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"Chiral-at-Metal" Octahedral Ruthenium(II) Complexes with Achiral Ligands: A New Type of Enantioselective Catalyst

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cis-$[Ru(dmp)_2(CH_3CN)_2][PF_6]_2$ (dmp = 2,9-dimethyl-1,10-phenanthroline), complex **1**$[PF_6]_2$, exists in two enantiomeric forms, Δ and Λ. During treatment with the chiral anion tris[tetrachlorobenzene-1,2-bis(olato)]phosphate(V), also named Trisphat, in dichloromethane it has been possible to selectively precipitate each enantiomer, associated with Trisphat in the form of the heterochiral pair. This *enantiomerically pure* compound has been characterized in solution by UV–visible, CD, ESI-MS, and NMR spectroscopy and by X-ray crystallography in the solid state. Trisphat was also used as an NMR chiral shift reagent to determine the enantiomeric excess of the complex preparations. The "chiral-at-metal" ruthenium complex has been evaluated as a catalyst for the oxidation of sulfides to sulfoxides by hydrogen peroxide. The reactions displayed a low but significant level of enantioselectivity (18% ee in the case of 4-bromophenyl methyl sulfide). Our results thus provide the first demonstration that the chiral information carried by a stereogenic metal center can be *catalytically* transferred to molecules during stereoselective oxidation.

Catalytic enantioselective oxidation of organic compounds is currently one of the most challenging chemical reactions.[1] In general the catalyst is a metal complex in which the metal ion is coordinated by chiral ligands designed to generate the desired selectivity. However, the metal ion itself can be an element of chirality but whether such a stereogenic metal center can control the stereoselectivity of catalytic oxidations has not been demonstrated yet.

To provide an experimental validation of the concept of asymmetric induction by stereogenic metal centers during enantioselective catalytic oxidations, we selected bis(diimine)ruthenium complexes, *cis*-$[Ru(N{-}N)_2(S)_2]^{2+}$ (N−N = diimine ligand; S = H_2O, CH_3CN, ...), as catalysts. Indeed, such complexes, containing labile coordination sites required for catalysis, were previously shown to display good catalytic activity during oxidation reactions.[2] Mechanistic studies suggested that these oxidations proceeded via high-valent Ru−oxo intermediate species.[3] Interestingly, using the sterically crowded 2,9-dimethyl-1,10-phenanthroline (dmp) as the diimine ligand (Chart 1), large turnover numbers were obtained for both the oxidation of alkanes by hydrogen peroxide and the epoxidation of alkenes by molecular oxygen.[4] Involvement of free radicals during epoxidation was excluded, implying oxygen atom transfer processes from the intermediate Ru−oxo complex. Furthermore, bis(diimine)-ruthenium complexes such as *cis*-$[Ru(N{-}N)_2(S)_2]^{2+}$ are octahedral complexes in which the only asymmetric center is the metal itself and which thus exists in two enantiomeric forms, named Λ and Δ (Chart 1).[5] Obviously, such complexes are in general prepared as a racemic mixture of the two enantiomers and evaluated for their catalytic properties in the racemic form. This was indeed the case for the *cis*-$[Ru(dmp)_2(S)_2]^{2+}$ (S = H_2O, CH_3CN) complexes discussed above. To evaluate their potential in asymmetric catalysis

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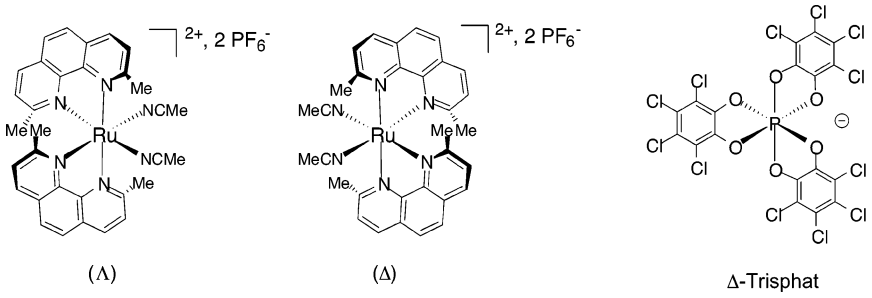
Chart 1. Structures of the Two Enantiomers of Ruthenium Complex **1**$[PF_6]_2$ and of the Trisphat Anion of Δ Configuration



during oxidation reactions such complexes must be prepared in an enantiomerically pure form.

A key step in this approach indeed resides in the preparation of enantiopure catalysts, which, in the absence of chiral ligands, remains challenging. In addition methods are required for simple, rapid, and accurate determination of the enantiomeric purity of these ruthenium complexes. In general, the procedures used for the preparation of optically pure bis(diimine)- or tris(diimine)ruthenium complexes rely on chromatographic chiral stationnary phase (HPLC) separation[6] or diastereoisomeric salt formation using chiral anions followed by crystallization[7] or chromatographic resolution.[8] These techniques have been applied for the preparation of *cis*-$[Ru(bipy)_2(py)_2]^{2+}$, *cis*-$[Ru(bipy)_2(CO)_2]^{2+}$, or *cis*-$[Ru(bipy)_2(DMSO)(Cl)]^+$ complexes, which proved useful as chiral building blocks or precursors for synthesis of a variety of other chiral ruthenium complexes. Stereoretentive methods for monosubstitutions,[9] as well as disubstitutions of the monodentate ligands of these precursors to generate tris(diimine)ruthenium complexes,[6b,7] have been reported. Recently, an anionic $\{[MnCo(oxalate)_3]^-\}_n$ polymeric network with cavities for enantioselective recognition was used for the resolution of the $[Ru(bipy)_2(ppy$ = phenylpyridine$)]^{2+}$ complex.[10]

