Inorg. Chem. **2003**, *42*, 1378−1385

Enantiospecific Synthesis of Δ and Λ $[Ru(bpy)_2ppy]^+$ and $[Ru(bpy)_2quo]^+$ (bpy = 2,2′-Bipyridine, ppy = Phenylpyridine-H^+, quo = 8-Hydroxyquinolate): ^1H and ^{13}C NMR Studies and X-ray Structure Determination of *rac*-$[Ru(bpy)_2quo]PF_6$

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Received October 22, 2002

In this paper, we describe the enantiospecific synthesis and the complete characterization of the two hexacoordinated ruthenium(II) monocations $[Ru(bpy)_2ppy]^+$ and $[Ru(bpy)_2quo]^+$ (bpy = 2,2′-bipyridine, ppy = phenylpyridine-H^+, quo = 8-hydroxyquinolate) in their enantiomeric Δ and Λ forms. The corresponding enantiomeric excesses (ee's) are determined by ^1H NMR using pure Δ-Trisphat (tris(tetrachlorobenzenedialato)phosphate(V) anion) as a chiral ^1H NMR shift reagent. A complete ^1H and ^{13}C NMR study has been carried out on *rac*-$[Ru(bpy)_2ppy]PF_6$ and *rac*-$[Ru(bpy)_2quo]PF_6$. Additionally, the X-ray molecular structure of *rac*-$[Ru(bpy)_2quo]PF_6$ is reported; this latter species crystallizes in the monoclinic *C*2/*c* space group (a = 22.079 Å, b = 16.874 Å, c = 17.533 Å, $\alpha = 90°$, $\beta = 109.08°$, $\gamma = 90°$).

Introduction

In the flourishing research in the field of polyfunctional materials, we are currently investigating the rational design of optically active molecular-based magnets.[1] These materials are bimetallic oxalato-bridged anionic frameworks of the general formula $\{[M^{III}M^{II}(C_2O_4)_3]_n\}^{n-}$, in which the negative charge is balanced by a monocationic counterpart. Furthermore, to achieve three-dimensional (3D) structures, the chiral template cation and the anionic block $[M^{III}(C_2O_4)]^{3-}$ must have both a quasi-D_3 symmetry.[1a,b] According to these requirements, our attention was focused on ruthenium(II) hexacoordinated salts. Such complexes, with three bidentate bipyridyl ligands either substituted or not, are largely described in the literature.[2] As dications, many of them are known in their enantiomerically pure Δ and Λ forms.[3] They can be obtained in optically active form, either by the classical fractional diastereomeric crystallization using tartrate salts,[4] or by direct chiral chromatography techniques.[5] Another way proceeds through enantiomeric synthesis, by replacement of two monodentate ligands by a bidentate one, starting from a previously resolved Δ or Λ $[Ru^{II}(bpy)_2L1L2]^{2+}$

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10.1021/ic026121c CCC: $25.00
Published on Web 01/24/2003

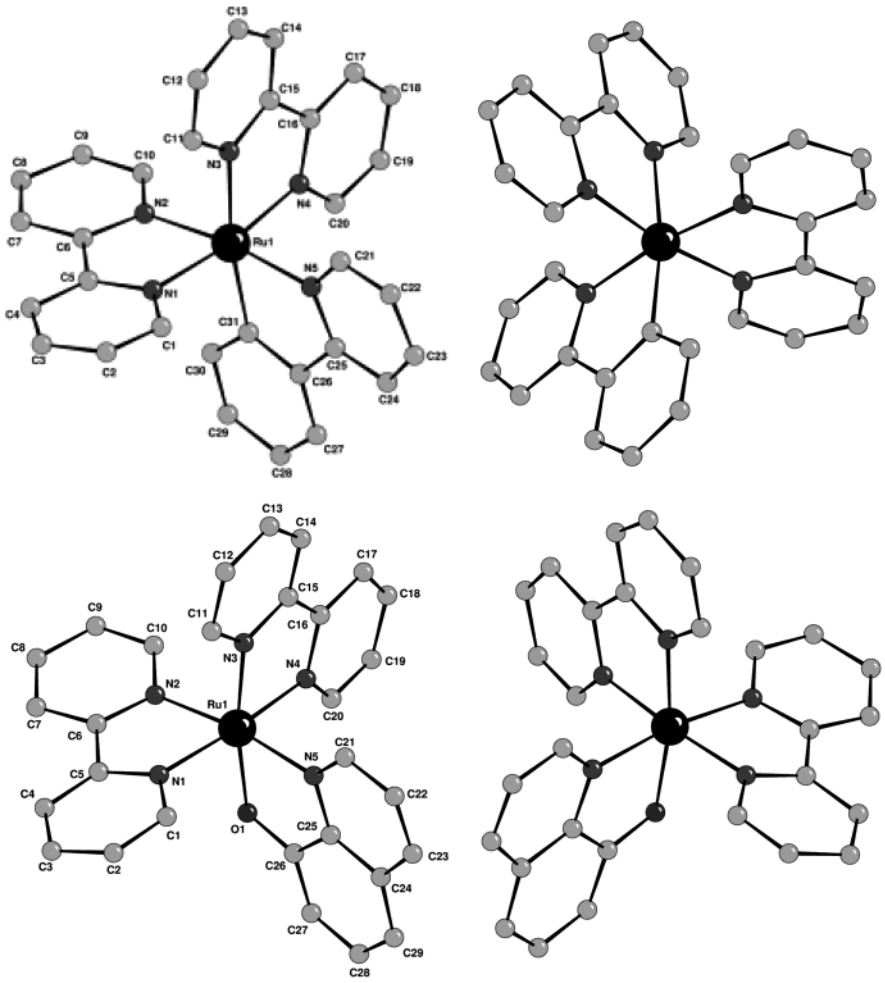

Figure 1. Schematic representation of $[Ru(bpy)_2ppy]^+$ (**1**) (top) and $[Ru(bpy)_2quo]^+$ (**2**) (bottom) in their Δ (left) and Λ (right) enantiomeric forms.

