Crystallization-Induced Asymmetric Transformation of Chiral-at-metal Ruthenium(II) Complexes Bearing Achiral Ligands

Olivier Hamelin,*[a] Jacques Pécaut,[b] and Marc Fontecave*[a]

Abstract: Recently, we observed that the enantiopure Λ form of the tributylammonium salt of the chiral anion tris[tetrachlorobenzene-1,2-bis(olato)]phosphate, also named Trisphat, was able to induce an efficient resolution of a Δ,Λ racemic mixture of *cis*-$[Ru(dmp)_2(NCCH_3)_2](PF_6)_2$ (dmp = 2,9-dimethyl-1,10-phenanthroline) due to the spontaneous and selective precipitation of the heterochiral pair $[\Delta\text{-}Ru(dmp)_2(CH_3CN)_2][\Lambda\text{-Trisphat}]_2$. We report here that the combination of such a stereoselective precipitation process and irradiation results in the *quantitative* conversion of the initial $[Ru(dmp)_2(NCCH_3)_2]^{2+}$ racemate into only one of the two enantiomers. This is the first example in inorganic chemistry of an asymmetric transformation that leads to a chiral complex with no chiral ligand. Finally, three new racemic ruthenium bis(diimine) complexes, namely $[Ru(dmp)_2(NCCH_3)Py](PF_6)_2$ (Py = pyridine), $[Ru(dmp)_2(1,3\text{-diaminopropane})](PF_6)_2$, and $[Ru(dmp)_2(\text{ethylenediamine})](PF_6)_2$ were synthesized. For all of them, crystallization-induced asymmetric transformation proved to be an efficient way of obtaining the corresponding optically active chiral-at-metal complexes in high yields and with excellent stereoselectivities.

Keywords: asymmetric synthesis · chiral-at-metal complexes · crystallization · ruthenium

Optically pure compounds are of importance in many domains of chemistry. However, while stereochemistry has been developed to a high level in organic chemistry, only a few studies concerning inorganic complexes have been reported, even if the synthetic approaches and the difficulties are very similar. Octahedral complexes bearing two or three bidentate achiral ligands exist in two enantiomeric forms, namely, Δ and Λ.[1] In spite of recent progress in this area, the control of the chirality at the metal center during the synthesis remains an attractive challenge.

In most cases, the preparation of optically pure ruthenium bis- and tris(diimine) complexes involves an initial racemic synthesis, followed by a resolution process. The separation of the optically active compounds from the racemic product mixtures is achieved by various methods including chiral chromatography techniques[2] (HPLC with a chiral stationary phase) and fractional diastereomeric crystallization with chiral anions as the resolving agents.[3] Tartrate salts are commonly used but Trisphat (tris[tetrachlorobenzene-1,2-bis(olato)]phosphate) is gaining recognition as a very efficient and versatile NMR chiral-shift and resolving agent.[4] However, by definition, the theoretical maximum yield in a resolution cannot exceed 50% for each of the two pure enantiomers. To overcome this limitation, stereoselective synthetic methods have been developed that allow the preparation of optically active ruthenium bis(bipyridine) complexes. For instance, Von Zelewsky and co-workers[5] and more recently the groups of Inoue[6] and of Balavoine[7] have used a chiral "chiragen" ligand and enantiopure methyl-*p*-tolyl sulfoxide, respectively, as chiral auxiliaries to prepare optically active ruthenium(II) bis(diimine) complexes with high diastereoselectivities. However, the preparation of chiral-at-metal complexes with only achiral ligands required a subsequent step to substitute the optically active ligands with achiral ones and this has to be achieved without any racemization.[8]

Considering these problems and with the aim of preparing optically active chiral-at-metal ruthenium(II) bis(diimine) complexes bearing only achiral ligands,[9] we investigated a new strategy allowing the efficient preparation of such complexes from racemic mixtures. This is an original and rare reaction in coordination chemistry, namely, an asymmetric transformation induced by light and selective crystallization in the presence of the chiral Trisphat anion. For this purpose, we prepared novel bis(diimine) ruthenium complexes that are described in this paper.