In this work, we were able to isolate each enantiomer of the ruthenium cation $[Ru(dmp)_2(CH_3CN)_2]^{2+}$, complex **1**, using selective crystallization techniques. In combination with tris[tetrachlorobenzene-1,2-bis(olato)]phosphate(V),[11] a chiral anion also named Trisphat (Chart 1), the heterochiral pairs were obtained in pure form and their structure determined. Finally, preliminary results demonstrate for the first time the potential of the "chiral-at-metal" *cis*-$[Ru(dmp)_2(CH_3CN)_2]^{2+}$ complex, with achiral phenanthroline ligands, in pure enantiomeric form, as a catalyst for enantioselective sulfoxidation by hydrogen peroxide. Even though the enantiomeric excesses are small, this work provides the first experimental demonstration that the chiral information carried by a stereogenic metal center can be *catalytically* transferred to molecules during stereoselective oxidation.

Experimental Section

Materials. $RuCl_3 \cdot 3H_2O$ and *cis*-$[Ru(bpy)_2Cl_2 \cdot 2H_2O$ were purchased from Strem Chemicals, and 2,9-dimethyl-1,10-phenanthroline (neocuproine) was from Aldrich. $Ru(dmp)_2Cl_2$[4a] and methyl naphthyl sulfide[12] were prepared according to described procedures. All sulfides used as substrates for the oxidation tests were commercially available from Aldrich. We thank J. Lacour for a gift of chiral Trisphat ([*n*-Bu_3NH][Λ-T] and [*n*-Bu_4N][Δ-T] salts). Commercial hydrogen peroxide 30% in water from Aldrich was used and titrated before utilization. Solvents used in synthetic procedures were analytical grade.

All the experiments were carried out under dark conditions to avoid any racemization process.

Instruments. NMR spectra were recorded on a Bruker Avance DPX 300 MHz spectrometer. Electrospray mass spectrometry was performed on a Finnigan LC-Q instrument. Absorption spectra were recorded with a Hewlett-Packard 8453 spectrophotometer. Circular dichroism spectra were recorded on a JASCO J-810 spectropolarimeter at 25 °C with a 0.1 cm path length cell. GC-MS analysis was done with a Perkin-Elmer autosystem X coupled to a turbomass spectrometer. HPLC analysis was performed using a HP 1100 system. The enantiomeric purity of the sulfoxides was also checked by analysis with a (*R,R)* Whelk-O2 HPLC column (4.6 mm × 25 cm × 10 μm): typical mobile phase, CH_2Cl_2/*i*-PrOH/cyclohexane (2:19:79); flow rate, 1 mL/min; detection, UV 254 nm.

X-ray Crystallography. Suitable yellow crystals were prepared by diffusion of dichloromethane in an acetonitrile solution of the precipitate obtained by reaction of **1**$[PF_6]_2$ with the Δ-Trisphat anion. Data collection was performed at 298 K using a Bruker SMART diffractometer with a charged-couple device (CCD) area detector, with graphite monochromated Mo Kα radiation (λ = 0.710 73 Å). Molecular structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques using SHELX TL package with anisotropic thermal parameters. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed in ideal positions and refined as riding atoms with individual isotropic displacement parameters. Pertinent crystallographic data are summarized in Table 1: orthorhombic, $C222_1$, No. 20; a = 23.3535 ± 0.0014, b = 30.7830 ± 0.0018, c = 14.5083 ± 0.0009 Å; V = 10429.9 ± 0.1 Å^3; Z = 4; R = 0.0474, R_w = 0.1432.

Preparation of *cis*-$[Ru(dmp)_2(CH_3CN)_2][PF_6]_2$, $1[PF_6]_2$. Complex **1**$[PF_6]_2$ was prepared by chloride displacement by CH_3CN from $Ru(dmp)_2Cl_2$. To 201 mg (0.35 mmol) of *cis*-$Ru(dmp)_2Cl_2$

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Table 1. Selected Bond Lengths (Å) and Angles (deg) for Complex [Λ-**1**][Δ-Trisphat]$_2$[a]

Ru−N(1)	2.113(4)	N(1)−Ru−N(1A)	81.6(2)
Ru−N(1A)	2.113(4)	N(1)−Ru−N(2)	79.30(17)
Ru−N(2)	2.0108(5)	N(1)−Ru−N(2A)	94.70(17)
Ru−N(2A)	2.108(5)	N(1)−Ru−N(3)	174.34(17)
Ru−N(3)	2.038(4)	N(1)−Ru−N(3A)	92.99(15)
Ru−N(3A)	2.038(4)	N(2)−Ru−N(1A)	94.70(17)
N(2)−Ru−N(3)	99.65(18)	N(2)−Ru−N(2A)	172.1(2)
N(2)−Ru−N(3A)	85.83(18)	N(3)−Ru−N(1A)	92.99(15)

[a] Estimated standard deviations in the least significant digits are given in parentheses.

dissolved in 20 mL of CH_3CN was added 693 mg of $AgNO_3 \cdot H_2O$ (10 equiv), and the mixture was stirred for 0.5 h. AgCl was filtered off, and the resulting orange solution was evaporated. After dissolution of the yellow powder in a minimum of EtOH and 20 mL of water, an excess of NH_4PF_6 was added. The resulting yellow precipitate of *cis*-$[Ru(dmp)_2(CH_3CN)_2][PF_6]_2$ was washed with water and Et_2O (yield = 94%). Recrystallization could be achieved in an CH_3CN/toluene mixture.