dication (bpy = 2,2′-bipyridine, L1 = L2 = CO,[6] L1 = Cl, L2 = DMSO[7]). Recently, von Zelewsky and Hua[8] have proposed a general elegant and efficient route to obtain Ru^{2+} salts having at least one substituted bypyridyl ligand, using as starting material the Δ or Λ $[Ru^{II}(bpy)_2py_2]^{2+}$ dication (py = pyridine). If the synthesis of optically active dicationic hexacoordinated ruthenium(II) salts is very well documented, in contrast, this is not the case for ruthenium(II) monocations. Nevertheless, some of them are described in the literature in their racemic form, as is the case for *rac*-$[Ru(bpy)_2ppy]^+$[9] and *rac*-$[Ru(bpy)_2quo]^+$ (ppy = phenylpyridine-H^+, quo = 8-hydroxyquinolate).[10] We have previously described[11] the partial resolution of the Δ and Λ $[Ru^{II}(bpy)_2ppy]^+$ (**1**) and Δ and Λ $[Ru^{II}(bpy)_2quo]^+$ (**2**) monocations, using the stereoselective self-assembly of a chiral 3D anionic framework. Following this procedure, the resulting enantiomeric excesses are, however, limited to 50%.

Herein we describe the synthesis of the Δ and Λ enantiomers of the monocations $[Ru^{II}(bpy)_2ppy]^+$ (**1**) and $[Ru^{II}(bpy)_2quo]^+$ (**2**) starting from Δ and Λ $[Ru^{II}(bpy)_2py_2]^{2+}$ (Figure 1). In addition, we propose a complete spectroscopic ^1H and ^{13}C NMR description of *rac*-**1** and *rac*-**2** and the X-ray structure of the *rac*-$[Ru^{II}(bpy)_2quo]^+$ monocation *rac*-**2**. For **1** and **2**, the enantiomeric excesses (ee's) were measured by ^1H NMR, using pure optically active anion Δ-Trisphat (tris(tetrachlorobenzenedialato)phosphate(V) anion),[12] as chiral shift reagent.

Experimental Section

The following compounds were prepared according to literature methods: Δ or Λ $[[Ru^{II}(bpy)_2py_2][PF_6]_2]$,[9] $[Ru^{II}(bpy)_2Cl_2]$,[7d] and

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$[N_nBu_4(\Delta\text{-Trisphat})]$.[12] Other reagents are commercially available and were used as purchased.

General Procedure. The IR spectra were recorded on a Bio-Rad IRFT spectrometer as KBr pellets in the 4000−250 cm^{-1} region. Elemental analyses were performed at the SIARE-UPMC Paris. Circular dichroism curves were recorded using a Jasco model J-710 spectropolarimeter. Measurements were carried out in CH_2Cl_2 solutions for Δ- and Λ-**1** and for Δ- and Λ-**2** ($c = 8.5 \times 10^{-5}$ mol·L^{-1}) in a 1 mm cuvette. The baseline correction was performed with the spectrum of a pure solvent prepared under the same conditions. Spectra were recorded in the 200−700 nm wavelength range for all compounds.

NMR Spectroscopy. NMR spectra were recorded on a Bruker Avance DMX500 spectrometer, operating at a ^1H resonance frequency of 500.13 MHz. Samples were dissolved in 500 μL of acetone-d_6 or CD_2Cl_2, at concentrations of ca. 10 mM. Chemical shifts are given in ppm/TMS by using the residual solvent ^1H and ^{13}C signals as internal references: 2.09 and 29.5 ppm in acetone-d_6, 5.32 and 54.0 ppm in CD_2Cl_2, respectively. Unless otherwise indicated, all ^1H two-dimensional experiments were acquired in the phase-sensitive mode with the time-proportional phase incrementation of the initial pulse.[13a] A relaxation delay of 1.2−2 s was used. There were 256−400 t_1 increments and 2048 complex data points in t_2 recorded for a spectral width of 2000 Hz in the two dimensions. Prior to Fourier transform, the signal was multiplied by a shifted square sine-bell window function. For TOCSY experiments,[13b] a MLEV17 mixing scheme of different lengths (from 10 to 80 ms) with a 10 kHz spin-locking field strength were used in order to define direct and long-range correlations. Two-dimensional heteronuclear experiments were performed by using the standard Bruker software. In $^{13}C-^1H$ HSQC and HMBC[13c,b] sequences, delays were optimized for coupling constants around 150 and 10 Hz, respectively. One-dimensional NOE experiments were recorded in difference mode by subtracting one spectrum with irradiation on resonance and another one with irradiation off resonance: in this experiment, a relaxation delay of 3 s was used. NOESY experiments were carried out by using mixing times of 1.2 s and relaxation delays of 3 s.

^1H NMR spectra for enantiomeric excess determination were obtained at 300 K on an AC300 Bruker spectrometer in 5 mm o.d. tubes. Concentration of the complex was 0.014 mol·L^{-1} in acetone-d_6 and CD_2Cl_2 for **1**PF6 and **2**PF6, respectively. Successive spectra were acquired after addition of aliquots of $[N^nBu_4(\Delta\text{-Trisphat})]$.

