Chiral Supramolecular Triangular Hosts: Anion Metathesis, Solution Behavior, and High Stability of the Metal Configuration

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The chiral supramolecular rhodium triangular hosts [Li⊂(*R*,*R*,*R*)-{Cp*Rh(5-chloro-2,3-dioxopyridine)}$_3$][Δ-Trisphat] (**8a**) and [Li⊂(*S*,*S*,*S*)-{Cp*Rh(5-chloro-2,3-dioxopyridine)}$_3$][Δ-Trisphat] (**8b**) have been prepared and separated by fractional crystallization. ^{1}H NMR studies carried out on **8b** showed that a slow epimerization process occurs at room temperature, which after 90 days produces approximately a 1:1 mixture of **8a**,**b**, suggesting that the configurational stability is highly enhanced in the trimer host compared to analogous chiral mononuclear species.

Introduction

Half-sandwich compounds with three-legged piano stool geometry with different substituents are archetypal examples of optically active chiral-at-metal complexes.[1] Pioneering work of Brunner et al. on the preparation and resolution of the racemate (*R*,*S*)-[CpMn(CO)(NO)(PPh$_3$)][PF$_6$] by converting the pair of enantiomers into a pair of diastereomers using the optically active alcohol (1*R*,3*R*,4*S*)-menthol gave an impetus to the development of modern chiral organometallic chemistry.[2] Another important contribution to this field was provided by Gladysz et al. on the preparation of optically active organorhenium Lewis acid complexes [CpRe(L)(NO)(PPh$_3$)][BF$_4$] (L = CH$_2$Cl$_2$, C$_6$H$_5$Cl) and their use in chiral recognition toward alkenes, aldehydes, and ketones.[1a,3] Although examples of chiral control in mononuclear systems are well known, less is known about chiral control in self-assembled supramolecular cages incorporating half-sandwich metal subunits.[4] We note, however, 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.[5] Self-assembly of chiral metallo-macrocycles and their use as hosts for metal catalysts are considered a hot, challenging field.[6]

Pursuing our research in the area of self-assembly of chiral metallo-macrocycles, we prepared several neutral trimers of the general formula [(η-ring)ML]$_3$ {with (η-ring)M = Cp*Rh (**1**), Cp*Ir (**2**), and (*p*-cymene)Ru (**3**)}, which are obtained as racemic mixture.[7,9a] The aim of this work is to investigate the homochiral self-assembly in this class of supramolecular triangular hosts as well as the epimerization process ($R_MR_MR_M \leftrightarrows S_MS_MS_M$) using an external optically pure anion (Figure 1) that can form a strong ion-pairing with the supramolecular cationic species and acts as a chiral probe to monitor the racemization process of the cationic part. To our knowledge, this is the only known example where the trimer assembly exhibits a $\pi-\pi$ interaction with the external chiral probe. All previous studies on related tricationic rhodium and iridium species featured chiral bridging ligands that are part of the supramolecular complex and therefore cannot provide a detailed study on the epimerization at the metal center, which is controlled by the chiral nature of the bridging ligand.[8]

In this work we present the general synthetic approach that leads to the formation of a 1:1 mixture of the two diastereomers of triangular metallo-macrocycles [Li⊂(*R*,*R*,*R*)-{(η-ring)ML}$_3$][Δ-Trisphat] and [Li⊂(*S*,*S*,*S*)-{(η-ring)ML}$_3$][Δ-Trisphat]. The key step in this synthesis is the metathesis of the triflate anion of the racemic precursors [Li⊂{(η-ring)ML}$_3$][OTf] by the chiral anion Δ-Trisphat (Figure 1) to give the target 1:1 mixture of the two diastereomeric complexes. Among the chiral triangular hosts investigated, only the rhodium metallo-macrocycle undergoes a smooth anion metathesis reaction, providing a 1:1 mixture of the two diastereomers of triangular metallo-macrocycles [Li⊂(*R*,*R*,*R*)-{Cp*Rh(5-chloro-2,3-dioxopyridine)}$_3$][Δ-Trisphat] (**8a**) and [Li⊂(*S*,*S*,*S*)-{Cp*Rh(5-chloro-2,3-dioxopyridine)}$_3$][Δ-Trisphat] (**8b**). The quest for successful anion metathesis and ion-pairing in this family of triangular hosts is presented and discussed. Part of this work has been recently