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DOI: 10.1002/chem.200305749

Results

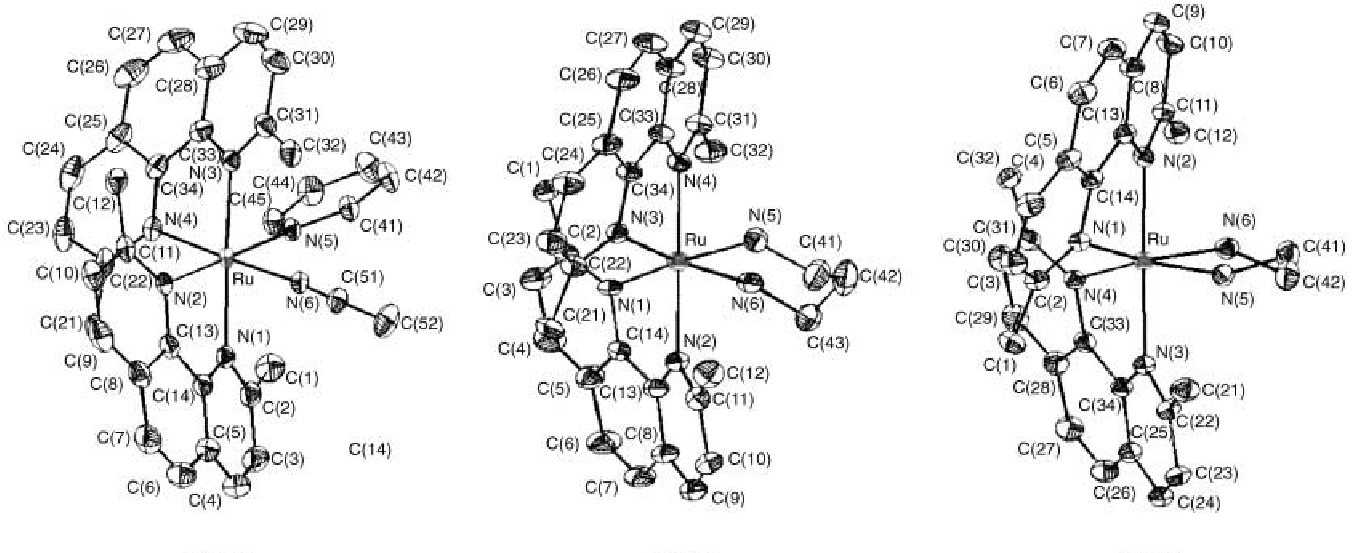
Preparation of the complexes: The racemic complex $[Ru(dmp)_2(NCCH_3)_2][PF_6]_2$ (**1**-$(PF_6)_2$, dmp = 2,9-dimethyl-1,10-phenanthroline) was prepared according to a described procedure.[9] Three new complexes, namely, *rac*-$[Ru(dmp)_2(NCCH_3)Py](PF_6)_2$ **2**-$(PF_6)_2$, Py = pyridine), $[Ru(dmp)_2$(1,3-diaminopropane)]$(PF_6)_2$ (**3**-$(PF_6)_2$), and $[Ru(dmp)_2$(ethylenediamine)]$(PF_6)_2$ (**4**-$(PF_6)_2$), used in this study have also been prepared for the first time and fully characterized. The synthesis of **2**-$(PF_6)_2$ was achieved from **1**-$(PF_6)_2$ by selective substitution of one acetonitrile ligand by a pyridine one in ethanol at 50 °C for 8 h in 90 % yield. Crystals of **2**-$(PF_6)_2$ suitable for X-ray analysis were grown by slow evaporation of dichloromethane from a concentrated solution of **2**-$(PF_6)_2$ in a dichloromethane/ethanol mixture. The molecular structure of the dication **2** is shown in Figure 1. The *cis* N(2)-Ru-N(3) and N(1)-Ru-N(4) angles are increased by as much as 12° with regard to those of a pure octahedron because of the steric repulsion generated by one of the two methyl groups of each of the dmp ligands in combination with the fact that the bite angle of the phenanthroline chelates is less than 90°. The same effects were also observed for the pyridine and the acetonitrile ligands that face the two other methyl groups, with *cis* angles of 98.45° and 101.20° for N(3)-Ru-N(6) and N(1)-Ru-N(5), respectively (Table 1). Interestingly, each phenanthroline presents an important curvature centered around the methyl group of the other diimine ligand. Indeed, the angles formed by the average planes of the two pyridinyl moieties of the same phenanthroline are 8.8° in one case and 12.6° in the other.

Table 1. Selected bond lengths [Å] and angles [°] for complexes **2**-$(PF_6)_2$, **3**-$(PF_6)_2$, and **4**-$(PF_6)_2$.[a]

Complex	Bond [Å]		Angle [°]	
2-$(PF_6)_2$	Ru–N(1)	2.116(3)	N(1)-Ru-N(3)	177.73(9)
	Ru–N(2)	2.087(2)	N(2)-Ru-N(3)	101.26(10)
	Ru–N(3)	2.090(3)	N(1)-Ru-N(4)	102.70(10)
	Ru–N(4)	2.075(3)	N(3)-Ru-N(6)	98.49(10)
	Ru–N(5)	2.128(3)	N(1)-Ru-N(5)	101.20(10)
	Ru–N(6)	2.035(3)	N(5)-Ru-N(6)	90.65(10)
3-$(PF_6)_2$	Ru–N(1)	2.101(3)	N(2)-Ru-N(4)	179.77(15)
	Ru–N(2)	2.046(3)	N(2)-Ru-N(3)	101.15(13)
	Ru–N(3)	2.077(3)	N(1)-Ru-N(4)	100.62(11)
	Ru–N(4)	2.050(3)	N(4)-Ru-N(6)	96.90(12)
	Ru–N(5)	2.128(4)	N(2)-Ru-N(5)	97.87(14)
	Ru–N(6)	2.117(3)	N(5)-Ru-N(6)	85.84(13)
4-$(PF_6)_2$	Ru–N(1)	2.117(2)	N(2)-Ru-N(3)	179.25(8)
	Ru–N(2)	2.086(3)	N(1)-Ru-N(3)	101.69(9)
	Ru–N(3)	2.113(2)	N(2)-Ru-N(4)	101.04(9)
	Ru–N(4)	2.079(3)	N(2)-Ru-N(5)	97.97(8)
	Ru–N(5)	2.147(3)	N(3)-Ru-N(6)	96.83(9)
	Ru–N(6)	2.130(3)	N(5)-Ru-N(6)	79.57(9)

[a] The estimated standard deviations in the least-significant digits are given in parentheses.

Complexes **3**-$(PF_6)_2$ and **4**-$(PF_6)_2$ were efficiently prepared from $[Ru(dmp)_2Cl_2]$ by substitution of both chloride ligands by 1,3-diaminopropane and ethylenediamine, respectively, in refluxing ethanol followed by an anion metathesis with NH_4PF_6 in water. The structures of both complexes were also determined by X-ray analysis from single crystals obtained by slow evaporation of acetone from an acetone/ethanol/cyclohexane solution for **3**-$(PF_6)_2$ and by slow diffusion of diethyl ether into a solution of acetone for **4**-$(PF_6)_2$ (Figure 1). In both structures, as was observed for **2**-$(PF_6)_2$, the *cis* N-Ru-N angles between the two nitrogen atoms of two different dmp ligands and between the nitrogen atom of one dmp ligand and the amine nitrogen atom located in front of the methyl substituents are increased by about 10° and 8°, respectively (that is, N(2)-Ru-N(3) and N(2)-Ru-N(5) for **3**-$(PF_6)_2$; Table 1). The steric hindrance generated by the methyl groups is probably also at the origin of the curvatures observed for every phenanthroline, with angles of 14.5–17.1° between the two planes of the pyridinyl moiet-



2-$(PF_6)_2$ **3**-$(PF_6)_2$ **4**-$(PF_6)_2$

Figure 1. ORTEP views of the structures of the following cations: $[Ru(dmp)_2(NCCH_3)Py]^{2+}$ (**2**), $[Ru(dmp)_2$(1,3-diaminopropane)$]^{2+}$ (**3**), $[Ru(dmp)_2$(ethylenediamine)$]^{2+}$ (**4**) with PF_6^- counterions. Hydrogen atoms have been omitted for clarity.

ies of the same phenanthroline. Moreover, while the six-membered ring formed by the diaminopropane ligand and the ruthenium center adopts a boat conformation with an N(5)-Ru-N(6) angle of 88.84°; this *cis* angle drops to 79.57° with the ethylenediamine ligand, which shows a twist conformation. Bond lengths are those expected for this type of Ru^{II} complex.