X-ray Crystallographic Analysis. Accurate cell dimensions and orientation matrix were obtained by least-squares refinement of 25 accurately centered reflections. Rather weak decays (10%) were observed in the intensities of two checked reflections during data collection; data were accordingly scaled. Absorption corrections were applied using DIFABS ($T_{min} = 0.84$ and $T_{max} = 0.94$). Computations were performed by using the PC version of CRYSTALS.[14a] The data were corrected for Lorentz and polarization effects. Scattering factors were taken from the International Table for X-ray Crystallography.[14b] The structures were solved by direct methods (SHELXS)[14c] and Fourier maps technique. Refinements on F were carried out by full-matrix least-squares using anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were introduced in calculated positions, and only one overall isotropic displacement parameter was refined. Selected crystallographic data and diffraction parameters are listed in Tables 1 and 2.

Table 1. Crystal Data for *rac*-$[Ru(bpy)_2quo]PF_6$

formula	$C_{29}H_{22}N_5ORu, PF_6$
cryst class	monoclinic
space group	*C*2/*c*
a (Å)	22.079(11)
b (Å)	16.874(3)
c (Å)	17.533(8)
α (deg)	90
β (deg)	109.08(3)
γ (deg)	90
V (Å^3)	6173(4)
Z	8
radiation type	Mo Kα
wavelength (Å)	0.710690
D	1.51
M (g·mol^{-1})	702.56
μ (mm^{-1})	0.627
T (K)	295
size (mm^3)	0.4 × 0.4 × 0.3
color	brown
shape	parallelepiped
diffractometer	Enraf-Nonius Cad-4
scan type	2*θ*/*ω*
reflns measured	6433
indep reflns	6039
R_{int}	0.02
θ_{min}, θ_{max}	1, 26.00
h_{min}, h_{max}	0, 27
k_{min}, k_{max}	0, 20
l_{min}, l_{max}	−21, 20
% decay	0.104
refinement on *F*	
R-factor[a]	0.0830
weighted *R*-factor[b]	0.0842
$\Delta\rho_{min}$ (e/Å^3)	−2.30
$\Delta\rho_{max}$ (e/Å^3)	1.45
reflns used	3297
$\sigma(I)$ limit	3.00
no. params	389
GOF	1.031

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|| F_o| - |F_c||)^2/\sum wF_o^2]^{1/2}$. Weighting scheme of the form $w = w'[1 - ((||F_o| - |F_c||)/6\sigma(F_o))^2]^2$ with $w' = 1/\sum_r A_r T_r(X)$ with coefficients 2.07, 1.53, and 1.51 for a Chebychev series for which $X = F_c/F_c(max)$.

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for *rac*-$[Ru(bpy)_2quo]PF_6$

Ru(1)−O(1)	2.064(6)	Ru(1)−N(1)	2.059(7)
Ru(1)−N(2)	2.031(7)	Ru(1)−N(3)	2.023(6)
Ru(1)−N(4)	2.027(7)	Ru(1)−N(5)	2.050(6)
O(1)−C(26)	1.305(11)		

O(1)−Ru(1)−N(1)	88.6(3)	N(1)−Ru(1)−N(2)	78.0(2)
N(2)−Ru(1)−N(3)	92.5(3)	N(3)−Ru(1)−N(4)	80.8(3)
O(1)−Ru(1)−N(5)	80.1(2)	N(4)−Ru(1)−N(5)	90.3(3)
Ru(1)−O(1)−C(26)	112.5(5)		

Preparation of *rac*-1PF$_6$ and *rac*-2PF$_6$. *rac*-**1**PF_6 was prepared as described previously.[9] *rac*-**2**PF_6 was synthesized according to a modified procedure from ref 10. A solution of 100 mg (1.9×10^{-4} mol) of $Ru^{II}(bpy)_2Cl_2$, 60 mg of 8-hydroxyquinoline (4.1×10^{-4} mol), and 100 mg of sodium acetate in 30 mL of absolute ethanol was heated to gentle reflux. $AgBF_4$ [75 mg (3.8×10^{-4} mol)] was progressively added, and the reflux was continued for 18 h, whereupon the solution turned red. After cooling, the solution was

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filtered on paper, and 31 mg (1.9×10^{-4} mol) of NH_4PF_6 in 20 mL of acetone solution was added to the filtrate. After removal of the solvent, the obtained red oil was purified by chromatography on a neutral alumina column (Φ 4 cm, *L* 10 cm) with, successively, CH_2Cl_2, THF, and MeOH as eluents. After evaporation of the solvent, the residue was dissolved in CH_2Cl_2 and reprecipitated by addition of cold diethyl ether, and 116 mg (86% yield) of *rac*-**2**PF_6 was obtained.

IR KBr pellet (cm^{-1}): 1654(m), 1568(s), 1497(m), 1458(s), 1378(s), 1322(m), 842(vs), 762(s), 729(m), 557(s). ^1H and ^{13}C NMR: see Table 4.

Analysis for $C_{29}F_6H_{22}N_5OPRu$ Calcd: C 49.58, H 3.16, N 9.97. Found: C 49.66, H 3.25, N 9.80.

