Inorganic Chemistry

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Proline as Chiral Auxiliary for the Economical Asymmetric Synthesis of Ruthenium(II) Polypyridyl Complexes

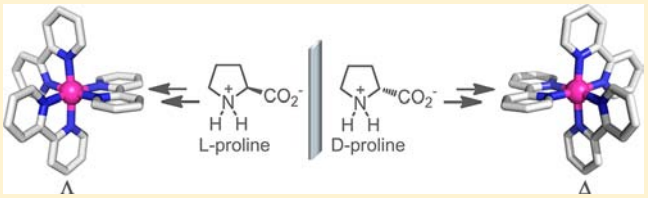
Chen Fu,[†] Marianne Wenzel,[†] Elisabeth Treutlein,[†] Klaus Harms,[†] and Eric Meggers*[,†,‡]

[†]Fachbereich Chemie, Philipps-Universität Marburg, Hans-Meerwein-Strasse, 35043 Marburg, Germany

[‡]Department of Chemical Biology, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, P. R. China

Supporting Information

ABSTRACT: A straightforward method for the synthesis of virtually enantiomerically pure ruthenium(II) polypyridyl complexes [Ru(pp)(pp′)(pp″)]$(PF_6)_2$, pp = bidentate polypyridyl has been developed. The synthesis draws from the readily available racemic starting material *cis*-[Ru(pp)(pp′)Cl_2] and the natural amino acids L- or D-proline and relies on a dynamic asymmetric transformation under thermodynamic control.



INTRODUCTION

Chiral octahedral metal complexes play an important role for the design of nucleic acid probes and enzyme inhibitors, among others, and for such applications of selective molecular recognition, single enantiomers are typically desired.[1,2] To address this need without applying time-consuming and inefficient chiral separation techniques, we recently developed a series of chiral auxiliaries for the asymmetric synthesis of chiral ruthenium complexes.[3,4] However, the practical use of these chiral auxiliaries is somewhat limited because either their synthesis is lengthy and expensive such as for enantiomerically pure 2-diphenylphosphino-2′-hydroxy-1,1′-binaphthyl (**HO-MOP**)[5] and 2-sulfinylphenols (**SO**),[6] the asymmetric coordination chemistry needs specialized photochemical equipment such as for chiral salicyloxazolines (**Salox**),[7] or the scaling-up of a procedure needs a careful adjustment of reaction parameters such as for the chiral *N*-acetyl-*tert*-butanesulfinamide (**ASA**)[8] (Figure 1). We were therefore seeking a simplified strategy for the generation of nonracemic ruthenium complexes that could be applied without specialized equipment and for which the required reagents are readily available. We turned our attention to the amino acid proline because it has been demonstrated over the past decade or so, that proline is a highly versatile catalyst for asymmetric organic transformations (asymmetric organocatalysis)[9] and we imagined that it could also serve as a cheap and readily available powerful chiral auxiliary for asymmetric coordination chemistry.[10−13]

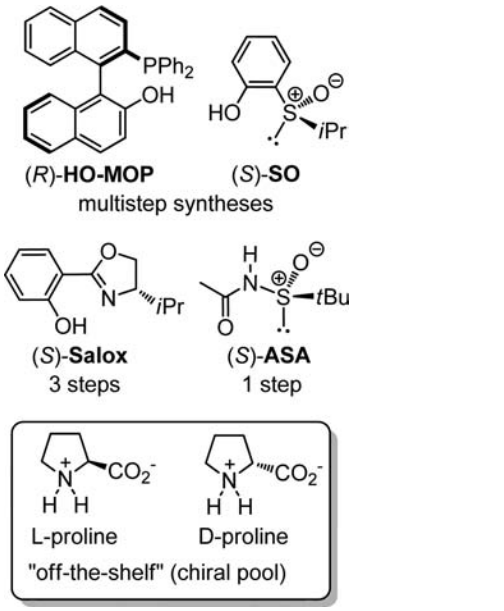


Figure 1. Synthetic accessibility of some chiral auxiliaries (previous work) as compared to the natural amino acids L- and D-proline (this study).