^{1}H NMR (300 MHz, acetone-d_6; δ (ppm)): 8.80 (d, 2H, J = 8.4 Hz); 8.38 (d, 2H, J = 8.4 Hz); 8.19 (d, 2H, J = 8.8 Hz); 8.11 (d, 2H, J = 8.4 Hz); 8.05 (d, 2H, J = 8.8 Hz); 7.44 (d, 2H, J = 8.4 Hz); 3.54 (s, 6H); 2.53 (s, 6H); 1.82 (s, 6H).

ESI-MS (CH_3CN; m/z): 745, $\{Ru(dmp)_2(CH_3CN)_2(PF_6)\}^+$; 704, $\{Ru(dmp)_2(CH_3CN)(PF_6)\}^+$; 663, $\{Ru(dmp)_2(PF_6)\}^+$; 299, $\{Ru(dmp)_2(CH_3CN)_2\}^{2+}$; 279, $\{Ru(dmp)_2(CH_3CN)\}^{2+}$; 259, $\{Ru(dmp)_2\}^{2+}$.

UV−vis (CH_3CN; λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 442 (7220); 365 (7000); 305 (15 200); 265 (54 300).

Preparation of *cis*-[Δ-Ru(dmp)$_2$(CH$_3$CN)$_2$][Λ-Trisphat]$_2$ or *cis*-[Λ-Ru(dmp)$_2$(CH$_3$CN)$_2$][Δ-Trisphat]$_2$. All experiments should be performed in the dark to avoid light-induced racemization. Racemization was also observed but to a lesser extent upon heating.

To a 5 mM solution of racemic *cis*-$[Ru(dmp)_2(CH_3CN)_2][PF_6]_2$ in 15 mL of CH_2Cl_2 was added 1 equiv of Trisphat salt in CH_2Cl_2 (either ([*n*-Bu_3NH][Λ-Trisphat] or [*n*-Bu_4N][Δ-Trisphat]) dropwise from a concentrated solution (≈30 mM) at room temperature. The immediately formed crystalline precipitate, consisting of [Δ-**1**][Λ-Trisphat]$_2$ or [Λ-**1**][Δ-Trisphat]$_2$, was filtered off. The yield of the selective crystallization was between 45 and 50%. The filtrate was then used for the isolation of the corresponding cationic enantiomer [Λ-**1**][PF_6]$_2$ or [Δ-**1**][PF_6]$_2$ (see below). The crystals were dried under vacuum.

ESI-MS (CH_3CN; m/z): 1368, $\{Ru(dmp)_2(CH_3CN)_2(Trisphat)\}^+$; 1325, $\{Ru(dmp)_2(CH_3CN)(Trisphat)\}^+$; 1287, $\{Ru(dmp)_2(Trisphat)\}^+$; 299, $\{Ru(dmp)_2(CH_3CN)_2\}^{2+}$; 279, $\{Ru(dmp)_2(CH_3CN)\}^{2+}$; 259, $\{Ru(dmp)_2\}^{2+}$.

CD for [Δ-**1**][Λ-Trisphat]$_2$ (CH_3CN; λ_{max}, nm ($\Delta\epsilon$, M^{-1} cm^{-1})): 211 (−584), 220 (+673), 243 (+176), 258 (+129), 276 (−65), 307 (−59), 376 (3), 458 (4) (e.d. by ^{1}H NMR: 98%).

Anal. Calcd for $Ru(C_{14}H_{12}N_2)_2(C_2H_3N)_2(C_{18}O_6Cl_{12}P)_2$, $C_{68}H_{30}N_6O_{12}Cl_{24}P_2Ru$ (MW = 2136.7): C, 38.20; H, 1.40; N, 3.93; Cl, 39.82; P, 2.89; Ru, 4.73. Found: C, 38.13; H, 1.60; N, 4.00; Cl, 40.34; P, 2.73; Ru, 4.35.

Isolation of *cis*-[Λ-Ru(dmp)$_2$(CH$_3$CN)$_2$][PF$_6$]$_2$ or *cis*-[Δ-Ru(dmp)$_2$(CH$_3$CN)$_2$][PF$_6$]$_2$. The second enantiomer of **1**$[PF_6]_2$ was recovered from the filtrate by precipitation using Et_2O.

CD for [Λ-**1**]$[PF_6]_2$ (CH_3CN; λ_{max}, nm ($\Delta\epsilon$, M^{-1} cm^{-1})): 229 (−40), 259 (−80), 276 (+61), 307 (+52), 375 (−3), 458 (−4). (ee by ^{1}H NMR: 88%). ES-MS (CH_3CN; m/z (relative intensity)): 745 (50), $\{Ru(dmp)_2(CH_3CN)_2(PF_6)\}^+$; 300 (30), $\{Ru(dmp)_2(CH_3CN)_2\}^{2+}$; 279 (100) $\{Ru(dmp)_2(CH_3CN)\}^{2+}$. No trace of Trisphat salt could be detected.