Preparation of Δ-, Λ-1PF_6 and Δ-, Λ-2PF_6. Δ-**1**PF_6: 409 mg (3.4×10^{-4} mol) of Δ-[Ru(bpy)$_2$py$_2$](D) dibenzoyl-tartrate, prepared according to the procedure described by von Zelewsky,[8] in 10.6 mL of ethylene glycol and 106 mg (7.4×10^{-3} mol) of phenylpyridine were heated for 6 h at 120 °C. The solution turned violet. After cooling, an aqueous solution of NH_4PF_6 (44.5 mg in 20 mL) was added, and subsequent addition of 200 mL of water resulted in the precipitation of a violet powder. The precipitate was filtered, and then dissolved in a minimum of CH_2Cl_2. Addition of pentane led to the precipitation of the ruthenium salt, which was filtered. These operations were repeated until the complete elimination of the unreacted phenylpyridine as checked by ^1H NMR. After being washed with water and diethyl ether, the powder was dried under vacuum leading to 226 mg (93% yield) of Δ-**1**PF_6 (ee = 0.50, determined by ^1H NMR using [N_nBu$_4$(Δ-Trisphat)] as chiral shift reagent). The Λ-**1**PF_6 enantiomeric form is obtained in a similar way starting from the Λ-[Ru(bpy)$_2$py$_2$](L) dibenzoyl-tartrate (ee = 0.73).[8]

Natural circular dichroism (NCD) Δ-**1**PF_6 (CH_2Cl_2, $c = 8 \times 10^{-5}$ mol·L^{-1}): 577(−), 488(+), 431(+), 298(−), 284(+), 260(+). Λ-**1**PF_6 (CH_2Cl_2, $c = 8 \times 10^{-5}$ mol·L^{-1}): 577(+), 488(−), 431(−), 298(+), 284(−), 260(−).

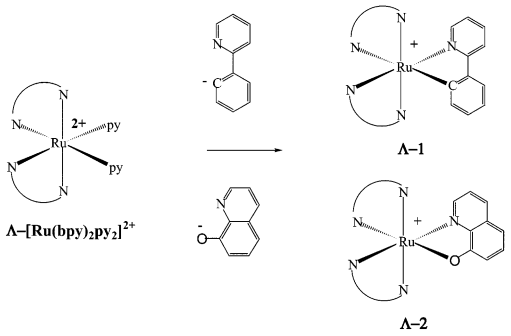
Synthesis of Δ-**2**PF_6: Δ-[Ru(bpy)$_2$py$_2$](D) dibenzoyl-tartrate [409 mg (3.4×10^{-4} mol)] in 10.6 mL of ethylene glycol, 108 mg (7.5×10^{-4} mol) of 8-hydroxyquinoline, and 180 mg of sodium acetate were heated for 18 h at 120 °C. The solution turned red. After cooling, a solution of NH_4PF_6 in acetone (5.6 mg/10 mL) was added. After evaporation of the solvent, the residue was purified by chromatography on a neutral alumina column (Φ 4 cm, *L* 10 cm), with CH_2Cl_2 as eluent, by collecting the red band. After removing the solvent, the residue was dissolved in a minimum of acetone, and further addition of cold diethyl ether led to the precipitation of a red powder. The powder is dried under vacuum to give 201 mg of Δ-**2**PF_6 in 84% yield (ee = 0.98). The Λ-**2**PF_6 enantiomeric form is obtained similarly, starting from the Λ-[Ru(bpy)$_2$py$_2$](L) dibenzoyl-tartrate (ee = 0.98).[8]

NCD Δ-**2**PF_6 (CH_2Cl_2, $c = 8 \times 10^{-5}$ mol·L^{-1}): 590(−), 523(−), 480(+), 411(+), 378(−), 359(+), 336(−), 298(−), 277(+), 260(+), 247(−). Λ-**2**PF_6 (CH_2Cl_2, $c = 8 \times 10^{-5}$ mol·L^{-1}): 590(+), 523(+), 480(−), 411(−), 378(+), 359(−), 336(+), 298(+), 277(−), 260(−), 247(+).

Results and Discussion

Synthesis. The racemic compounds *rac*-**1** and *rac*-**2** were obtained according to a modified procedure from the literature.[9,10] The two Δ and Λ enantiomers of **1** and **2** were obtained starting from the pure Δ or Λ forms of the dication $[Ru^{II}(bpy)_2py_2]^{2+}$ prepared following the procedure described previously[8] according to Scheme 1.

Scheme 1. Enantiospecific Substitution of the Pyridine Ligands from Δ or Λ $[Ru(bpy)_2py_2]^{2+}$ with ppy(-H^+) or quo Ligands



The phenylpyridine or 8-hydroxyquinoline is warmed to 120 °C in ethylene glycol in the presence of the Δ or Λ $[Ru^{II}(bpy)_2py_2]^{2+}$ for 6 or 18 h to give compounds **1** and **2**, respectively. The final compounds are recovered as PF_6 salts in 93% and 84% yield by adding an aqueous or acetone solution of NH_4PF_6 for **1** and **2**, respectively. The dramatic difference in enantiospecificity between the two cations **1** and **2** can be correlated to the nature of the incoming chelating ligand which replaces the two pyridines in the $[Ru(bpy)_2(py)_2]^{2+}$ starting material. Actually, in the case of 8-hydroxyquinoline, the abstraction of the phenolic proton is easier than removing an aromatic proton from the phenylpyridine.

X-ray Crystallographic Studies for *rac*-2PF_6. Suitable crystals for X-ray studies of *rac*-**2**PF_6 were obtained by slow diffusion of diethyl ether into an acetonitrile solution of *rac*-**2**PF_6. *rac*-**2**PF_6 crystallizes in the monoclinic *C*2/*c* space group with $Z = 8$. Crystallographic data and selected distances and angles are reported in Tables 1 and 2, respectively. The CAMERON view of **2** is shown in Figure 2.