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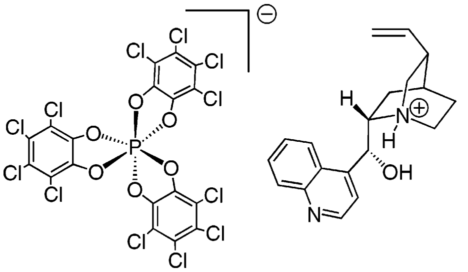

Figure 1. [Cinchonidinium][Δ-Trisphat].

published.[9a] Further ^{1}H NMR studies carried out on **8b** in a sealed NMR tube showed that a slow racemization process occurs at 290 K ($k = 1.682 \times 10^{-7}$ s^{-1}; $\Delta G^{\ddagger} = 108.6$ kJ mol^{-1}), which after 90 days produces approximately a 1:1 mixture of **8a**,**b**, suggesting that the configurational stability of the metal center is high in the trimer host compared to analogous chiral mononuclear species.

Results and Discussion

(1) Synthesis, Characterization, and X-ray Molecular Structures of 2 and 8a. The racemic triangular metallo-macrocycles (**1**−**3**) were prepared as described by previous procedures. Complexes **1** and **3** were already reported by us[9] and others,[7] and the iridium complex [Cp*IrL]$_3$ (**2**) was obtained in quantitative yield from [Cp*Ir(μ-Cl)Cl]$_2$ and 5-chloro-2,3-dihydroxypyridine (**LH$_2$**) in the presence of Cs_2CO_3 in MeOH. The X-ray molecular structure of **2** was determined (Figure 2) and confirms the formation of the metallo-macrocycle. Complex **2** crystallizes in the monoclinic unit cell with space group $P2_1/n$. Toluene molecules are also present in the crystals. As in previous structures of this family, the assembling ligand **L** chelates one metal center by two oxygen atoms and acts as a monodentate ligand to the adjacent metal through the nitrogen atom. The three "Cp*Ir^{2+}" dicationic moieties and the three dianionic ligands are arranged in an alternate fashion, thus providing a neutral metallo-macrocycle.

Surprisingly, reaction of **2** with LiCl led to the formation of labile [(Cp*IrL)$_3$LiCl], which existed in equilibrium with the starting material **2**. In contrast, the ruthenium and rhodium macrocycles provided stable complexes [(Cp*RhL)$_3$LiCl] (**4**) and [((*p*-cymene)RuL)$_3$LiCl] (**5**) (Scheme 1).

In complexes **4** and **5**, abstraction of the chloride was achieved by treatment with AgOTf, giving the related compounds [{Cp*RhL}$_3$LiOTf] (**6**) and [{(*p*-cymene)RuL}$_3$LiOTf] (**7**). The novel compound **7** was completely characterized by spectroscopic methods and elemental analysis (see Experimental Section). Most remarkably the ^{7}Li NMR showed a singlet at δ −0.68 ppm, diagnostic of lithium bound by the neutral host.[7,9]

Conversion of the racemic precursors **6** and **7** to a 1:1 mixture of two diastereomeric macrocycles [Li⊂(*R*,*R*,*R*)-{(ring)ML}$_3$][Δ-Trisphat] and [Li⊂(*S*,*S*,*S*)-{(ring)ML}$_3$][Δ-Trisphat] was attempted by eluting a mixture of **6** or **7** and an excess of [cinchonidinium][Δ-Trisphat] through a neutral alumina column (Scheme 1). Surprisingly in complex **7**, the exchange of the triflate anion by the Δ-Trisphat was not successful. However the rhodium macrocycle [{Cp*RhL}$_3$LiOTf] (**6**) provided a 1:1 mixture of the target complexes [(R_{Rh}, R_{Rh}, R_{Rh}), Δ] (**8a**) and [(S_{Rh}, S_{Rh}, S_{Rh}), Δ] (**8b**) after anion exchange. Fractional crystallization of the 1:1 mixture of **8ab** from CH_2Cl_2/Et_2O provided, after several days, orange crystals, which were separated and dried under vacuum. The sample was analyzed by ^{1}H NMR in CD_2Cl_2/toluene-d_8 (75:25) and showed the presence of a major singlet at δ 1.883 ppm attributed to the methyl protons of "Cp*Rh" and identified as enriched [(S_{Rh}, S_{Rh}, S_{Rh}), Δ] (**8b**) (de ≈ 95%), while most of the other diastereomer remained in solution. We note that in this mixture of deuterated solvent the ion-pairing is strong enough to allow a differentiation between **8a** and **8b**.