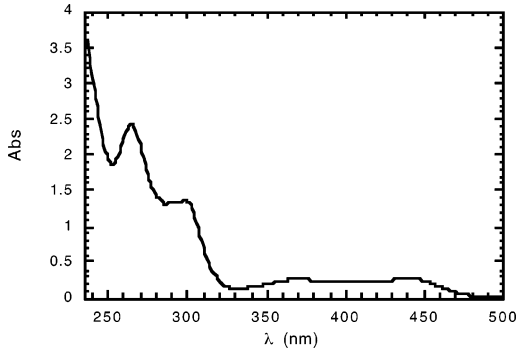

Figure 1. UV−visible spectrum of a CH_3CN solution of the precipitate ([Λ-**1**][Δ-Trisphat]$_2$] = 0.2 mM). **1**$[PF_6]_2$ was treated with Δ-Trisphat in a CH_2Cl_2 solution, and the precipitate was dissolved in CH_3CN.

General Procedure for the Catalytic Oxidation Reactions. To a MeOH solution of catalyst **1**$[PF_6]_2$ or **1**$[Trisphat]_2$ (0.5 mM) was added 50 equiv of the sulfide, and the reaction was initiated by addition of 150 equiv of H_2O_2. The reaction in air or under argon was monitored by GC from the amount of sulfoxide formed using acetophenone as internal standard.

Enantiomeric Excesses Determination. Enantiomeric excesses for ruthenium complexes were determined by NMR analysis in acetone-d_6 (sample concentration ≈ 3 mM). To get the largest splitting of the NMR signals, 2−4 equiv of Trisphat salt was added. Enantiomeric excesses of the sulfoxides were determined by HPLC analysis and by ^{1}H NMR in $CDCl_3$ for the purified compounds. In the latter case, 1−2 equiv of chiral (*R*)-(+)-2,2′-binaphthol was added by small portions until a good splitting of the CH_3 singlet (between 2.7 and 3.0 ppm) was obtained. Enantiomeric excess was calculated from the deconvolution of these two peaks.[13]

Results and Discussion

Isolation of the Δ and Λ Enantiomers of *cis*-[Ru(dmp)$_2$(CH$_3$CN)$_2$]$^{2+}$. The racemic complex *cis*-$[Ru(dmp)_2(CH_3CN)_2][PF_6]_2$, complex **1**$[PF_6]_2$, was synthesized from *cis*-$Ru(dmp)_2Cl_2$[4a] by displacement of the chloride ligands with $AgNO_3$ in acetonitrile followed by anion metathesis with methanolic NH_4PF_6. Addition to complex **1**$[PF_6]_2$ in CH_2Cl_2 of 1 equiv of [*n*Bu_3NH][Λ-Trisphat], the tributylammonium salt of Trisphat, a chiral anion in the Λ enantiomeric form, resulted in the formation of a crystalline precipitate.

Redissolution of the precipitate in CH_3CN gave a yellow solution with absorption bands consistent with a bis(diimine)-ruthenium(II) complex (Figure 1).

The ESI-MS spectrum of that solution displayed a peak at m/z = 1368 corresponding to the $[Ru(dmp)_2(CH_3CN)_2]$-$[Trisphat]^+$ fragment and no peak for a fragment containing PF_6. The CD spectrum in acetonitrile shown in Figure 2a demonstrated a large enrichment in one diastereoisomer resulting from the stereoselective precipitation of one enantiomer of cation **1** in association with Λ-Trisphat. This spectrum displayed bands between 200 and 250 nm characteristic for the Trisphat anion of Λ configuration, whereas the absorption bands between 250 and 550 nm are charac-

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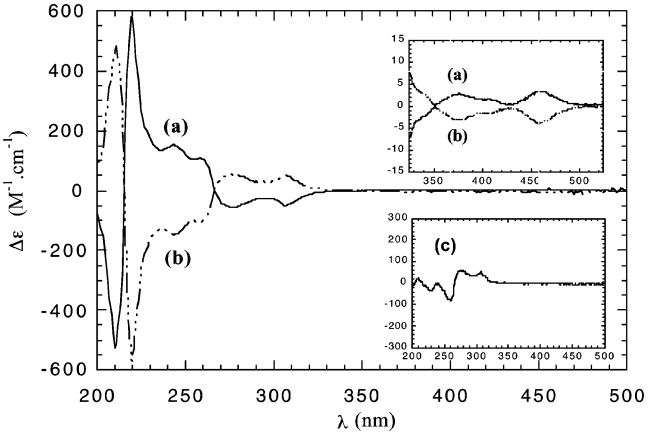

Figure 2. Circular dichroïsm spectra in CH_3CN of (a) [Δ-**1**][Λ-Trisphat]$_2$, (b) [Λ-**1**][Δ-Trisphat]$_2$, and (c) [Λ-**1**][PF_6]$_2$ isolated from the filtrate. Inset: Expansion of the wavelength region between 325 and 525 nm for (a) and (b).

teristic for cation **1**. The absolute configuration was derived from the sign of the ligand-centered transition at 266 nm: a positive Cotton effect at high energy and negative at lower energy is characteristic for a Δ configuration at the metal center.[6,14] The precipitation is therefore selective for the heterochiral diastereoisomer [Δ-Ru(dmp)$_2$(CH_3CN)$_2$][Λ-Trisphat]$_2$ ([Δ-**1**][Λ-Trisphat]$_2$).

