -577 ( $c = 0.0156$ ,  $\text{CH}_2\text{Cl}_2$ ). The last sample did not show any crystals even after several weeks. The solvent was removed under vacuum (ee 28% in **3b**,  $m = 26$  mg).

**X-ray Crystallography for 1.** Red crystals were grown by slow diffusion of pentane into a toluene solution **1**. The selected crystal was protected by paratone oil and Araldite and then mounted onto the top of a glass rod. The data were collected at room temperature on a Nonius KappaCCD diffractometer with graphite-monochromated Mo K $\alpha$  radiation. The Nonius Supergui program package was used for cell refinement and data reduction. The structure was solved by direct methods and subsequent difference Fourier

syntheses and refined by full-matrix least squares on  $F$  using the programs of the PC version of CRYSTALS.<sup>16</sup> All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced in calculated positions in the last refinements and were allocated an overall refinable isotropic thermal parameter. See Tables 1 and 2.

**X-ray Crystallography for 3a.** Red crystals were grown by slow evaporation of a toluene/ $\text{CH}_2\text{Cl}_2$  solution of sample 2. The crystals were fragile and easily loose included solvent upon exposure to air. The selected crystal was protected by paratone oil and Araldite and then mounted onto the top of a glass rod. The data were collected at 180 K on a Nonius KappaCCD diffractometer with graphite-monochromated Mo K $\alpha$  radiation. The Nonius Supergui program package was used for cell refinement and data reduction. The structure was solved by direct methods and subsequent difference Fourier syntheses and refined by full-matrix least-squares on  $F$  using the programs of the PC version of CRYSTALS.<sup>16</sup> The asymmetric unit contained the rhodium complex, the  $\Delta$ -Trisphat anion, three toluene molecules, one  $\text{CH}_2\text{Cl}_2$  molecule, and 2.5  $\text{H}_2\text{O}$  molecules. Rhodium, phosphorus, and chlorine atoms were refined anisotropically. Other atoms were refined isotropically. Hydrogen atoms were introduced in calculated positions in the last refinements and were allocated an overall refinable isotropic thermal parameter.

**Acknowledgment.** This research was made possible by a grant to L.M. from the MRT (Ministère de la Recherche et de la Technologie), to whom we are very grateful. We thank Professor Kamal Boubekeur for much help in X-ray crystallography and the CNRS and UPMC for supporting this work.

**Supporting Information Available:** X-ray data (in CIF format) for **1** and **3a**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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