Asymmetric transformation: We recently observed that addition of a small excess of the tributylammonium salt of the enantiopure Λ form of the Trisphat anion to a dichloromethane solution of a Δ,Λ racemic mixture of *cis*-$[Ru(dmp)_2(NCCH_3)_2](PF_6)_2$ (**1**-$(PF_6)_2$) resulted in the immediate selective precipitation of the heterochiral ion pair [Δ-**1**][Λ-Trisphat]$_2$ (98% *de*, 48% yield), while the homochiral ion pair [Λ-**1**][Λ-Trisphat]$_2$ remained in solution.[9]

To evaluate its photochemical stability, the isolated optically pure [Δ-**1**][Λ-Trisphat]$_2$ was dissolved in acetonitrile and then irradiated with a standard light (40 W tungsten filament). After a 2 h irradiation period, the solution was dried and the crude residue was dissolved in [D$_6$]acetone. Conversion of [Δ-**1**] into [Λ-**1**] can be easily monitored by ^{1}H NMR spectroscopy in [D$_6$]acetone since both enantiomers are associated in solution with Trisphat and the resulting diastereomeric ion pairs have different chemical shifts in their NMR spectra.[9] The best resolution was obtained with acetone as the solvent and in the presence of a small excess of [nBu$_3$NH][Λ-Trisphat] (2.1 equiv). As shown in Figure 2a,b, under these conditions, most signals in the aromatic region of the spectrum of the racemic **1**-$(PF_6)_2$ were indeed split into two signals of equal intensity. NMR analysis of the reaction mixture after irradiation thus showed the presence of an equimolar mixture of [Λ-**1**][Λ-Trisphat]$_2$ and [Δ-**1**][Λ-Trisphat]$_2$ as the result of the isomerization of the chiral metal center (data not shown). The *trans* isomer, defined as the complex with the two acetonitrile ligands trans to each other, could not be formed, probably because of the steric hindrance created by the methyl groups of the dmp ligands.

These results, namely, the selective crystallization of the heterochiral pair and the light-dependent racemization, led us to use the following strategy for converting the racemic **1**-$(PF_6)_2$ complex into a unique optically active diastereomer. [nBu$_3$NH][Λ-Trisphat] (2.1 equiv) was added to a dichloromethane solution of the complex **1**-$(PF_6)_2$ and the resulting suspension was then irradiated as described above. The composition of the suspension was monitored at time intervals by NMR spectroscopy of a concentrated aliquot after redissolution in [D$_6$]acetone. During the reaction, modifications in the spectrum were observed that indicate the slow disappearance of the homochiral isomers (Figure 2c–f). After an irradiation period of 3 h, the conversion was nearly complete. The precipitate was then filtered off and dissolved in [D$_6$]acetone, then two additional equivalents of Λ-Trisphat were added for an optimal resolution in the NMR spectrum (Figure 2g). Integration of the peaks in the region $\delta = 7.30$–7.50 ppm, peaks that correspond to the two H8 protons of the dmp ligands, revealed diastereoselectivity of up to 98%. In addition, the yield of the isolated salt was almost quantitative; this was also confirmed by NMR measurements of the filtrate, in which no complex could be detected.

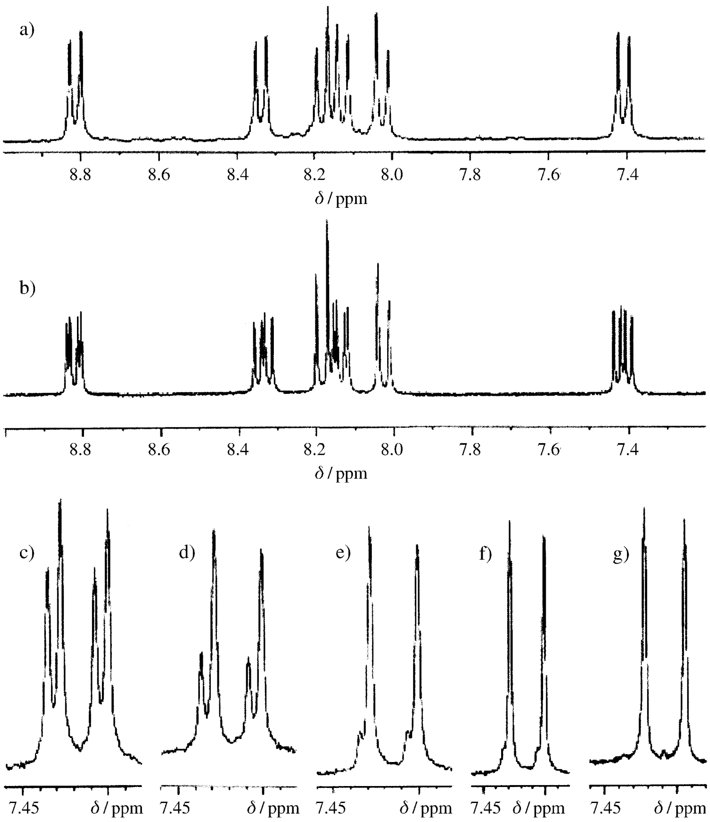


Figure 2. ^{1}H NMR spectra (300 MHz, [D$_6$]acetone) of the aromatic protons for the racemic **1**-$(PF_6)_2$ complex a) in the absence and b) in the presence of [nBu$_3$NH][Λ-Trisphat] (2.1 equiv). Expansion of the $\delta = 7.38$–7.46 ppm region of the ^{1}H NMR spectra for the reaction mixture after c) 15 min, d) 45 min, e) 2.25 h, and f) 3 h of exposure to light. g) Expansion of the $\delta = 7.38$–7.46 ppm region of the ^{1}H NMR spectrum of the isolated precipitate in the presence of two additional equivalents of [nBu$_3$NH][Λ-Trisphat].