The molecular structure is in accordance with the proposed formula. The Ru−N distances [2.059 Å Ru(1)−N(1), 2.031 Å Ru(1)−N(2), 2.023 Å Ru(1)−N(3), 2.027 Å Ru(1)−N(4), 2.050 Å Ru(1)−N(5), and 2.064 Å Ru(1)−(1)O] indicate that the ruthenium atom lies in a distorted octahedral en-

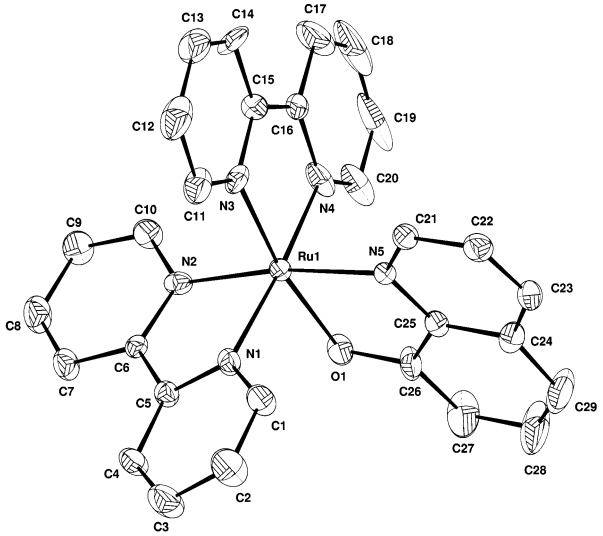


Figure 2. CAMERON view of the monocation *rac*-[Ru(bpy)$_2$quo]$^+$ **2**.

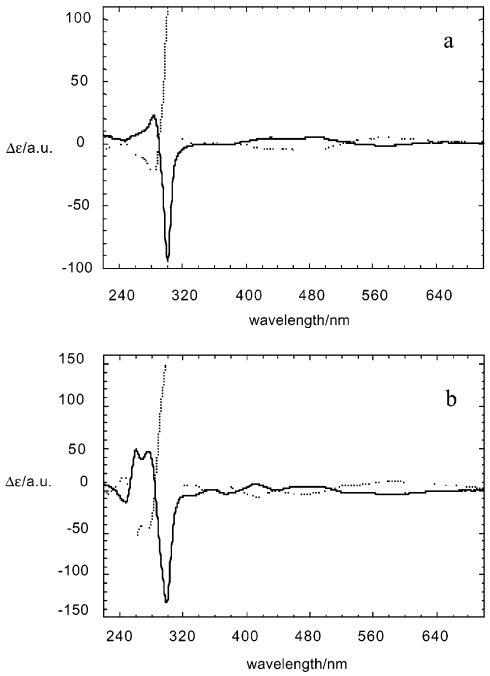


Figure 3. NCD curves for the two enantiomers of (a) **1**PF_6 and (b) **2**PF_6: Δ enantiomer (—) and Λ enantiomer (···).

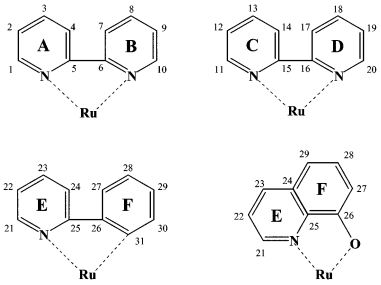
vironment. The N(1)RuN(2), N(3)RuN(4), and O(1)RuN(5) angles are quite similar with bond angles of 78.0(2)°, 80.8(3)°, and 80.1(2)°, respectively.

Cotton Effect for Δ-, Λ-1PF_6 and Δ-, Λ-2PF_6. Dichroism curves were recorded in 8.5×10^{-5} mol·L^{-1} CH_2Cl_2 solutions. The absolute configurations were determined by comparison with the CD curves obtained for the starting Δ or Λ $\{[Ru^{II}(bpy)_2py_2][PF_6]_2\}$[8] complexes. This correlation is based on the principle that related optically active compounds are of the same absolute configuration if they give a Cotton effect of the same sign in the absorption wavelength region of an electronic transition common to both molecules.[15] The CD curves for the Δ and Λ enantiomers of **1** and **2** are shown in Figure 3a,b.

Both complexes show optical activity and opposite signals typical for two enantiomers. The absolute configurations Δ and Λ were assigned according to the sign of the intense MLCT transition at 301 nm for **1**PF_6 and 298 nm for **2**PF_6. A positive sign corresponds to the Λ configuration, a negative sign to the Δ one.[8]

Determination of the Enantiomeric Excess (ee). The very deep purple color of the $[Ru(bpy)_2(ppy)]^+$ (**1**) and $[Ru(bpy)_2quo]^+$ (**2**) complexes (due to the intraligand bipyridine transitions) prevented all attempts to measure the optical rotation, $[\alpha]_D$. Therefore, the enantiomeric excesses were determined using ^{1}H NMR. Since the discovery by Lacour[12] of $[N_nBu_4(\Delta\text{-Trisphat})]$ as a ^{1}H NMR chiral shift reagent,[16] this method has been used to determine the ee of some hexacoordinated metal cations, as well as of charged or noncharged chiral organometallic compounds with different types of chirality: planar, chiral clusters, for example.[16] We have previously shown that this is a good method to determine the ee for Δ-**1**, Λ-**1** and Δ-**2**, Λ-**2** when partially resolved by using the stereoselective self-assembly of a chiral 3D anionic framework. It is evident that the determination of the protons affected by the chiral Δ-Trisphat anion requires the complete assignment of the ^{1}H NMR spectra.