RESULTS AND DISCUSSION

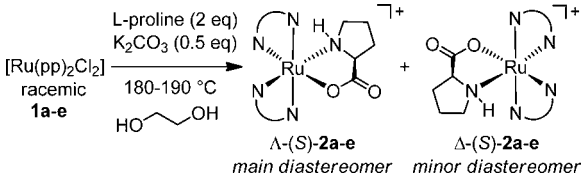
Our new synthetic strategy is inspired by investigations of Vagg and Williams, who reported that in (*S*)-aminoacidate complexes of the type Δ,Λ-[Ru(pp)$_2${(*S*)-aminoacidate}]$^+$, pp = bidentate polypyridyl ligand, the Λ-diastereomer is typically thermodynamically more stable and the authors explained this observation with an interligand repulsion between the α-pyridyl proton of one diimine ligand and the α-side chain of the aminoacidate ligand in the less favored Δ-propeller.[14] We speculated that this thermodynamic difference between the Λ- and Δ-diastereomer should be most pronounced in the related ruthenium-prolinate complexes which might enable us to develop an asymmetric synthesis of ruthenium polypyridyl complexes by a dynamic transformation based on an equilibrium between two diastereomers of significantly different stabilities. Indeed, when racemic *cis*-[Ru(bpy)$_2$$Cl_2$] (**1a**), bpy =

Received: July 12, 2012
Published: September 4, 2012

   dx.doi.org/10.1021/ic3015157 | *Inorg. Chem.* 2012, 51, 10004−10011

2,2′-bipyridine, was reacted with 2 equiv of L-proline in ethylene glycol and in the presence of 0.5 equiv of K_2CO_3 at 190 °C for a few minutes, Λ-[Ru(bpy)$_2$(L-Pro)]PF_6 {Λ-(*S*)-**2a**} formed as the main product with a crude diastereoselectivity between the Λ- and Δ-diastereomer of ≥20:1 (Scheme 1).[15]

Scheme 1. Diastereoselective Synthesis of the Ruthenium(II)-Prolinate Complexes Λ-(*S*)-2a−e



Silica gel column chromatography then afforded Λ-(*S*)-**2a** in an isolated yield of 74% and a d.r. value of at least 100:1 as determined by ^{1}H NMR (Table 1 and Figure 2). The minor diastereomer Δ-(*S*)-**2a** could only be isolated in small quantities, and the CD spectra of the two resolved diastereomers are displayed in Figure 3. Since this reaction started with racemic **1a**, these results demonstrate that in the course of the reaction a significant amount of the Δ-configured ruthenium starting material converted its metal-centered configuration to Λ. Analogous results were obtained with the racemic starting complexes *cis*-[Ru(pp)$_2$Cl$_2$], pp = 5,5′-dimethyl-2,2′-bipyridine (dmb, **1b**), 1,10-phenanthroline (phen, **1c**), and 2,2′-biquinoline (biq, **1d**), providing Λ-(*S*)-**2b** (70%), Λ-(*S*)-**2c** (67%), and Λ-(*S*)-**2d** (72%) as single diastereomers (Scheme 1 and Table 1).

Regarding the mechanism of this reaction, we assume that both diastereomers, e.g. Λ-(*S*)-**2a** and Δ-(*S*)-**2a** are initially formed but that under the optimized high temperature reaction conditions, the diastereomer Δ-(*S*)-**2a** is unstable and reversibly releases the proline ligand. Since under these high temperature reaction conditions the two enantiomers of the starting material **1a** must be in an equilibrium with each other through the dissociation of one or two chlorides and the formation of coordinatively unsaturated intermediates, the unstable and reversibly formed diastereomer Δ-(*S*)-**2a** can convert to the thermodynamically more stable diastereomer Λ-(*S*)-**2a**. This would constitute a dynamic resolution under thermodynamic control, similar to related conversions with the chiral auxiliaries **SO** and **ASA**.[6b,8,16] This proposed mechanism is supported by an experiment in which we heated the minor diastereomer Δ-(*S*)-**2a** in ethylene glycol at 190 °C under argon for 10 min and found a conversion to the major diastereomer Λ-(*S*)-**2a** with a crude d.r. of ≥20:1 and an isolated yield of 60% (d.r. > 100:1). This thermally induced Δ→Λ conversion most likely involves the dissociation or at least labilization of the coordinated L-prolinate ligand because the yield for this isomerization increased to 82% if the Δ→Λ conversion was performed in the presence of additional L-proline (10 equiv) for 20 min, thereby most likely suppressing side reactions of coordinatively unsaturated ruthenium intermediates after the dissociation of proline from Δ-(*S*)-**2a**.