CD spectroscopy (Figure 2c) analysis of the filtrate indicated the absence of Trisphat anion and an enrichment in the enantiomer cation of opposite configuration in association with the anion PF_6^-, namely the *cis*-[Λ-Ru(dmp)$_2$(CH_3CN)$_2$][PF_6]$_2$ complex ([Λ-**1**][PF_6]$_2$). The formula of the complex was confirmed by ESI-MS. Different experiments carried out by varying the initial concentration in **1**[PF_6]$_2$ revealed that the largest precipitation yield was obtained for 5 mM of **1**[PF_6]$_2$ in CH_2Cl_2. Under these conditions, almost half of the ruthenium complex was selectively precipitated by addition of 1 equiv of Trisphat. Using 2 equiv of the Trisphat anion did not modify the diastereoselectivity observed in the precipitation.

NMR Spectroscopy: Determination of the Enantiomeric Purity. Trisphat is fully silent in ^{1}H NMR spectroscopy and was previously reported to be an efficient chiral shift reagent for tris(diimine)ruthenium (II) complexes such as [Ru(bipy)$_3$]$^{2+}$ or [Ru(phen)$_3$]$^{2+}$.[15] Whether Trisphat could be used also for bis(diimine)ruthenium complexes was unknown. Addition of an enantiomerically pure form of Trisphat to these complexes might indeed also result in the formation of diastereoisomeric ion pairs with different chemical shifts in their NMR spectra.

Since CD_2Cl_2 could not be used as a solvent, we decided to use acetone-d_6 instead since no precipitation was observed. This solvent had previously been used for determining the enantiomeric excess of the cation [Ru(bpy)$_2$(ppy)]$^+$.[10] Upon sequential addition of 1−4 equiv of the tetrabutylammonium salt of the Λ form of Trisphat (Λ-Trisphat) to a 3 mM solution of complex **1**[PF_6]$_2$ in acetone-d_6, the two diastereoisomers ([Δ-**1**][Λ-Trisphat]$_2$) and ([Λ-**1**][Λ-Trisphat]$_2$) became distinguishable. The spectra are shown in Figure 3 and are compared to that of the same solution in the absence of Trisphat (Figure 3a). Most of the resonances present in the spectrum of the racemic mixture were split into two doublets. The signals between 7.40 and 7.45 ppm, corresponding to one H8 proton of the dmp ligands, were used for determining diastereoisomeric excesses of enriched solutions (see below) as they displayed the largest splitting.

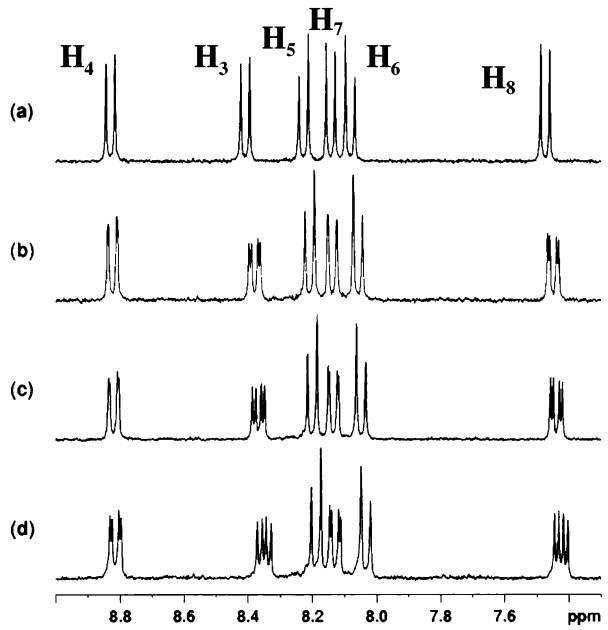

Figure 3. Aromatic region of the ^{1}H NMR spectrum of the racemic *cis*-[Ru(dmp)$_2$(CH_3CN)$_2$][PF_6]$_2$ complex, **1**[PF_6]$_2$, (a) in the absence and in the presence of (b) 1, (c) 2, and (d) 4 equiv of [*n*-Bu_3NH][Λ-Trisphat], in acetone-d_6.

Trisphat appears to be an efficient NMR shift reagent not only for tris(diimine) as previously reported[14] but also for a bis(diimine)ruthenium complex such as **1**[PF_6]$_2$. Very few such reagents are available so far for this class of complexes. In the case of [Ru(bipy or phen)$_2$(CO)$_2$] complexes a chiral europium(III) reagent was used[7b] whereas in the case of [Ru(bipy or phen)$_2$(py)$_2$]$^{2+}$ the substitution of pyridines by an optically active bidentate ligand, 1,2-diaminocyclohexane, with complete retention of configuration, was necessary to afford two diastereoisomers that could be distinguished by NMR spectroscopy.[7a]

The stereoselectivity of the precipitation of *cis*-[Ru(dmp)$_2$(CH_3CN)$_2$][PF_6]$_2$ during treatment with Λ-Trisphat in CH_2Cl_2 described above could thus be determined by NMR spectroscopy. This was achieved after dissolution of the precipitate in acetone-d_6 and addition of 2 equiv of [*n*Bu_3NH][Λ-Trisphat] for optimal resolution. A diastereoisomeric excess value of 98% for the [Δ-**1**][Λ-Trisphat]$_2$ diastereoisomer was derived from integration of the peaks at 7.40−7.45 ppm (Figure 4a). On the basis of this value and of the amount of solid that was recovered by precipitation (47% yield), an enantiomeric excess of about 88% for the complex present in the filtrate was expected. This was indeed what we found by NMR analysis (Figure 4b).