Scheme 2. Carbon Atom Numbering for the Aromatic Rings of $[Ru(bpy)_2ppy]^+$ and $[Ru(bpy)_2quo]^+$[a]



[a] A−B and C−D = bipyridyl, E−F = phenylpyridyl (left) or 8-hydroxyquinolate (right).

^{1}H and ^{13}C NMR studies of *rac*-1PF_6 and *rac*-2PF_6. Complex **1** was investigated many years ago by Constable et al.:[9] they determined ^{1}H chemical shifts at 5.9 T on the basis of homodecoupling and NOE experiments. At that field, many proton resonances are overlapping, and the resulting assignment may be questioned. Consequently, we decided to reconsider the problem by using a set of 2D ^{1}H and ^{13}C correlation methods at higher field. Given the good dispersion of protons in acetone solutions, these studies were carried out in this solvent.

The assignment strategy was as follows: (i) determination of proton connectivities in each of the six aromatic rings from COSY and TOCSY experiments, (ii) assignment of methine carbons from HSQC and HSQC-TOCSY experiments and of quaternary carbons from HMBC spectra, (iii) ring pairing (A−B, C−D, and E−F, Scheme 2) and relative spatial orientations of the three ligands from 1D and 2D NOE measurements.

By using TOCSY, it is easy to establish the connectivity sequence of the four protons (d, t, t, d) in each of the six aromatic rings; however, because of strong mutual ring-current effects in such compact metallo complexes, ^{1}H chemical shifts cannot be directly deduced from those of the free bipyridine and phenylpyridine ligands. This remains possible for ^{13}C assignment: actually, the 1D ^{13}C spectrum of **1** exhibits around 150 ppm five deshielded CH signals which correspond to the methine groups in α position of N atoms (C_1, C_{10}, C_{11}, C_{20}, and C_{21}) in the five pyridine rings A, B, C, D, and E. The related protons are then unambiguously determined from HSQC spectra. At this stage, HSQC-TOCSY experiments allow us to determine all the resonances corresponding to each aromatic ring and show that the four deshielded doublets around 8.7 ppm correspond to the

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"facing" protons H_4, H_7, H_{14}, and H_{17} (Scheme 2). Moreover, the strong NOE observed between the doublets at 8.60 and 8.62 ppm and the one between the doublets at 8.77 and 8.69 ppm allow us to associate the rings (A−B and C−D) of the two bpy ligands (d_{H-H} around 2.1 Å). Similarly, the strong NOE observed between the protons at 8.18 and 7.94 ppm is in agreement with the short distance (2.08 Å) between the facing protons H_{24} and H_{27} in the (E−F) ppy ligand. The next step is the quaternary carbons assignment by HMBC spectra: among the corresponding resonances, five signals between 155 and 168 ppm are assigned to the carbon atoms in the α position of N atoms (C_5, C_6, C_{15}, C_{16}, and C_{25}). On the basis of long-range coupling constants, the strongly deshielded signal at 193.1 ppm corresponds to C_{31}, directly bonded to the Ru center, and the last one at 145.9 ppm corresponds to C_{26} in the same ring.

The relative position of the three ligands (two bpy and one ppy) is finally inferred from the observation of inter-ring NOEs. Actually, according to the X-ray data, there are two sets of three protons belonging to different rings (A, C, E and B, D, F) for which the H−H distances are close to 3.2 Å. This value explains the medium intensity observed for the correlations between H_1, H_{11}, H_{21} and between H_{10}, H_{20}, H_{30} in the NOESY spectrum (see Table 3). Finally, the presence of weak NOEs between the protons at 8.77 and 7.74 ppm and between those at 8.62 and 6.52 ppm is in agreement with interproton distances around 4.5 Å ($d_{H_7-H_{30}} = 4.50$ Å and $d_{H_{14}-H_{21}} = 4.16$ Å). These observations lead to assign the corresponding protons and to discriminate the two bpy ligands.

When compared to the dication $[Ru(bpy)_3]^{2+}$,[17] all the protons (except H_{20}) of the pyridine rings in monocation **1** are shielded, and the largest negative shifts (−0.3 to −0.6 ppm) are observed for the pyridine ring E. This may be explained by the different electronic distribution induced by pairing with the phenyl ring F in the ppy ligand.

For complex **2**, the TOCSY spectrum makes evident two sequences of three coupled protons immediately assigned to the quo ligand. The presence of a strong NOE and a small ^4J coupling constant (<1 Hz)[18] between the protons at 8.12 and 6.90 ppm allows us to assign these resonances to the *peri* protons H_{23} and H_{29}, respectively. As described previously, CH pairs of the pyridine rings are determined from HSQC and HSQC-TOCSY spectra: again, the four facing protons of the bpy ligands, H_4, H_7, H_{14}, and H_{17}, are characterized by strong NOEs. However, because of the degeneracy at 8.76 ppm, it is necessary to use the three inter-ring NOEs implying H_1, H_{11}, and H_{21} (distances 3.2 Å) to associate by pairs the pyridine rings and simultaneously to determine the relative orientations of the bpy and quo ligands. Let us remark that the low symmetry of **2** leads to different inter-ring distances between protons H_{10}, H_{20}, and H_{27}, and consequently, only two NOEs implying these protons are observed (see Table 2). As in the previous description, the weak NOE between protons at 7.58 ppm (H_{21}) and 8.73 ppm allows us to discriminate the two bpy ligands, according to a distance of 4.48 Å between H_{14} and H_{21}. Two other weak NOEs implying in one part H_{10}, H_{11} and in another part H_{10}, H_{17} are in agreement with the X-ray distances (see Table 4).