Figure 4 displays a crystal structure of the preferred diastereomer Λ-(*S*)-**2a**, whereas Figure 5 depicts the main and minor diastereomers Λ-(*S*)-**2d** and Δ-(*S*)-**2d**, respectively, of the reaction of **1d** with L-proline. These structures indicate the thermodynamic preference for the Λ-(*S*) diastereomer since the Δ-(*S*) diastereomer contains a steric repulsion between the CH_2-group next to the coordinated nitrogen of L-prolinate and one of the coordinated bipyridyl ligands as apparent in the structure of Δ-(*S*)-**2d**. This is consistent with the thermodynamic preference of the Λ-diastereomer in ruthenium(II) polypyridyl (*S*)-aminoacidate complexes.[14]

Next, we investigated the removal of the coordinated L-prolinate auxiliary and we expected an acid-lability of the N,O-chelate through a protonation of the coordinated carboxylate group. Indeed, when Λ-(*S*)-**2a** was treated with trifluoroacetic acid (TFA) (8 equiv) in the presence of an excess of bpy (15 equiv) in MeCN at 110 °C for 2.5 h, Λ-[Ru(bpy)$_3$]$(PF_6)_2$ (Λ-**3a**) was obtained after workup, silica gel chromatography, and hexafluorophosphate precipitation in a yield of 79% with 99:1 e.r. as determined by chiral HPLC (entry 1 in Table 2, Figure 6). Analogous results were obtained with the substrates Λ-(*S*)-**2b**,**c** (Table 2, entries 2 and 3), whereas Λ-(*S*)-**2d** (Table 2, entry 4) was converted to [Ru(biq)$_2$(bpy)]$(PF_6)_2$ (**3d**) upon reaction with bpy and TFA with a Λ/Δ-ratio of only 3:2 and a low yield of 15%, revealing a limited scope of this and related methods for the asymmetric synthesis of ruthenium polypyridyl complexes with sterically highly demanding ligands.

This new and economical method was next applied to the asymmetric synthesis of *tris*-heteroleptic ruthenium polypyridyl complexes. Accordingly, racemic *cis*-[Ru(bpy)(dmb)Cl$_2$] (**1e**) was reacted with L-proline (2 equiv) and K_2CO_3 (0.5 equiv) in ethylene glycol under argon for several minutes at 190 °C, affording after silica gel chromatography Λ-(*S*)-**2e** in a yield of 75% as a mixture of two diastereomers with Λ-configuration at the metal (Table 1, entry 5). The following reaction of Λ-(*S*)-**2e** with phen (15 equiv) or 4,4′-di-*tert*-butyl-2,2′-bipyridine (dbb) (15 equiv) and TFA (8 equiv) in MeCN at 110 °C for 2.5 h afforded the *tris*-heteroleptic complexes Λ-[Ru(bpy)(dmb)(phen)]$(PF_6)_2$ (Λ-**3e**) (82% yield) and Λ-[Ru(bpy)-

Table 1. Synthesis of the L-Prolinate Complexes Λ-(*S*)-2a−e

entry	*rac*-[Ru(pp)(pp′)Cl$_2$][a]	temperature[b]	main product	crude d.r.[c]	yield[d]
1	pp = pp′ = bpy (**1a**)	190 °C	Λ-(*S*)-**2a**	≥20:1	74%
2	pp = pp′ = dmb (**1b**)	190 °C	Λ-(*S*)-**2b**	≥35:1	70%
3	pp = pp′ = phen (**1c**)	190 °C	Λ-(*S*)-**2c**	≥25:1	67%
4	pp = pp′ = biq (**1d**)	180 °C	Λ-(*S*)-**2d**	≥30:1	72%
5	pp = bpy, pp′ = dmb (**1e**)	190 °C	Λ-(*S*)-**2e**	≥40:1[e]	75%