The thermal behavior of the racemic complex **1** in the presence of Trisphat was also examined under dark conditions. The initial dichloromethane suspension resulting from the addition of enantiopure Λ-Trisphat (2 equiv) to the racemic mixture was refluxed in the dark. The transformations were monitored by ^{1}H NMR spectroscopy as discussed above. Interestingly, the isomerization was shown to occur but the reaction proved much slower than under conditions with irradiation: after 38 h the [Δ-**1**][Λ-Trisphat]$_2$:[Λ-**1**][Λ-Trisphat]$_2$ diastereomeric ratio was only 84:16 (79:21 after 18 h; data not shown).

For the sake of testing the generality of the photochemical reaction, complexes **2**-$(PF_6)_2$, **3**-$(PF_6)_2$,and **4**-$(PF_6)_2$, for which resolution by Trisphat had also proved to be successful, were irradiated in the presence of [nBu$_3$NH][Λ-Trisphat] under the conditions used for **1**-$(PF_6)_2$ (dichloromethane, 40 W). Exposure of **2**-$(PF_6)_2$ to light resulted in the formation of a large quantity of [Δ-**1**][Λ-Trisphat]$_2$, a result illustrating the relatively high photolability of the pyridine ligand. Consequently, to avoid release of pyridine, the reaction was performed under dark conditions at room temperature (20–25 °C). After 4 days, the two diastereoisomers were isolated by precipitation in diethyl ether in a good yield (74%) and with a good stereoselectivity (75.0% *de*; 65.5% *de* after 2.5 days; ^{1}H NMR spectroscopic determination; Table 2). It is noteworthy that the optically pure complex can be obtained by filtration of the precipitate formed after irradiation in reasonable yield. The CD spectrum of the complex dissolved in acetonitrile showed, from the sign of the ligand-centered transition at 270 nm, a positive Cotton effect at higher energy and a negative effect at lower energy, which is characteristic for a Δ configuration of the $[Ru(dmp)_2(NCCH_3)Py]^{2+}$ ion (Figure 3).[10] Consequently, as was observed for **1**-$(PF_6)_2$, addition of one enantiomer of the tributylammonium Trisphat salt to *rac*-[**2**]$(PF_6)_2$ resulted in the stereoselective precipitation of the heterochiral pair [Δ-**2**][Λ-Trisphat]$_2$.

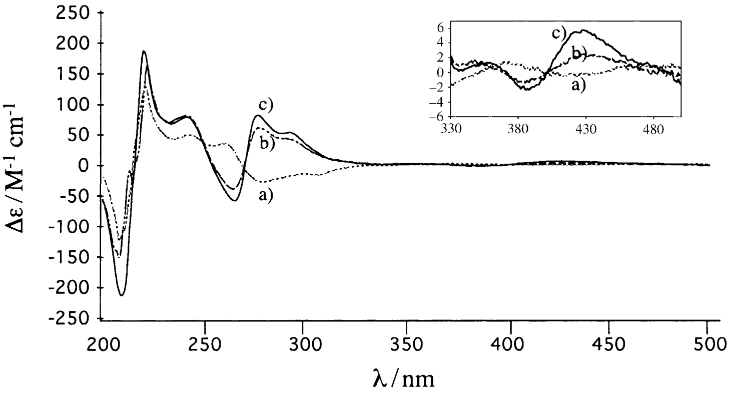


Figure 3. Circular dichroism spectra in CH_3CN of a) [Δ-$Ru(dmp)_2(NCCH_3)Py$][Λ-Trisphat]$_2$, b) [Λ-$Ru(dmp)_2$(1,3-diaminopropane)][Λ-Trisphat]$_2$, and c) [Λ-$Ru(dmp)_2$(ethylenediamine)][Λ-Trisphat]$_2$. Inset: Expansion of $\lambda = 330$–500 nm region for the same compounds.

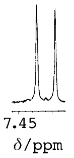
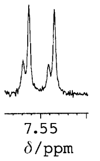
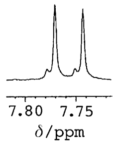
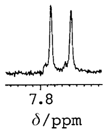
As expected, because of the lower lability of the diamino ligands, more intense irradiation was needed to observe a reaction with **3**-$(PF_6)_2$ and **4**-$(PF_6)_2$. Moreover, because of the higher solubility of the corresponding Trisphat salts, a 1:1 mixture of CH_2Cl_2 and $CHCl_3$ was used as the solvent. Thus, exposure of **3**-$(PF_6)_2$ or **4**-$(PF_6)_2$ in the presence of a small excess of [*n*Bu_3NH][Λ-Trisphat] to a 250 W halogen lamp resulted in reactions with stereoselectivities of 91.8 and 95.0% after reaction for 10 and 24 h, respectively. Complexes [**3**][Λ-Trisphat]$_2$ and [**4**][Λ-Trisphat]$_2$ were isolated by precipitation in diethyl ether in 81 and 79% yields, respectively (Table 2). The lower diastereoselectivities, relative to the reaction with **1**-$(PF_6)_2$, can be explained by the larger solubilities of the less-soluble ion pairs. However, as for [**1**][Λ-Trisphat]$_2$ and [**2**][Λ-Trisphat]$_2$, optically pure complexes can be obtained by filtration of the precipitate formed after irradiation (100% *de* and 60% yield for [**3**][Λ-Trisphat]$_2$ after 5.5 h). The absolute configurations of the final complexes obtained from **3**-$(PF_6)_2$ and **4**-$(PF_6)_2$ were also determined by CD spectroscopy, after irradiation, by comparison with the CD spectra obtained for [Δ-**1**][Λ-Trisphat]$_2$ and [Δ-**2**][Λ-Trisphat]$_2$. Both showed Cotton effects of the opposite sign from the transition at 275 nm, a result suggesting the selective formation of the homochiral [Λ-**3**][Λ-Trisphat]$_2$ and [Λ-**4**][Λ-Trisphat]$_2$ pairs (Figure 3).

Discussion

The results reported here provide a rare example of an asymmetric transformation in coordination chemistry. In the case studied here, it leads to the preparation of chiral ruthenium bis(diimine) complexes in high yields and with excellent optical purities. The reaction used is based on the two following properties of this class of complexes.