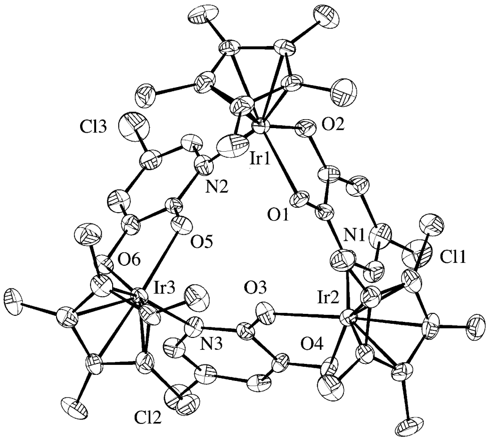

Figure 2. CAMERON view of **2** at the 30% probability level showing the atom-numbering system. Selected bond distances (Å) and angles (deg): Ir(1)−O(1) 2.111(7), Ir(1)−O(2) 2.064(8), Ir(2)−O(3) 2.112(8), Ir(2)−O(4) 2.065(7), Ir(3)−O(5) 2.113(7), Ir(3)−O(6) 2.076(8), Ir(1)−N(3) 2.129(9), Ir(2)−N(1) 2.096(9), Ir(3)−N(2) 2.138(9); O(1)−Ir(1)−N(3) 87.8(3), N(1)−Ir(2)−O(3) 86.9(3), O(5)−Ir(3)−N(2) 84.8(3).

The X-ray molecular structure of **8a** was recently reported by us[7] (see Figure 3) and shows, as an outstanding feature, a chiral recognition between the Δ-Trisphat anion and a single enantiomer cation, [Li⊂(*R*,*R*,*R*){Cp*Rh(5-chloro-2,3-dioxopyridine)}$_3$]$^+$, manifested through a $\pi-\pi$ interaction. Complex **8a** crystallizes in the chiral space group $P2_12_12_1$. The absolute configuration of the molecules in the structure was confirmed by refining the Flack's *x* parameter, which was equal to 0.01(7), attesting to the enantiopure character of the crystal. This example represented the first direct evidence of chiral recognition in the solid state between the chiral Δ-Trisphat anion and the supramolecular metallo-macrocycle.[9] Although several examples have been reported in the literature[10] and in recent reviews[11] in which the chiral Δ-Trisphat anion was used to differentiate between enantiomers of organometallic and coordination complexes, none of these examples featured a chiral host−guest supramolecular system.

(2) Anion Metathesis. In order to understand the reasons that govern the success or failure of the anion metathesis process in this family of chiral triangular hosts, we investigated and compared the structures of the triflate precursors [{Cp*RhL}$_3$LiOTf] (**6**) and [{(*p*-cymene)RuL}$_3$LiOTf] (**7**). We feel that a strong interaction or a covalent bond Li−X ($X^- = Cl^-$, OTf^-) versus an ionic form Li^+/X^- in solution could be important in the success of replacement of the anion X by

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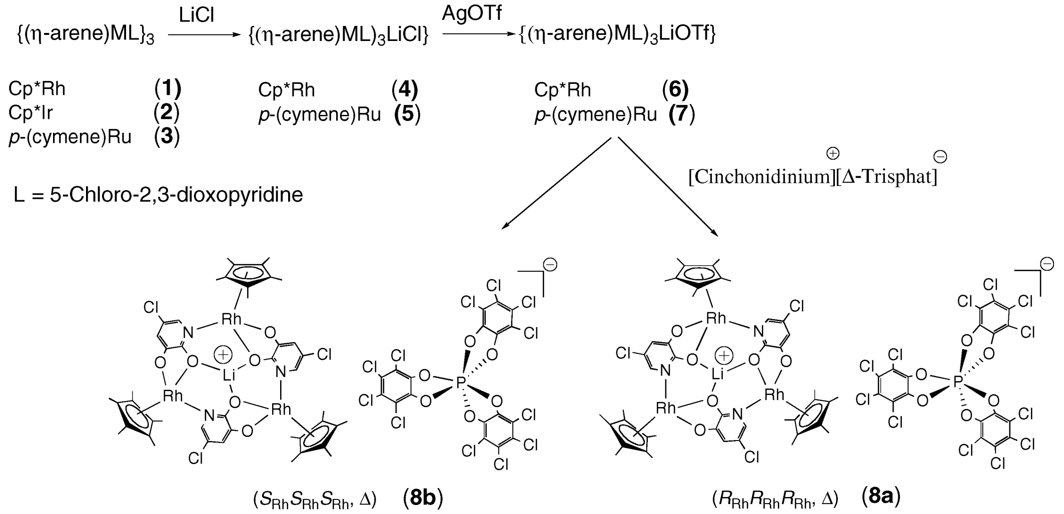
Scheme 1