[a]bpy =2,2′-bipyridine, dmb =5,5′-dimethyl-2,2′-bipyridine, phen =1,10-phenanthroline, biq =2,2′-biquinoline. [b]General reaction conditions: The racemic ruthenium complexes (200 mM) with L-proline (400 mM), and K_2CO_3 (100 mM) were heated in ethylene glycol under argon for several min at the indicated oil bath temperature. See Experimental Section for more details. [c]Determined from the crude product by ^{1}H NMR. [d]Isolated yield of the hexafluorophosphate salt of the Λ-(*S*)-diastereomer(s) after silica gel chromatography with final d.r. ≥ 100:1. [e]Ratio Λ-(*S*)/Δ-(*S*). The two Λ-(*S*)-diastereomers formed in a ratio of 5:2.

dx.doi.org/10.1021/ic3015157 | *Inorg. Chem.* 2012, 51, 10004−10011

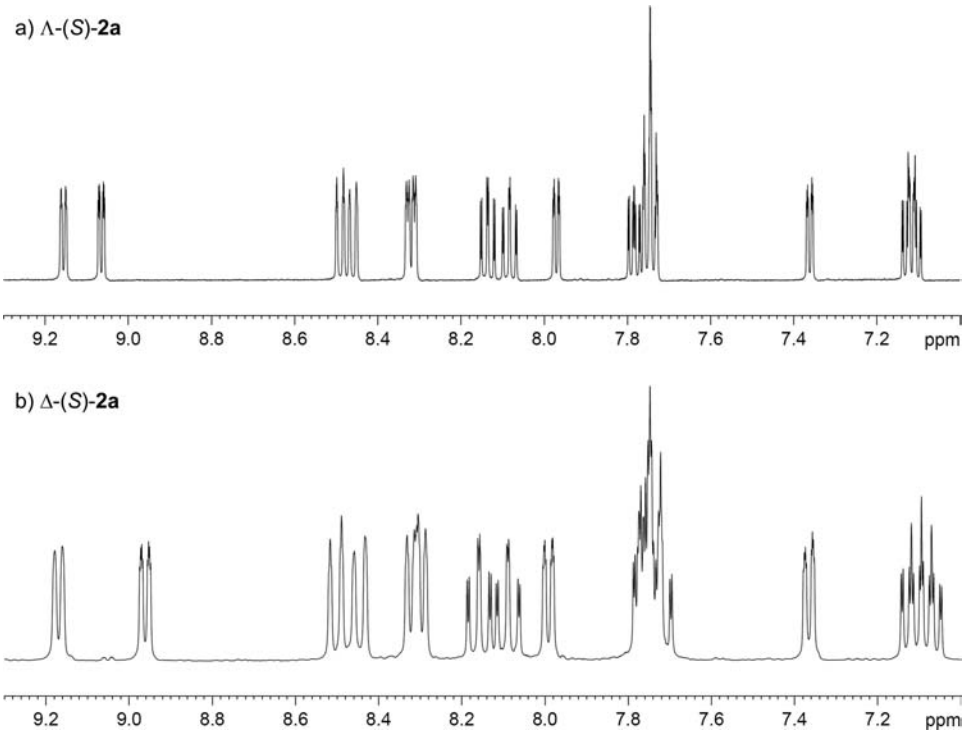


Figure 2. Main and minor product of the high-temperature-transformation *rac*-**1a**→**2a**. Excerpts of the aromatic region of the ^{1}H NMR spectra (300 MHz, CD_3CN) are shown. (a) Main diastereomer Λ-(*S*)-**2a** after silica gel purification. (b) Isolated minor diastereomer Δ-(*S*)-**2a**. ^{1}H NMR signals differ significantly for one of the protons in α-position to the coordinating nitrogen of the 2,2′-bipyridine (δ = 9.06 ppm versus 8.97 ppm for Λ-(*S*)-**2a** and Δ-(*S*)-**2a**, respectively). Integration of these protons were used to determine d.r. values of crude reactions and purified products.