First, ruthenium bis(diimine) complexes are known to be light-sensitive, undergoing slow transformation under prolonged exposure to light. In particular, the exchange of ligands and racemization can occur upon irradiation. The exchange of ligands has been rather extensively studied. For example, Sauvage and co-workers[11] showed that visible-light irradiation of mixed ruthenium(II) complexes containing 1,10-phenanthroline and a sterically hindered bidentate ligand leads to the clean and selective substitution of the latter by acetonitrile solvent molecules. Under controlled irradiation in either the ligand-centered (LC) or metal-to-ligand charge transfer (MLCT) bands, the dmso ligand of enantiopure *cis*-$[Ru(bpy)_2(dmso)Cl][PF_6]$ (dmso = dimethylsulfoxide, bpy = bipyridine) can also be substituted by a variety of ligands with complete retention of configuration.[12] In contrast, photoracemization reactions have seldom been reported. One can mention the observation by Inoue and co-workers that the enantiomeric excess of a sample of purified optically active $[Ru(bpy)_2Cl(dmso)]^+$ slowly decreases on standing as a result of photodegradation.[13] This explains

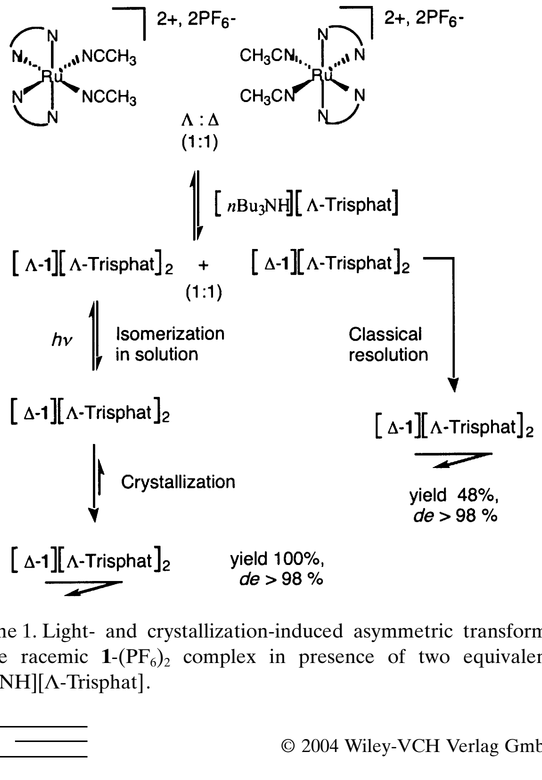
Table 2. Light-induced asymmetric transformation of **1**-$(PF_6)_2$, **2**-$(PF_6)_2$, **3**-$(PF_6)_2$, and **4**-$(PF_6)_2$ in the presence of [*n*Bu_3NH][Λ-Trisphat].

	1-$(PF_6)_2$	**2**-$(PF_6)_2$	**3**-$(PF_6)_2$	**4**-$(PF_6)_2$
conditions	CH_2Cl_2, 40 W, 3 h	CH_2Cl_2, dark, 4 d	$CH_2Cl_2/CHCl_3$ (1:1), 250 W, 10 h	$CH_2Cl_2/CHCl_3$ (1:1), 250 W, 24 h
diastereoselectivity	>98:2	3:1	11.2:1	>19:1
expansion of an aromatic region of the ^{1}H NMR spectrum of the diastereomeric mixture with an excess of [*n*Bu_3NH][Λ-Trisphat] in [D$_6$]acetone.				
absolute configuration of the product	[Δ-**1**][Λ-Trisphat]$_2$	[Δ-**2**][Λ-Trisphat]$_2$	[Λ-**3**][Λ-Trisphat]$_2$	[Λ-**4**][Λ-Trisphat]$_2$
yield [%]	quantitative	74.2	81.1	79.1

why chiral ruthenium complexes are generally used and stored under dark conditions. The racemization reaction probably occurs by the photodissociation of at least one of the ligands and the rearrangement of the pentacoordinate intermediate before return of the released ligand into the coordination sphere.

Second, the two cationic enantiomers ($[\Delta$-(**1**–**4**)$]^{2+}$ and $[\Lambda$-(**1**–**4**)$]^{2+}$) of complexes **1**–**4** give, upon association with Λ-Trisphat, the heterochiral [Δ-(**1**–**4**)][Λ-Trisphat]$_2$ and homochiral [Λ-(**1**–**4**)][Λ-Trisphat]$_2$ pairs, which have very different solubilities. This allows the selective precipitation of one of the two diastereoisomers. Further physicochemical and structural studies are required to understand why, in the case of complexes **1** and **2** containing acetonitrile ligands, precipitation of the heterochiral pair is favored whereas, in the case of complexes **3** and **4** containing diamine ligands, the homochiral pair preferentially precipitates, as shown by CD spectroscopy.

As a consequence of these two properties, it is possible to convert, in the presence of enantiopure Trisphat with a clever choice of solvent and upon exposure to light, one cationic enantiomer from a racemic mixture of ruthenium bis(diimine) complexes into the other with good to excellent yields. This is beautifully shown here with complex **1**-$(PF_6)_2$. The reaction is summarized in Scheme 1. Upon addition of two equivalents of [*n*Bu$_3$NH][Λ-Trisphat] to a racemic mixture of **1**-$(PF_6)_2$, anion metathesis leads to a 1:1 mixture of the homochiral [Λ-**1**][Λ-Trisphat]$_2$ and heterochiral [Δ-**1**][Λ-Trisphat]$_2$ complexes. Classical resolution was achieved because of the highly selective precipitation of the latter (*de* > 98 %) with only the more soluble homochiral isomer left in solution. Exposure of the solution to light results in the slow racemization of the $[\Lambda$-**1**$]^{2+}$ ion and leads to the formation of the less soluble [Δ-**1**][Λ-Trisphat]$_2$ complex, which thus precipitates continuously to allow its quantitative preparation.



Scheme 1. Light- and crystallization-induced asymmetric transformation of the racemic **1**-$(PF_6)_2$ complex in presence of two equivalents of [*n*Bu$_3$NH][Λ-Trisphat].

Such a process, commonly observed in organic chemistry, can be defined as an *asymmetric transformation of the second kind*, also named a crystallization-induced asymmetric transformation.[14] To the best of our knowledge, such an asymmetric transformation has never been reported for the synthesis of a chiral-at-metal complex with achiral ligands. Recently, Brunner and co-workers reported a diastereoselective preparation of Ir and Rh chiral-at-metal complexes by crystallization-induced asymmetric transformation.[15] However, the optically active bidentate Schiff base ligand was present in the coordination sphere in order to control the stereoselective isomerization of the chiral metal center during the crystallization.