Δ-Trisphat. The structure of [{(*p*-cymene)RuL}$_3$LiCl} (**5**) has been reported[7a] and shows that in the solid state the encapsulated Li$^+$ is also bonded to the chloride atom. Further the ^{7}Li NMR spectrum recorded in CD$_2$Cl$_2$ for **5** shows a singlet at δ −0.64 ppm, which is very close to that of [{(*p*-cymene)RuL}$_3$LiOTf] (**7**), with δ −0.68 ppm. The ^{19}F NMR of **7** recorded in CD$_2$Cl$_2$ showed a signal at δ −77.4 ppm diagnostic of coordinated triflate, while **6** under the same conditions gave a signal at δ −79.2 ppm.[12] These results may suggest that the ion-pairing between Li/OTf in **7** is much stronger than that in **6**, and hence anionic metathesis with Δ-Trisphat occurs only with a rhodium triangular host and not the analogous ruthenium macrocycle. Chromatography of **7** in the presence of even 10 equiv. of [cinchonidinium][Δ-Trisphat] led to the formation of a small amount of [{(*p*-cymene)RuL}$_3$Li][Δ-Trisphat] (ca. 10%) and recovery of the starting material **7**. Attempts to separate the Δ-Trisphat complex from **7** by successive chromatography led to the decomposition of the ruthenium metallo-macrocycle.

NMR Analysis of the Epimerization Process of the Triangular Rhodium Hosts 8a,b. Previous studies of the solution behavior of chiral trimers [(η-ring)M(Aa)]$_3$[BF$_4$]$_3$ where Aa is an optically pure amino acidate with either L or D configuration have been reported.[8] In fact the metal centers in these trimers adopted a preferential configuration imposed by the optically pure ligand. For instance in the solid state $R_MR_MR_M$ diastereomers were observed for rhodium and iridium centers with various amino acidate ligands; however for prolinate compounds the $S_MS_MS_M$ diastereomers were favored. In our system the chiral auxiliary Δ-Trisphat is a free anion and not covalently linked to the trimer structure as in the previous examples. Thus it acts as a chiral probe for a detailed analysis of the cation racemization process ($R_MR_MR_M \leftrightarrows S_MS_MS_M$).

When a sealed NMR tube of **8b** was left at 60 °C overnight, complete epimerization was observed by ^{1}H NMR spectroscopy, which showed a new singlet at δ 1.887 ppm attributed to the η^5-Cp*Rh of [(R_{Rh}, R_{Rh}, R_{Rh}), Δ] (**8a**). One of the two pyridine protons showed partial splitting, which is consistent with the inequivalence of the η^5-Cp*Rh protons of the diasteriosomers due to $\pi-\pi$ stacking with a phenyl ring of the Δ-Trisphat anion as observed in the X-ray molecular structure;[9] however due to overlap of signals, this signal could not be used to quantitatively analyze the epimerization process.

Monitoring the kinetic evolution of the spectrum in a sealed NMR tube for a period of 90 days thermostated at 290 K allowed us to observe a slow epimerization process of **8b** and the formation of the diastereomer [(R_{Rh}, R_{Rh}, R_{Rh}), Δ] (**8a**) with a new singlet at δ 1.887 ppm that gradually increased during racemization (Figure 4).

Due to the overlap of the two C$_5$Me$_5$ signals, integration could not be reliably used to obtain their relative intensities, and fitting to two Lorentzian curves was used (see Figure 4b). The fit[13b] yielded a first-order rate constant of 1.5×10^{-2} d^{-1} or 1.7×10^{-7} s^{-1}. This corresponds to a $\Delta G^{\ddagger} = 109$ kJ mol^{-1} and the half-life of **8b** in CD$_2$Cl$_2$/CD$_3$C$_6$D$_5$ solution at 290 K is 19 days on the basis of going halfway to equilibrium. The experimental mole fractions and calculated curves for χ_{Rh-S} and χ_{Rh-R} (see Supporting Information) are given in Figure 5.