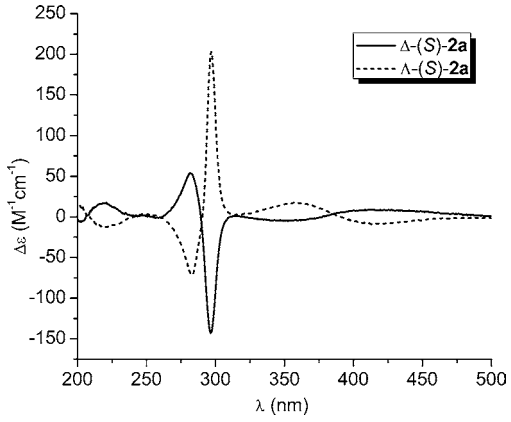


Figure 3. CD spectra of the purified complexes Λ-(*S*)-**2a** and Δ-(*S*)-**2a** in CH_3CN (0.1 mM).

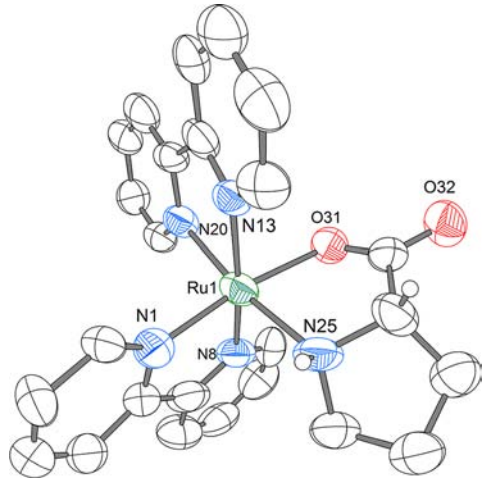


Figure 4. Crystal structures of the diastereomer Λ-(*S*)-**2a**. ORTEP drawing with 50% probability thermal ellipsoids. Only one of two independent ruthenium complexes is shown. A nitrate counterion and water molecules are omitted for clarity. Hydrogens are shown at the stereogenic carbon (*S*) and nitrogen (*S*).

(dmb)(dbb)]$(PF_6)_2$ (Λ-**3f**) (85% yield), respectively, both with 98:2 e.r. (Table 2, entries 5 and 6).

Finally, we used the convenient proline-based asymmetric synthesis of ruthenium polypyridyl complexes to investigate their rate of racemization under typical laboratory conditions (organic solvents, slightly elevated temperature, visible light). For this, enantiomerically pure Λ-[Ru(bpy)$_3$]$(PF_6)_2$ (98:2 e.r.) was kept in MeCN, DMF, or MeOH at room temperature or at 45 °C for one week under exclusion of light. As expected, no signs of racemization were detected under these conditions which is due to the thermal kinetic inertness of ruthenium polypyridyl complexes. However, when the same experiments were performed under exposure to visible light (7 W LED reflector lamp), complete racemization occurred. Figure 7 demonstrates the temperature dependence of the racemization rate: Whereas at room temperature complete racemization is observed within 2 d (k = 0.099 h^{-1}), at 50 °C racemization is even completed within 10 h (k = 0.541 h^{-1}), thus confirming the well established light-induced racemization of ruthenium polypyridyl complexes in aqueous solution.[17]