By using three additional ruthenium bis(diimine) complexes with different light sensitivities, we have demonstrated that this reaction displays some kind of generality and may have broad applicability. Certainly, the degree of stereoselectivity of the transformation highly depends on the difference between the solubilities of the homochiral [Λ-Ru][Λ-Trisphat]$_2$ and heterochiral [Δ-Ru][Λ-Trisphat]$_2$ diastereomeric pairs. This in turn depends on the ligands at positions 5 and 6, as illustrated by the results obtained with **2**, **3**, and **4**.

Conclusion

We demonstrate here that the photolabilization of ligands combined with a selective crystallization allows the highly diastereoselective preparation of inorganic chiral-at-metal complexes with achiral ligands through an efficient asymmetric transformation in the presence of Trisphat as a chiral auxiliary agent. We guess that most of the resolution methods used to access these chiral ruthenium bis(diimine) complexes could be turned into this straightforward technique. One application of such complexes is catalysis. We recently reported that an optically pure ruthenium bis(diimine) complex (Δ- or Λ-$[\mathbf{1}]^{2+}$) with achiral ligands was able to catalyze the enantioselective oxidation of sulfides by H_2O_2. Even if the enantiomeric excesses were relatively low (less than 18 %), we demonstrated for the first time that the chiral information carried by the stereogenic reactive metal center could be catalytically transferred to substrates. Catalytic asymmetric epoxidations with isolated optically pure or enriched chiral-at-metal complexes are currently under investigation.

Experimental Section

$[Ru(dmp)_2Cl_2]$[16] and $[Ru(dmp)_2(CH_3CN)_2](PF_6)_2$[9] (**1**-$(PF_6)_2$) were prepared according to previously described procedures. Solvents used in synthetic procedures were analytical grade. Dichloromethane and chloroform were distilled over $CaCl_2$. Ethylenediamine and 1,3-diaminopropane were purchased from Aldrich and pyridine wa spurchased from SDS. [*n*Bu$_3$NH][Λ-Trisphat] was provided by J. Lacour (University of Genève, Geneva, Switzerland). All the preparations of the complexes were carried out in dark conditions and under argon.

Instruments: NMR spectra were recorded on a Bruker EMX-300 apparatus at 300 MHz. Electrospray mass spectrometry was performed on a Finnigan LC-Q instrument. Absorption spectra were recorded with a Hewlett–Packard 8453 spectrometer. Circular dichroism spectra were recorded on a JASCO J-810 spectropolarimeter at 25 °C with a 0.1-cm pathlength cell. Data collection was performed at 298 K by using a Bruker SMART diffractometer with a charged couple device area detector, with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). Molecular structures was solved by direct methods and refined on F^2 by full-matrix least-squares techniques with the SHELXTL package with anisotropic thermal parameters. All non-hydrogen atoms were refined anisotropically; hydrogen atoms were placed in ideal positions and refined as riding atoms with individual isotopic displacement parameters. Pertinent crystallographic data are summarized in Table 1.

Diastereomeric excesses of the ruthenium complexes were determined by NMR analysis after dissolution of the isolated precipitate in $[D_6]$acetone, in the presence of an excess of Trisphat salt to obtain a good splitting pattern.

Preparation of $[Ru(dmp)_2(NCCH_3)Py](PF_6)_2$ (2-$(PF_6)_2$): Pyridine (45.4 µL, 562.0 µmol, 10 equiv) was added to a solution of **1**-$(PF_6)_2$ (50.0 mg, 56.2 µmol) in absolute ethanol (22.0 mL) and the mixture was heated to 50 °C for 8 h under an argon atmosphere and in the dark. The resulting light-brown suspension was then cooled to room temperature and stirred for 12 h. The suspension was concentrated in vacuo. Crystallization by slow diffusion of diethyl ether into a concentrated solution in acetone afforded **2**-$(PF_6)_2$ (46.7 mg, 90 % yield) as brown crystals. Suitable single crystals for X-ray analysis were obtained by slow evaporation of dichloromethane from a solution of **2**-$(PF_6)_2$ in a dichloromethane/ethanol mixture. ^{1}H NMR (300 MHz, CD_2Cl_2): $\delta = 8.53$ (d, 1 H, $J = 8.3$ Hz), 8.37 (d, 1 H, $J = 8.3$ Hz), 8.30 (d, 1 H, $J = 8.3$ Hz), 8.29 (d, 1 H, $J = 8.3$ Hz), 8.15–7.80 (m, 6 H), 7.74 (t, 2 H, $J = 7.9$ Hz), 7.59 (tt, 1 H, $J = 7.8$, 1.4 Hz), 7.56 (d, 1 H, $J = 8.3$ Hz), 7.40 (d, 1 H, $J = 8.3$ Hz), 7.11 (pseudo t, 2 H, $J = 7.1$ Hz), 3.18 (s, 3 H), 2.57 (s, 3 H), 2.21 (s, 3 H), 1.94 (s, 3 H), 1.76 (s, 3 H) ppm; MS (ESI, acetone, 30 °C): m/z (%): 783 $[\mathbf{2}\text{-}(PF_6)]^+$ (92), 616 $[Ru(dmp)_2PyF]^+$ (70), 579 $[Ru(dmp)_2(NCCH_3)F]^+$ (52), 299 $[Ru(dmp)_2Py]^{2+}$ (100), 259 $[Ru(dmp)_2]^{2+}$ (74); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 234 (41 546), 272 (49 197), 293 (24 156), 306 (18 093), 392 (7706), 455 nm (7400 $M^{-1}cm^{-1}$); elemental analysis: calcd (%) for $C_{35}H_{36}N_6O_2F_{12}P_2Ru$ ($[Ru(dmp)_2(NCCH_3)Py](PF_6)_2 \cdot 2H_2O$): C 45.08, H 3.48, N 8.53, F 23.13, P 6.28, Ru 10.25; found: C 44.90, H 3.46, N 8.81, F 22.61, P 6.48, Ru 9.55; crystallographic data: triclinic, $P\bar{1}$, $a = 8.2916(17)$, $b = 10.851(2)$, $c = 20.890(4)$ Å, $V = 1826.2(6)$ Å^3, $Z = 2$, $R = 0.0453$, $Rw = 0.1152$.