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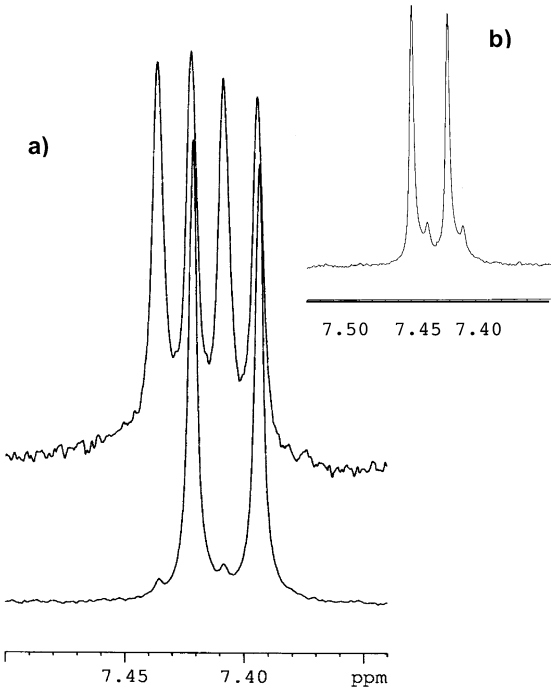


Figure 4. Analysis by ^{1}H NMR spectroscopy in acetone-d_6 of the stereoselectivity of the precipitation of *cis*-$[Ru(dmp)_2(CH_3CN)_2][PF_6]_2$, by Λ-Trisphat in CH_2Cl_2. The signal of the proton H8 of the dmp ligand is displayed: (a) (top spectrum) racemic **1**$[PF_6]_2$ in the presence of 4 equiv of [*n*-Bu_3NH][Λ-Trisphat] and (bottom spectrum) solution of the precipitate after dissolution in acetone-d_6 (the major doublet corresponds to [Δ-**1**][Λ-Trisphat]$_2$); (b) solution of the filtrate after evaporation and dissolution in acetone-d_6 in the presence of 2 equiv of [*n*-Bu_3NH][Λ-Trisphat] (the major doublet corresponds to [Λ-**1**][Λ -Trisphat]$_2$).

In a parallel experiment a crystalline precipitate was also obtained upon addition of the Trisphat anion of opposite configuration Δ to a solution of complex **1**$[PF_6]_2$. The CD spectrum of the precipitate dissolved in CH_3CN is shown in Figure 2b. It is indeed the mirror image of the spectrum of the [Δ-**1**][Λ-Trisphat]$_2$ pair (Figure 2a) confirming a comparable enrichment in the Λ enantiomer of the $[Ru(dmp)_2(CH_3CN)_2]^{2+}$ cation, under these precipitation conditions.

Three-Dimensional Structure of *cis*-[Λ-Ru(dmp)$_2$-(CH$_3$CN)$_2$][Δ-Trisphat]$_2$. The heterochiral selectivity has been fully confirmed by X-ray analysis. Suitable crystals were prepared by diffusion of CH_2Cl_2 in an CH_3CN solution of the precipitate obtained by reaction of complex **1**$[PF_6]_2$ with the Trisphat anion of absolute configuration Δ. The structure of the complex is shown in Figure 5. The complex crystallizes in the orthorhombic *C*222 space group, and the unit cell contains 4 complex cations, 8 Trisphat anions, and 48 other molecules (H_2O and CH_2Cl_2). The R1 value after final refinement is 0.05. Bond lengths and angles are typical for this class of complexes (Table 1). The absolute configuration of the ruthenium center was unambiguously assigned as Λ, due to the presence of the Trisphat anion of known chirality Δ. Very few structural confirmations of this type have been done, and to the best of our knowledge, this is the first structure of a metal complex associated with the Trisphat anion. It shows that one aromatic ring of one dmp ligand of the cation and one catecholato ring of the anion are both in a relative orientation and at a distance (about 3.4 Å) consistent with a π-stacking interaction.[16] The second dmp ligand of the same cation is in a similar interaction with a catecholato ring of a second Trisphat (Figure 5). These interactions could account for the unusual heterochiral association observed.[17] Comparable π-stacking effects have been observed between the toluyl group and the phenanthroline ligand in the $[Ru(phen)_3][(+)$-*O*,*O*′-di-4-toluyl-D-tartrate] complex[8] or between the benzoyl ring and the bipyridine ligand in the $[Ru(bipy)_2(py)_2][(+)$-*O*,*O*′-dibenzoyl-D-tartrate] complex.[18]

In conclusion, the Trisphat anion appears to be an excellent chiral agent for selective crystallization of each enantiomer of complex **1** associated to Trisphat, in the form of the heterochiral pairs, [Λ-**1**][Δ-Trisphat]$_2$ or [Δ-**1**][Λ-Trisphat]$_2$. As a consequence, each enantiomer could also be obtained associated to PF_6^- from the CH_2Cl_2 filtrate, with a high enantiomeric excess. This is the first report of such an application of Trisphat, which has been shown to serve in a number of other useful applications.[19] The method reported here is simple, efficient, highly selective, and fast. Furthermore, the complexes obtained in this work might serve as precursors for synthesis of novel chiral ruthenium complexes. In comparison, resolution of the $[Ru(N-N)_2(py \text{ or } CO)_2]^{2+}$ building blocks was achieved by addition of chiral tartrate anions, but it required either 8−10 days incubation or many recrystallization steps to obtain crystals of pure enantiomers.