It has been reported that [(η^5-C$_5$Me$_5$)Rh(NH$_2$CHBu^{t}CO$_2$)(PPh$_3$)][BF$_4$] epimerizes with $\Delta H^{\ddagger} = 88.7$ kJ mol^{-1} and $\Delta S^{\ddagger} = -24.9$ JK^{-1} mol^{-1},[8] corresponding to $\Delta G^{\ddagger}_{290} = 95.9$ kJ mol^{-1}, which is comparable with $\Delta G^{\ddagger}_{290}$ for the cation racemization of **8**. The proposed mechanism involved ligand dissociation to give a 16-electron intermediate. It was also reported that a mixture of [{(η^5-C$_5$Me$_5$)Rh(NH$_2$CHBu^{t}CO$_2$)}$_3$][BF$_4$]$_3$ and [{(η^5-C$_5$Me$_5$)Ir(NH$_2$CHBu^{t}CO$_2$)}$_3$][BF$_4$]$_3$ readily equilibrates even at −84 °C to give a mixture of [{(η^5-C$_5$Me$_5$)Rh(NH$_2$CHBu^{t}CO$_2$)}$_{3-n}${(η^5-C$_5$Me$_5$)Ir(NH$_2$CHBu^{t}CO$_2$)}$_n$][BF$_4$]$_3$, $n = 0$ to 3, and a mechanism involving dissociation into monomers was suggested. It is probable that the first step of the racemization of the cationic part of **8** involves bond dissociation at one rhodium to give a 16-electron intermediate. In theory, this could produce [(S_{Rh}, R_{Rh}, R_{Rh}), Δ] and [(S_{Rh}, S_{Rh}, R_{Rh}), Δ] intermediates, but using molecular models, such species appear to be under high strain and are therefore unlikely. It therefore seems reasonable to propose a mechanism for **8** similar to that reported for the tricationic species (vide supra) which involves complete decoordination of the Li$^+$ followed by dissociation into monomers. Subsequent self-assembly produces the other diastereomer.

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[13] (a) Derived from eq 1.48 in: Wilkins, R. G. *Kinetics and Mechanisms of Reactions of Transition Metal Complexes*, 2nd ed.; VCH: Weinhein, 1991; p 13. (b) Excel was used to calculate $(\chi_{Rh-S})_t$ as a function of time, *t*, rate constant, *k*, $(\chi_{Rh-S})_0$, and $(\chi_{Rh-S})_e$. The sum of the squares of the error between calculated and experimental was minimized using the Solver function in Excel with *k*, $(\chi_{Rh-S})_0$, and $(\chi_{Rh-S})_e$ as variables. The best fit was obtained with χ_{Rh-S} (equilibrium) = 0.52, implying a small optical induction by the Δ-Trisphat anion. However, in view of the errors involved in determining the intensities of the diastereomers, this induction cannot be considered to be significant.

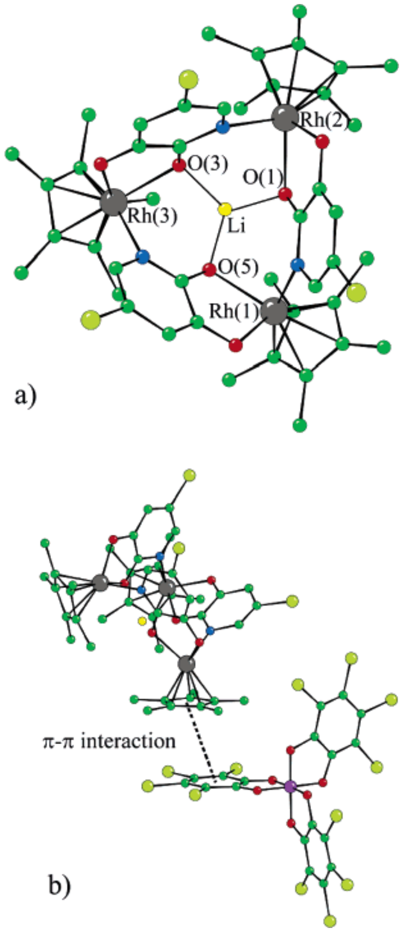

Figure 3. (a) Frontal projection of the cationic part of **8a** showing Li^+ encapsulation with the atom-numbering system and (b) sideways projection of **8a** showing the $\pi-\pi$ interaction between Δ-Trisphat and triangular host.

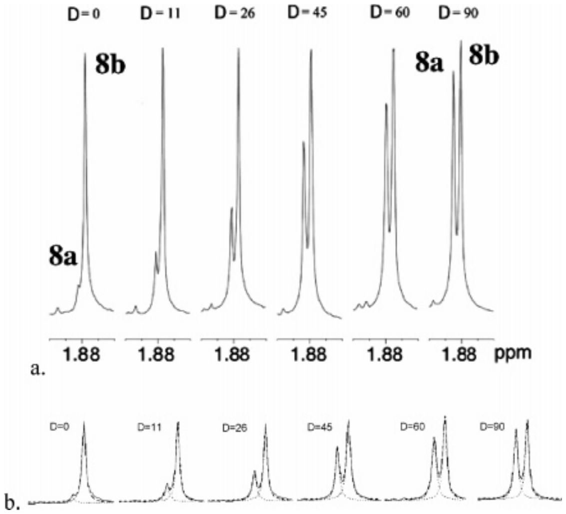

Figure 4. Partial 500 MHz ^{1}H NMR spectrum of **8b** in CD_2Cl_2/$CD_3C_6D_5$ at 290 K as a function of time showing the C_5Me_5 signal. D = days. (a) Experimental spectra. (b) Lorentzian fit of the two signals.