Preparation of $[Ru(dmp)_2(1,3\text{-diaminopropane})](PF_6)_2$ (3-$(PF_6)_2$): A solution of $[Ru(dmp)_2Cl_2]$ (100.0 mg, 170.0 µmol) and 1,3-diaminopropane (17.7 µL, 187.1 µmol, 1.1 equiv) in absolute ethanol (8.0 mL) was refluxed in the dark and under an argon atmosphere for 1.5 h. The resulting crimson-red solution was concentrated in vacuo and the residue was dissolved in water. Precipitation of the complex by addition of NH_4PF_6 (277.1 mg, 1.7 mmol, 10 equiv) and subsequent filtration and drying under high vacuum afforded **3**-$(PF_6)_2$ (135 mg, 153.2 µmol, 90 % yield) as a red-orange powder, which could be used without further purification. Crystallization by slow evaporation of acetone from an acetone/ethanol/cyclohexane solution of **3**-$(PF_6)_2$ afforded crystals suitable for X-ray analysis. ^{1}H NMR (300 MHz, CD_2Cl_2): $\delta = 8.49$ (d, 2 H, $J = 8.3$ Hz), 8.40 (d, 2 H, $J = 8.3$ Hz), 8.10 (d_{AB}, 4 H, $J = 8.8$ Hz), 7.83 (d, 2 H, $J = 8.3$ Hz), 7.59 (d, 2 H, $J = 8.3$ Hz), 3.25–3.05 (brs, 2 H), 2.98 (s, 6 H), 2.62–2.42 (brs, 2 H), 2.02 (s, 6 H), 1.80–1.60 (brs, 2 H), 1.27–1.47 (m, 4 H) ppm; MS (ESI, acetone): m/z (%): 737 $[\mathbf{3}\text{-}(PF_6)]^+$ (57), 611 $[Ru(dmp)_2(1,3\text{-diaminopropane})F]^+$ (46), 537 $[Ru(dmp)_2F]^+$ (100), 259 $[Ru(dmp)_2]^{2+}$ (19); UV/Vis (CH_3CN): λ_{max} (ε) = 220 (10 598), 234 (51 461), 275 (62 332), 293 (20 244), 420 (5158), 477 (6539), 506 nm (8677 $M^{-1}cm^{-1}$); elemental analysis: calcd (%) for $C_{31}H_{34}N_6F_{12}P_2Ru$: C 42.23, H 3.89, N 9.53; found: C 41.71, H 3.86, N 9.17; crystallographic data: orthorombic, $Fdd2$, $a = 33.504(7)$, $b = 46.670(9)$, $c = 12.509(3)$ Å, $V = 19\,560(7)$ Å^3, $Z = 16$, $R = 0.0689$, $Rw = 0.1683$.

Preparation of $[Ru(dmp)_2(\text{ethylenediamine})](PF_6)_2$ (4-$(PF_6)_2$): The complex **4**-$(PF_6)_2$ was prepared in a similar manner to **3**-$(PF_6)_2$ by using ethylenediamine instead of 1,3-diaminopropane and with a 90 % yield. Suitable crystals for X-ray analysis were prepared by diffusion of diethyl ether in a concentrated acetone solution of **4**-$(PF_6)_2$. ^{1}H NMR (300 MHz, CD_2Cl_2): $\delta = 8.49$ (d, 2 H, $J = 8.3$ Hz), 8.38 (d, 2 H, $J = 8.3$ Hz), 8.09 (s, 4 H), 7.81 (d, 2 H, $J = 8.3$ Hz), 7.59 (d, 2 H, $J = 8.3$ Hz), 3.65–3.55 (brs, 2 H), 2.97 (s, 6 H), 2.67–2.60(brs, 2 H), 2.21–2.14 (brs, 2 H), 2.02 (s, 6 H), 1.31–1.24 (brs, 2 H) ppm; MS (ESI, acetone): m/z (%): 723 $[\mathbf{4}\text{-}(PF_6)]^+$ (100), 537 $[Ru(dmp)_2F]^+$ (67), 289 $[Ru(dmp)_2(\text{ethylenediamine})]^{2+}$ (48), 259 $[Ru(dmp)_2]^{2+}$ (68); UV/Vis (CH_3CN): λ_{max} (ε) = 221 (12 409), 234 (50 339), 275 (64 067), 293 (29 417), 420 (7523), 476 (9836), 499 nm (12 243 $M^{-1}cm^{-1}$); elemental analysis: calcd (%) for $C_{32}H_{40}N_6O_2P_2F_{12}Ru$ ($[Ru(dmp)_2(\text{ethylenediamine})](PF_6)_2 \cdot H_2O \cdot EtOH$): C 41.25, H 4.33, N 9.02, F 24.47, P 6.65, Ru 10.85; found: C 40.93, H 3.94, N 9.09, F 24.01, P 7.14, Ru 10.85; crystallographic data: orthorhombic, $Fdd2$, $a = 33.788(7)$, $b = 45.439(9)$, $c = 12.639(3)$ Å, $V = 19\,404(7)$ Å^3, $Z = 16$, $R = 0.0337$, $Rw = 0.0873$.

Standard conditions for asymmetric transformation: Dichloromethane and chloroform were used after distillation over $CaCl_2$, filtration over a plug of basic alumina, and deoxygenation by argon bubbling. $[nBu_3NH][\Lambda\text{-Trisphat}]$ (2.1 equiv) was added to a solution of the complex in dichloromethane (1.4 mM for complexes **1** and **2**) or a 1:1 mixture of dichloromethane/chloroform (0.7 mM for complexes **3** and **4**). An immediate precipitate was observed in the cases of **1** and **2**, whereas 5–10 min were needed for precipitation with **3** and **4**. The resulting suspension was then stirred and exposed to a lamp (40 W tungsten filament for 3 h for **1**, 250 W halogen lamp for **3** (10 h) and **4** (24 h)) located 10 cm from the sample, while under an argon atmosphere. For complex **1**, the precipitate was filtered and washed successively with dichloromethane and diethyl ether. For **2**–**4**, the suspension was concentrated and dissolved in a minimum of acetone, then the complexes were precipitated by addition of the solution into a large volume of diethyl ether. The mixture was then filtered, washed with diethyl ether, and dried under high vacuum. Optically pure complexes can be obtained by filtration of the precipitate after irradiation.