Catalytic Oxidation of Sulfides by Hydrogen Peroxide.[20] The catalytic activity of complex **1**$[PF_6]_2$ (0.5 mM) was assayed during oxidation of methyl phenyl sulfide (25 mM) by hydrogen peroxide (75 mM). MeOH gave larger yields than CH_2Cl_2 or CH_3CN and larger selectivity (defined as the sulfoxide/sulfone ratio) than acetone. Indeed, in MeOH, after ca. 8 h of reaction at room temperature, the sulfide substrate was completely oxidized (100% conversion, 50 TON) to the corresponding sulfoxide and sulfone with a high selectivity (9:1 sulfoxide/sulfone). No inactivation of the catalyst could be observed, and addition of a second portion of sulfide and peroxide resulted in similar yields and selectivities. In the absence of the catalyst only about 10% of the sulfide was oxidized. Addition of the chiral tributylammonium Trisphat salt alone did not induce any enantioselectivity during the sulfoxidation.

Table 2 reports the enantiomeric excesses (ee's) for the sulfoxide products obtained during the oxidation of a variety of sulfides by H_2O_2 catalyzed by the enantiomerically pure

(16) Harrowfield, J. M. *J. Chem. Soc., Dalton Trans.* **1996**, 3165.
(17) Examples of homochiral association/selectivity with Trisphat: (a) Maury, O.; Lacour, J.; Le Bozec, H. *Eur. J. Inorg. Chem.* **2001**, 201. (b) Lacour, J.; Goujon-Ginglinger, C.; Torche-Haldimann, S.; Jodry, J. J. *Angew. Chem., Int. Ed.* **2000**, *39*, 3695.
(18) Kolp, B.; Viebrock, H.; von Zelewsky, A.; Abeln, D. *Inorg. Chem.* **2001**, *40*, 1196.
(19) Enantioselective extraction: (a) Reference 15(b). (b) Jodry, J. J.; Lacour, J. *Chem.—Eur. J.* **2000**, *6*, 4297. Ion pair chromatographic resolution: Lacour, J.; Torche-Haldimann, S.; Jodry, J. J.; Ginglinger, C.; Favarger, F. *Chem. Commun.* **1998**, 1733.
(20) For a review on asymmetric oxidation of sulfides, see: Kagan, H. B. In *asymmetric oxidation of sulfides*; Ojima, I., Ed.; Wiley-VCH: New York, 2000; p 327.

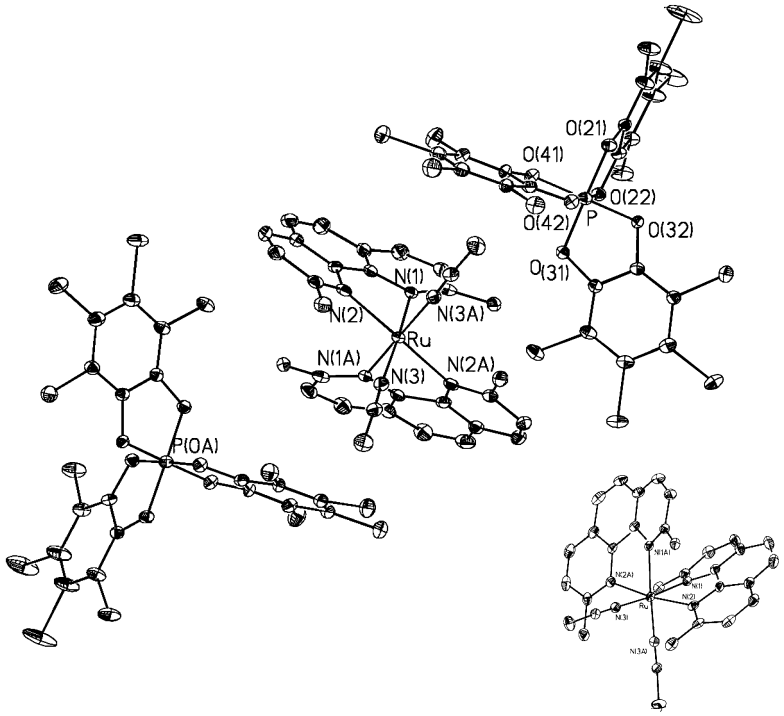


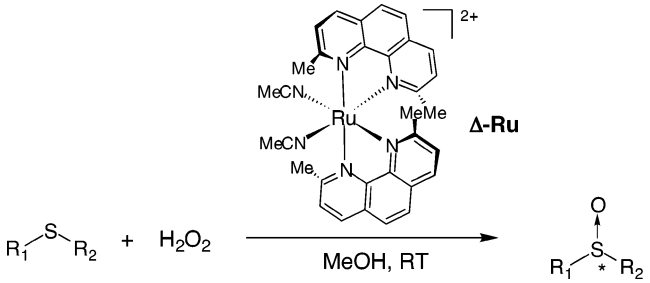
Figure 5. X-ray structure of *cis*-[Λ-Ru(dmp)$_2$(CH$_3$CN)$_2$][Δ-Trisphat]$_2$·10H$_2$O·2CH$_2$Cl$_2$. Hydrogen atoms have been omitted for clarity. Inset: ORTEP representation of the [Λ-Ru(dmp)$_2$(CH$_3$CN)$_2$]$^{2+}$ cation.