In summary we have reported the synthesis of a family of chiral triangular hosts [(η-ring)ML]$_3$ and their triflate salts [{Cp*RhL}$_3$LiOTf] (**6**) and [{(*p*-cymene)RuL}$_3$LiOTf] (**7**). Conversion to the 1:1 diastereomers is achieved by OTf metathesis by the Δ-Trisphat anion and depends on the strength and nature of the Li- - -OTf interaction. In this context complex **7** failed to react. In contrast, smooth conversion of **6** to 1:1 [Li⊂(*R*,*R*,*R*)-{Cp*Rh(5-chloro-2,3-dioxopyridine)}$_3$][Δ-Trisphat] (**8a**) and [Li⊂(*S*,*S*,*S*)-{Cp*Rh(5-chloro-2,3-dioxopyridine)}$_3$][Δ-Trisphat] (**8b**) occurred. Resolution of the chiral supramolecular rhodium trimer host (**8a**,**b**) was performed, and the epimerization process was monitored by ^{1}H NMR spectroscopy. Remarkably the configurational stability at the rhodium center in **8** is very high compared to the monomers of half-sandwich Cp*M compounds with three-legged piano stool geometry. In fact **8b**, at 290 K requires 90 days to achieve approximately a 1:1 mixture of the two diastereomers **8a**,**b**. A mechanism involving dissociation of the cationic [(R_{Rh}, R_{Rh}, R_{Rh})]$^+$ part of **8a** into monomers followed by epimerization and subsequent self-assembly providing the other enantiomer, [(S_{Rh}, S_{Rh}, S_{Rh})]$^+$, is proposed.

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(μ-Cl)Cl)]$_2$,[14] [Cp*Ir(μ-Cl)Cl]$_2$,[14] [{Cp*Rh(5-chloro-2,3-dioxopyridine)}$_3$] (**1**), [{(*p*-cymene)Ru(5-chloro-2,3-dioxopyridine)}$_3$] (**3**), [{Cp*Rh(5-chloro-2,3-dioxopyridine)}$_3$LiCl] (**4**), [{(*p*-cymene)Ru(5-chloro-2,3-dioxopyridine)}$_3$LiCl] (**5**), [{Cp*Rh(5-chloro-2,3-dioxopyridine)}$_3$ LiOTf] (**6**), [*n*-Bu$_4$N][Δ-Trisphat],[10h] and [cinchonidinium][Δ-Trisphat][15] were prepared by literature procedures.[7,9a] 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 Bruker 400 MHz and DRX-500 MHz instruments. NMR chemical shifts are reported in parts per million referenced to the residual solvent proton/carbon resonance [(^{1}H) CD_2Cl_2, 5.32; $CD_3C_6D_5$, 7.26]. Infrared spectra were obtained on a Bio-Rad IR-FT spectrophotometer from samples prepared on KBr disks. Elemental analyses were performed by the Microanalytical Laboratory of the Université Paris VI.

Synthesis of [{Cp*Ir(5-chloro-2,3-dioxopyridine)}$_3$] (2). [Cp*Ir(μ-Cl)Cl]$_2$ (0.402 g, 0.5 mmol), 5-chloro-2,3-dihydroxypyridine (**LH$_2$**) (0.152 g, 1.0 mmol), and Cs_2CO_3 (0.881 g, 2.7 mmol) were put in suspension in 25 mL of methanol. The mixture was stirred at room temperature for 12 h. Evaporation of methanol under reduced pressure gave a dark yellow solid. This solid was dissolved in CH_2Cl_2 and the suspension was filtered off. After evaporation under reduce pressure of CH_2Cl_2 and drying in vacuo, a yellow-orange product was obtained. Yield: 98% (0.461 g, 0.3 mmol). Anal. Calcd for $C_{45}H_{51}N_3O_6Ir_3Cl_3$ (1413 g mol^{-1}): C, 38.25; H, 3.64; N, 2.97. Found: C, 38.11; H, 3.52; N, 2.90. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.72 (1H, d, J = 2.5 Hz, H6), 6.23 (1H, d, J = 2.4 Hz, H4), 1.66 (s, 15H, Cp*). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 172.0 (C2), 159.7 (C3), 128.2 (C6), 117.2 (C5), 115.8 (C4), 81.5 (Cp*), 9.5 (CH_3, Cp*).