$[Ru(dmp)_2(NCCH_3)Py][\Lambda\text{-Trisphat}]_2$ ([2][Λ-Trisphat]$_2$): ^{1}H NMR (300 MHz, $[D_6]$acetone): $\delta = 8.82$ (d, 1 H, $J = 8.3$ Hz), 8.61 (d, 1 H, $J = 8.3$ Hz), 8.59 (d, 1 H, $J = 8.3$ Hz), 8.65–8.45 (brs, 3 H), 8.25 (d_{AB}, 1 H, $J = 8.7$ Hz), 8.17 (d_{AB}, 1 H, $J = 8.7$ Hz), 8.13 (s, 2 H), 7.99 (d, 1 H, $J = 8.3$ Hz), 7.96 (d, 1 H, $J = 8{,}3$ Hz), 7.77 (tt, 1 H, $J = 1.5$, 7.5 Hz), 7.72 (d, 1 H, $J = 8.3$ Hz), 7.58 (d, 1 H, $J = 8.3$ Hz), 7.18 (pseudo t, 2 H, $J = 7.5$ Hz), 3.37 (s, 3 H), 2.76 (s, 3 H), 2.41 (s, 3 H), 2.10–1.90 (s, 3 H, recovered by solvent peak), 1.87 (s, 3 H) ppm; MS (ESI, acetone, 30 °C): m/z (%): 1408 $\{[\mathbf{2}][\text{Trisphat}]\}^+$ (12), 1367 $\{[Ru(dmp)_2Py][\text{Trisphat}]\}^+$ (2), 1288 $\{[Ru(dmp)_2][\text{Trisphat}]\}^+$ (8), 579 $[Ru(dmp)_2(NCCH_3)F]^+$ (52), 299 $[Ru(dmp)_2Py]^{2+}$ (56), 259 $[Ru(dmp)_2]^{2+}$ (100+); CD for [**2**][Λ-Trisphat]$_2$ (CH_3CN): λ_{max} ($\Delta\varepsilon$) = 208 (−122), 221 (128), 237 (44), 243 (49), 255 (31), 260 (35), 280 (−27), 338 (−1), 374 (1.5), 414 nm (−0.5 $M^{-1}cm^{-1}$).

$[Ru(dmp)_2(1,3\text{-diaminopropane})][\Lambda\text{-Trisphat}]_2$ ([3][Λ-Trisphat]$_2$): ^{1}H NMR (300 MHz, $[D_6]$acetone): $\delta = 8.73$ (d, 2 H, $J = 8.3$ Hz), 8.58 (d, 2 H, $J = 8.3$ Hz), 8.23 (s, 4 H), 8.03 (d, 2 H, $J = 8.3$ Hz), 7.76 (d, 2 H, $J = 8.3$ Hz), 3.90–3.72 (m, 2 H), 3.21 (s, 6 H), 2.76 (s, 2 H), 2.70–2.40 (brs, 2 H), 2.12 (s, 6 H), 1.85–1.65 (m, 2 H), 1.60–1.45 (m, 2 H) ppm; MS (ESI, acetone): m/z (%): 1362 $\{[\mathbf{3}][\text{Trisphat}]\}^+$ (22), 1288 $\{[Ru(dmp)_2][\text{Trisphat}]\}^+$ (36), 553 $[Ru(dmp)_2Cl]^+$ (32), 267 $[Ru(dmp)_2(H_2O)]^{2+}$ (97, metastable species), 259 $[Ru(dmp)_2]^{2+}$ (100); CD for [**3**][Λ-Trisphat]$_2$ (CH_3CN): λ_{max} ($\Delta\varepsilon$) = 208 (−151), 222 (163), 233 (69), 241 (81), 264 (39), 277 (60), 342 (1), 353 (1.5), 385 (−1.5), 436 nm (2.42 $M^{-1}cm^{-1}$).

$[Ru(dmp)_2(\text{ethylenediamine})][\Lambda\text{-Trisphat}]_2$ ([4][Λ-Trisphat]$_2$): ^{1}H NMR (300 MHz, $[D_6]$acetone): $\delta = 8.70$ (d, 2 H, $J = 8.3$ Hz), 8.58 (d, 2 H, $J = 8.3$ Hz), 8.23 (s, 4 H), 8.02 (d, 2 H, $J = 8.3$ Hz), 7.78 (d, 2 H, $J = 8.3$ Hz), 4.50–4.30 (m, 2 H), 3.21 (s, 6 H), 2.76 (s, 2 H), 2.65–2.40 (m, 4 H), 2.15 (s, 6 H) ppm; MS (ESI, acetone): m/z (%): 1348 $\{[\mathbf{4}][\text{Trisphat}]\}^+$ (53), 1288 $\{[Ru(dmp)_2][\text{Trisphat}]\}^+$ (8), 267 $[Ru(dmp)_2(H_2O)]^{2+}$ (100, metastable species), 259 $[Ru(dmp)_2]^{2+}$ (66); CD for [**4**][Λ-Trisphat]$_2$ (CH_3CN): λ_{max} ($\Delta\varepsilon$) = 209 (−213), 220 (186), 234 (67), 241 (78), 265 (−58), 277 (82), 336 (0.2), 357 (1.5), 386 (−2.5), 428 nm (5.7 $M^{-1}cm^{-1}$).

Crystallographic data: CCDC-224443 (**2**-$(PF_6)_2$), CCDC-224444 (**3**-$(PF_6)_2$), and CCDC-224445 (**4**-$(PF_6)_2$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336033; or deposit@ccdc.cam.uk).

Acknowledgements

We are grateful to the "Ministère Français de la Recherche et de la Technologie" for an "ACI Jeunes Chercheurs 2000" grant. We also thank J. Lacour (University of Genève, Geneva, Switzerland) for a generous gift of Trisphat and C. Lebrun (DRFMC, CEA-Grenoble) for the ES-MS analysis.

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Received: November 26, 2003 [F5749]