Table 2. Enantioselective Oxidation of Sulfides R$_1$−S−R$_2$ (25 mM) by H$_2$O$_2$ in the Presence of **1** Catalyst (0.5 mM) in MeOH at Room Temperature

entry	R$_1$	R$_2$	catal	ee, %
1[a]	C$_6$H$_5$−	CH$_3$−	[Δ-**1**][Λ-Trisphat]$_2$	10 (*R*)
2[a]	C$_6$H$_5$−	CH$_3$CH$_2$−	[Δ-**1**][Λ-Trisphat]$_2$	7 (*R*)
3[a]	4-CH$_3$C$_6$H$_4$−	CH$_3$−	[Δ-**1**][Λ-Trisphat]$_2$	10 (*R*)
4[a]	2-naphthyl	CH$_3$−	[Δ-**1**][Λ-Trisphat]$_2$	14 (*R*)
5[a]	4-methyldibenzo-thiophene	C$_6$H$_4$−[d]	[Δ-**1**][Λ-Trisphat]$_2$	14 (nd)
6[b]	2-BrC$_6$H$_4$−	CH$_3$−	[Δ-**1**][Λ-Trisphat]$_2$	18 (*R*)
7[b]	2-BrC$_6$H$_4$−	CH$_3$−	[Λ-**1**][PF$_6$]$_2$	18 (*S*)
8[b]	2-BrC$_6$H$_4$−	CH$_3$−	*rac*-**1** + (Λ-Trisphat)[c]	0

[a] Catalyst:H$_2$O$_2$ ratio = 1:150. [b] Catalyst:H$_2$O$_2$ ratio = 1:75. [c] The catalyst is racemic complex **1**[PF$_6$]$_2$ in the presence of 4 equiv of [*n*-Bu$_3$NH][Λ-Trisphat]. nd = configuration not determined.

Scheme 1. Enantioselective Oxidation of Sulfides by H$_2$O$_2$ Catalyzed by a Chiral-at-Metal Ruthenium Complex



[Δ-**1**][Λ-Trisphat]$_2$ complex (Scheme 1). The same results were obtained whether the reactions were carried out under aerobic or anaerobic conditions. The ee values for the sulfoxide products were determined by ^{1}H NMR spectroscopy using (*R*)-(+)-2,2′-binaphthol as a chiral shift reagent and by chiral HPLC analysis. Table 2 shows that the oxidation reaction was enantioselective with all the studied substrates. Furthermore, addition of a second aliquot of H$_2$O$_2$ and substrate resulted in similar ee and yield, confirming the stability of the catalyst.

The obtained ee's were low but however significant, ranging from 7% to 18% (2-bromophenyl methyl sulfide). In the case of the latter substrate, the reaction catalyzed by the chiral cation of opposite metal configuration in association with PF$_6$, [Λ-**1**][PF$_6$]$_2$, thus in the absence of the chiral anion, gave the 2-bromophenyl methyl sulfoxide with the same enantiomeric excess but with the opposite configuration (entry 7). This experiment clearly demonstrated that the chiral Trisphat anion was not contributing to the observed enantioselectivity. As an additional proof, an experiment using racemic complex **1**[PF$_6$]$_2$ in the presence of 4 equiv of [*n*Bu$_3$NH][Λ-Trisphat] as a catalyst (entry 8) only led to a racemic mixture of sulfoxides. To exclude a possible contribution of a kinetic resolution process, we examined the ability of [Δ-**1**][Λ-Trisphat]$_2$ to catalyze the oxidation of sulfoxide to sulfone. The unreacted sulfoxide was checked at different reaction times and proved to remain racemic. Finally, the ee's were determined at different times during the course of the reaction and proved to be constant and similar to that of the purified product at the end of the reaction. This excluded an autoinduction by the chiral product. The enantioselectivity of the reaction is therefore exclusively controlled by the chiral metal center, and this control occurs during the oxygen transfer to the sulfide substrate. More experiments are required to establish the mechanism of the reaction and identify the oxygen active species. It should be noted that a partially optically active oxo complex *cis*-[Ru(bipy)$_2$(py)(O)]$^{2+}$ (bipy = bipyridine, py = pyridine) was shown to be able to oxidize sulfides to sulfoxides enantioselectively.[21]

We are fully aware that the selectivities reported in this preliminary study are too small to make this particular complex a useful catalyst. However, we draw attention to the fact that we provide here the first experimental validation of the concept that a "chiral-only-at-metal" complex has the potential to catalyze enantioselective oxidations. The simplicity of the achiral ligands used here as well as the great stability of the catalyst is remarkable. New possibilities regarding the design and development of stereoselective catalysts, with no requirement for the synthesis of complex chiral ligands, are opened.

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Supporting Information Available: Crystallographic data for $[\Lambda\text{-Ru(dmp)}_2(CH_3CN)_2][\Delta\text{-Trisphat}]_2$ (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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