As for **1**, it is worth noting that proton H_{20} is deshielded with respect to the corresponding one in $[Ru(bpy)_3]^{2+}$, but this effect is more pronounced than for **1** (0.86 and 0.13 ppm, respectively). This may result from differences in ring current effects. Actually, this proton H_{20} faces a pyridine ring in $[Ru(bpy)_3]^{2+}$, a phenyl ring in $[Ru(bpy)(ppy)]^+$: in $[Ru(bpy)_2(quo)]^+$, it may be perturbed by the presence of the oxygen atom.

Table 3. ^1H and ^{13}C NMR Data for $[Ru(bpy)_2ppy]^+$ (**1**)[a]

	δ C	δ H	NOE correlations	NOE intensity[b]	H−H distance[c]	HMBC correlations
			Ring A			
1	150.6	7.96				
2	126.9	7.39				
3	134.0	7.92				
4	123.5	8.60	8.62(H_7)	s	2.1	
5	157.5					H_7, H_4, H_3
			Ring B			
6	157.2			t		H_4
7	123.3	8.62	8.60(H_4)	s	2.1	
8	134.0	7.99				
9	126.6	7.41				
10	150.4	7.92				
			Ring C			
11	149.4	8.07	7.96(H_1), 7.74(H_{21})	m, m	3.17, 3.13	
12	127.6	7.62				
13	136.8	8.15				
14	123.6	8.77	8.69(H_{17})	s	2.11	
15	155.8					H_{14}, H_{17}
						H_{13}, H_{11}
			Ring D			
16	158.3					H_{17}, H_{14}
						H_{18}, H_{20}
17	123.9	8.69	8.77(H_{14})	s	2.11	
18	135.4	7.99				
19	126.6	7.40				
20	154.5	8.20	6.52(H_{30})			
			Ring E			
21	150.5	7.74	7.96(H_1)	m	3.06	
			8.07(H_{11})	m	3.13	
			8.77(H_{14})	w	4.16	
22	122.7	7.06				
23	136.1	7.80				
24	119.3	8.18	7.94 (H_{27})	s	2.08	
25	168.0					H_{24}, H_{27}
						H_{23}, H_{21}
			Ring F			
26	145.9					H_{27}, H_{30}
27	124.6	7.94	8.18(H_{24})	s	2.08	
28	121.1	6.92				
29	128.9	6.86				
30	135.6	6.52	8.20(H_{20})	m	3.27	
			7.92(H_{10})	m	3.21	
			8.62(H_7)	w	4.50	
31	193.1					H_{29}, H_{27}

[a] Chemical shifts in acetone-d_6 are given in ppm with respect to TMS by using the solvent peak as reference: 2.09 ppm for ^1H and 29.5 ppm for ^{13}C. Only unambiguous NOEs relevant for assignment are mentioned: they were obtained by 2D NOESY spectra (mixing times of 1 s and 1.2 s). Long-range correlations are given for quaternary carbons only and are deduced from HMBC spectra with optimization for coupling constants around 8 Hz. [b] s = strong; m = medium; w = weak. [c] In angstroms, from X-ray data.[11a]

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Table 4. ^{1}H and ^{13}C NMR Data for $[Ru(bpy)_2Quo]^+$ (**2**)[a]

	δ C	δ H	NOE correlations	NOE intensity[b]	H−H distance[c]	HMBC correlations
			Ring A			
1	151.0	8.10	8.19(H_{11})	m	3.21	
			7.58(H_{21})	m	3.20	
2	127.1	7.49				
3	136.5	8.07				
4	124.1	8.76	8.71(H_7)	s	2.06	
5	158.4					*d*
			Ring B			
6	158.5					*d*
7	123.7	8.71	8.76(H_4)	s	2.06	
8	136.3	8.01				
9	126.6	7.43				
10	152.2	7.92	8.93(H_{20})	m	3.50	
			8.19(H_{11})	w	4.83	
			8.76(H_{17})	w	4.16	
			Ring C			
11	153.5	8.19	8.10(H_1)	m	3.21	
			7.58(H_{21})	m	3.20	
			7.92(H_{10})	w.	4.83	
12	127.1	7.44				
13	135.6	8.02				
14	124.3	8.73	8.76(H_{17})	s	2.21	
			7.58(H_{21})	w	4.48	
15	159.7					H_{11}, H_{13}
						H_{14}, H_{17}
			Ring D			
16	158.1					H_{17}
17	123.9	8.76	8.73(H_{14})	s	2.21	
			8.19(H_{11})	w	4.83	
18	136.7	8.13				
19	127.2	7.66				
20	151.1	8.93	7.92(H_{10})	m	3.50	
			6.83(H_{27})	m	3.73	
			Ring E			
21	146.5	7.58	8.10(H_1)	m	3.20	
			8.19(H_{11})	m	3.20	
			8.73(H_{14})	w	4.48	
22	122.4	7.25				
23	136.2	8.12	6.90(H_{29})	s	2.58	
24	131.4					H_{22}, H_{28}
25	146.3					H_{23}, H_{27}, H_{29}
			Ring F			
26	170.5					H_{27}, H_{28}
27	115.8	6.83	8.93(H_{20})	m	3.73	
28	130.3	7.35				
29	110.4	6.90	8.12(H_{23})	s	2.58	

[a] Chemical shifts are given in ppm with respect to TMS by using the solvent peak as reference: 2.09 ppm for ^{1}H and 29.5 ppm for ^{13}C. Only NOEs relevant for assignment are mentioned: they were obtained by 2D NOESY spectra (mixing times of 1 s and 1.2 s.). Long-range correlations are given for quaternary carbons only and are deduced from HMBC spectra with optimization for coupling constants around 8 Hz. [b] s = strong; m = strong; w = weak. [c] In angstroms, from X-ray data. [d] Strong overlap.