Synthesis of [{(*p*-cymene)Ru(5-chloro-2,3-dioxopyridine)}$_3$ LiOTf] (7). [{(*p*-cymene)Ru(5-chloro-2,3-dioxopyridine)}$_3$LiCl] (**5**) (0.689 g, 0.585 mmol) and $AgCF_3SO_3$ (0.150 g, 0.585 mmol) were put in suspension in 20 mL of CH_2Cl_2. The orange suspension was stirred for 60 min and filtered off. After evaporation under reduce pressure of CH_2Cl_2 and drying in vacuo, an orange product was obtained. Yield: 99% (0.752 g, 0.58 mmol). Anal. Calcd for $C_{46}H_{48}N_3O_9Ru_3Cl_3LiF_3S$ (1291.6 g mol^{-1}): C, 42.75; H, 3.74; N, 3.25. Found: C, 42.88; H, 3.51; N, 3.02. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 6.72 (1H, d, J = 2.4 Hz, H6), 6.29 (1H, br, aromatic *p*-cymene), 5.85 (1H, d, J = 5.9 Hz, aromatic *p*-cymene), 5.80 (1H, d, J = 5.0 Hz, aromatic *p*-cymene) (1H, d, J = 2.3 Hz, H4), 4.93

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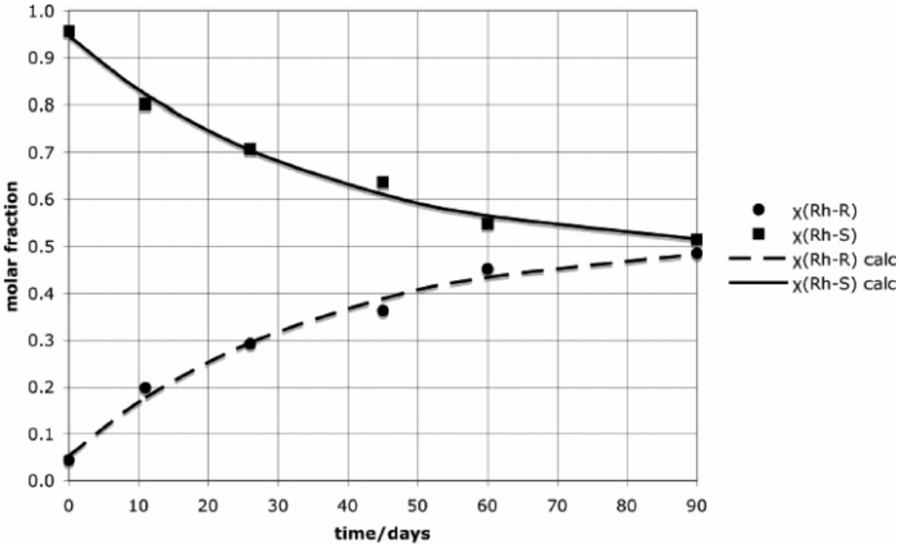

Figure 5. Plot of the relative mole fractions of [(R_{Rh}, R_{Rh}, R_{Rh}), Δ] (**8a**), ● χ(Rh−R), and [(S_{Rh}, S_{Rh}, S_{Rh}), Δ] (**8b**), ■ χ(Rh−S), as a function of time along with the best fit first-order kinetics at 290 K.

(1H, br, aromatic *p*-cymene), 2.76 (1H, m, H7, *p*-cymene), 1.74 (3H, s, H10, *p*-cymene), 1.32 (6H, dd, $J = 7.0$ Hz, $J = 9.8$ Hz, H8,9, *p*-cymene). ^{13}C{^{1}H} NMR (CD_2Cl_2, 100 MHz): δ 166.5 (C2), 156.2 (C3), 129.0 (C6), 119.3 (C5), 117.7 (C4), 99.0 (C1, *p*-cymene), 97.0 (C4, *p*-cymene), 84.0 (C3, *p*-cymene), 82.0 (C5, *p*-cymene), 77.0 (C6, *p*-cymene), 74.0 (C2, *p*-cymene), 31.1 (C7, *p*-cymene), 23.0 (C8 or C9, *p*-cymene), 21.5 (C8 or C9, *p*-cymene), 17.7 (C10, *p*-cymene). ^{7}Li NMR (CD_2Cl_2, 155 MHz, reference: δ ($LiOH/D_2O$) = 0 ppm): δ −0.68 (s, Li^+). ^{19}F NMR (CD_2Cl_2, 376 MHz, reference: δ ($CFCl_3/CDCl_3$) = 0 ppm): δ −77.9 (s, CF_3SO_3). IR (KBr disk, cm^{-1}): (ν_{C-F}) 1240, 1197; (ν_{SO}) 1035.