Enantiomeric Excesses for Δ-1PF_6, Λ-1PF_6 and Δ-2PF_6, Λ-2PF_6. Addition of 1 equiv of $[N_nBu_4(\Delta\text{-Trisphat})]$ to a solution (c = 0.014 mol·L^{-1}) of **1**PF_6 or **2**PF_6 induces dramatic changes in their ^{1}H NMR spectra. Among all signals, those corresponding to proton H_{12} in **1** and H_{22} in **2** are the most affected. These two protons are located at the periphery of the ruthenium complexes. Their multiplets split in two sets of signals. One set is deshielded and assigned to the diastereomeric pair Λ-**1**/Δ-Trisphat or Λ-**2**/Δ-Trisphat. The other one is shielded for the diastereomeric pair Δ-**1**/Δ-Trisphat or Δ-**2**/Δ-Trisphat. In each case, the clean separation between the two sets allows us to quantify the diastereomeric excess and consequently to determine the enantiomeric excess (ee).

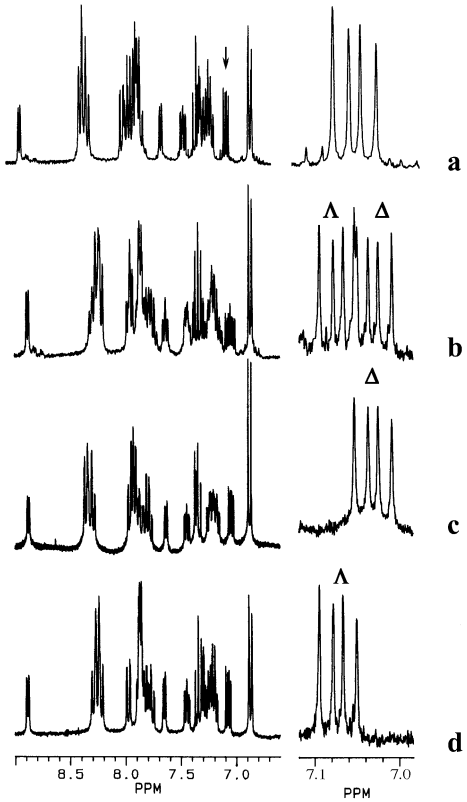

Figure 4. 300 MHz ^{1}H NMR spectra of **2** in CD_2Cl_2 solution (0.014 m·L^{-1}), with expansion of the H_{22} proton multiplet: from top to bottom: in the absence of $[N_nBu_4(\Delta\text{-Trisphat})]$ (a), in the presence of 1 equiv of $[N_nBu_4(\Delta\text{-Trisphat})]$ for *rac*-$[Ru(bpy)_2quo]^+$ (b), Δ-$[Ru(bpy)_2quo]^+$ (c), and Λ-$[Ru(bpy)_2quo]^+$ (d).

The ^{1}H NMR spectra[19] corresponding to H_{22} for *rac*-**2**PF_6, Δ-**2**PF_6, and Λ-**2**PF_6 are shown in Figure 4.

We have already shown that using the diastereoselective precipitation of a homochiral 3D network leads to the resolution of compounds **1** and **2**.[11] However, the ee values obtained for these monocations are modest, 0.45 for **1** and 0.20 for **2**. In contrast, following the procedure described in this paper, the ee's are higher, 0.50 and 0.73 for Δ-**1**PF_6 and Λ-**1**PF_6, respectively, and the resolution is nearly quantitative for Δ-**2**PF_6 and Λ-**2**PF_6 with ee values of 0.98. The difference in stereoselectivity observed between the two incoming ligands can be related to the nature of the bonds which have to be broken when substituting the pyridyl ligands. The hydroxyquinoline exists in equilibrium with the corresponding phenolate. Therefore, the phenolate, as well as the pyridine functions, is able to substitute directly the two pyridyl ligands. In contrast, for phenylpyridine, it is necessary to break heterolytically the high-energy C−H bond. This process occurs probably by insertion of the ruthenium in the C−H bond requiring a higher activation energy relative to the hydroquinoline. Hence, for phenylpyridine, a competitive decoordination between bipyrydyl

(19) This determination was performed in CD_2Cl_2 solutions: in these conditions, the H_{22} multiplet is well separated from the other signals. The assignment of the ^{1}H spectrum was obtained by comparison with acetone-d_6 spectrum and quickly checked by 2D methods.

and pyridyl occurs leading to a partial racemization. The difference in the ee measured for Δ-**1** and Λ-**1** may be the consequence of an uncontrolled racemization process during the synthesis.

Concluding Remarks

The reaction proposed by Hua and von Zelewsky is very efficient for obtaining optically active hexacoordinated ruthenium monocations. The optical purity of the synthesized compounds depends on the nature of the incoming third ligand. The measurement of the enantiomeric excesses using the ^{1}H NMR technique is possible on the basis of a complete attribution of the ^{1}H spectra. The use of the two ruthenium monocations as a chiral template in their enantiomeric forms is now in progress for the synthesis of optically active molecular-based magnets.

Acknowledgment. The authors thank CNRS, Université Pierre et Marie Curie, and NATO for financial support.

Supporting Information Available: Additional structural details and X-ray crystallographic files in CIF format for the structure determination of *rac*-[Ru(bpy)$_2$quo]PF_6. This material is available free of charge via the Internet at http://pubs.acs.org.

IC026121C