Separation of 8a and 8b by Fractional Crystallization. Fifty milligrams of **8a**,**b** was dissolved in CH_2Cl_2 (10 mL), and the system was left to crystallize with Et_2O through a slow evaporation method. After 8 days, orange crystals (sea urchin) were formed and filtered off (de 95% in **8b**, $m = 26$ mg). The filtrate was left to crystallize again. No crystals were formed; thus the solvent was removed by evaporation to yield enriched **8a**. Anal. Calcd for $C_{63}H_{51}N_3O_{12}Rh_3Cl_{15}LiP$ (1919.4 g mol^{-1}): C, 39.40; H, 2.68; N, 2.19. Found: C, 39.66; H, 3.03; N, 2.03. ^{1}H NMR (**8a**) (CD_2Cl_2/toluene-d_8 (75/25), 400 MHz): δ 7.02 (1H, d, $J = 2.4$ Hz, H6), 6.79 (1H, d, $J = 2.4$ Hz, H4), 1.887 (s, 15H, Cp*). ^{1}H NMR (**8b**) (CD_2Cl_2/toluene-d_8 (75/25), 400 MHz): δ 6.97 (1H, d, $J = 2.4$ Hz, H6), 6.74 (1H, d, $J = 2.3$ Hz, H4), 1.883 (s, 15H, Cp*). ^{7}Li NMR (CD_2Cl_2, 155 MHz, reference: δ ($LiOH/D_2O$) = 0 ppm): δ 0.2 (s, Li^+). ^{31}P NMR (CD_2Cl_2, 162 MHz): δ −79.9 (s, P, Δ-Trisphat). IR (KBr disk, cm^{-1}): ($\nu_{P-O,\ \Delta-Trisphat}$) 992, ($\nu_{C-Cl,\ \Delta-Trisphat}$) 825, ($\nu_{C-Cl,\ \Delta-Trisphat}$) 668.

X-ray Crystallography for 2. Orange crystals were grown by slow diffusion of pentane into a toluene solution of **2**. 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 Kα 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.[16] All non-hydrogen atoms were refined anisotropically except those of the toluene molecules. The hydrogen atoms were located in a difference map, but those attached to carbon atoms were repositioned geometrically. The positions were refined using a riding model. See Table 1.

Table 1. X-ray Data for the Metallo-macrocycle $(Cp^*IrL)_3$ (2)

formula	$[(Cp^*)Ir(C_5H_2ClNO_2)]_3\cdot 3/2(C_7H_8)$
unit cell	monoclinic
space group	$P2_1/n$
a (Å)	13.951(7)
b (Å)	15.198(5)
c (Å)	26.005(10)
α (deg)	90deg
β (deg)	100.69(4)
γ (deg)	90
volume (Å^3)	5418(4)
Z	4
λ(Mo Kα) (Å)	0.710730
density	1.90
M (g mol^{-1})	1551.15
temperature (K)	295
μ (mm^{-1})	7.550
$R(F_o)^a$	0.041
$R_w(F_o)^b$	0.047

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

NMR Measurements and Kinetics. NMR samples were prepared by dissolving the diastereoisomer **8b** (3.2 mg, 1.67×10^{-3} mmol) in 870 μL of a $CD_2Cl_2/CD_3C_6D_5$ solvent mixture (75/25). The spectra were recorded on a Bruker DRX-500 spectrometer equipped with a Silicon Graphics workstation. A 5 mm broadband probe with a shielded z-gradient was used. The temperature was monitored with a BCU 05 temperature unit and fixed at 290 K for the kinetic study as a function of time. Data were processed on Silicon Graphics stations with the help of GIFA (version 4.3).[17−18] Spectra were obtained in 64 scans of 16K data points over a 4 kHz spectral width. A presaturation (60 dB) of the $CHDCl_2$ residual signal was performed. Prior to the Fourier transformation, a zero-filling was added to increase the resolution. Then, the free induction decays were processed using standard Fourier transformation. Baselines were corrected using a polynomial function if necessary.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determination of **2** and **8a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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