■ CONCLUSION

We here introduced a straightforward and economical asymmetric synthesis of nonracemic ruthenium(II) polypyridyl complexes [Ru(pp)(pp′)(pp″)]$(PF_6)_2$ based on using the

dx.doi.org/10.1021/ic3015157 | *Inorg. Chem.* 2012, 51, 10004−10011

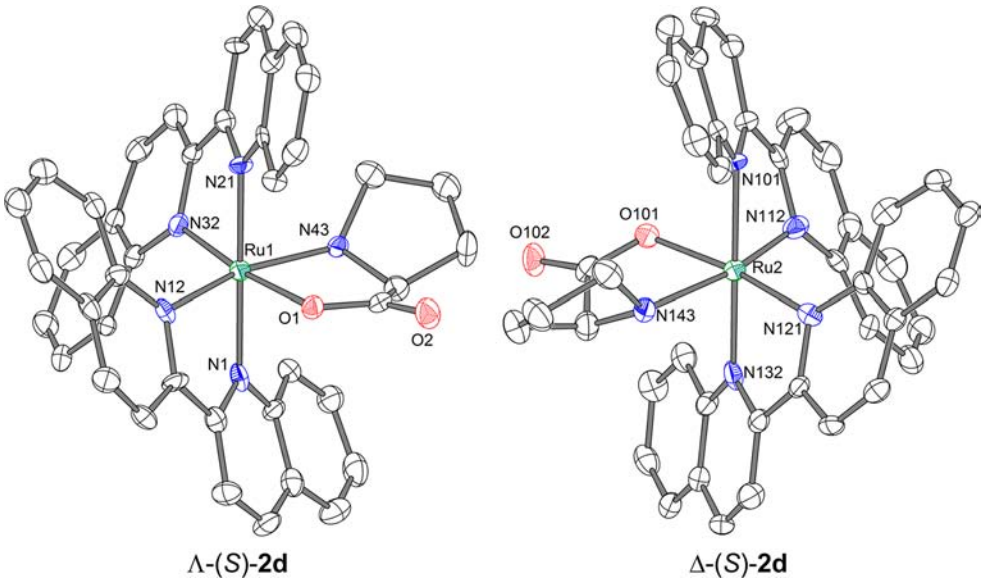
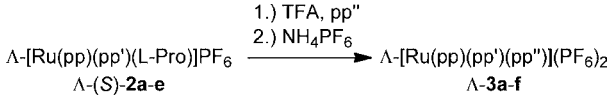


Figure 5. Structures of the two diastereomers Λ-(*S*)-**2d** (favored) and Δ-(*S*)-**2d** (disfavored), which cocrystallized from a mixture of diastereomers. ORTEP drawing with 50% probability thermal ellipsoids. Hexafluorophosphate counterions are omitted for clarity.

Table 2. TFA-Promoted Substitution of the L-Proline Auxiliary against Achiral Bidentate Ligands under Retention of Configuration[a]



entry	starting cpd	pp″[b]	product complex	yield	e.r.[c]
1	Λ-(*S*)-**2a**	bpy	Λ-[Ru(bpy)$_3$](PF$_6$)$_2$ (Λ-**3a**)	79%	99:1
2	Λ-(*S*)-**2b**	dmb	Λ-[Ru(dmb)$_3$](PF$_6$)$_2$ (Λ-**3b**)	83%	97:3
3	Λ-(*S*)-**2c**	phen	Λ-[Ru(phen)$_3$](PF$_6$)$_2$ (Λ-**3c**)	81%	99:1
4	Λ-(*S*)-**2d**	bpy	Λ/Δ-[Ru(biq)$_2$(bpy)](PF$_6$)$_2$ (**3d**)[d]	15%	ca. 3:2[e]
5	Λ-(*S*)-**2e**	phen	Λ-[Ru(bpy)(dmb)(phen)](PF$_6$)$_2$ (Λ-**3e**)	82%	98:2
6	Λ-(*S*)-**2e**	dbb	Λ-[Ru(bpy)(dmb)(dbb)](PF$_6$)$_2$ (Λ-**3f**)	85%	98:2

[a]General reaction conditions: Λ-(*S*)-**2a**−**e** (100 mM) in MeCN with TFA (8 equiv) and bipyridyl ligand (15 equiv) in a sealed brown glass vial under argon atmosphere at 110 °C for several hours. [b]bpy = 2,2′-bipyridine, dmb = 5,5′-dimethyl-2,2′-bipyridine, phen = 1,10-phenanthroline, biq = 2,2′-biquinoline, dbb = 4,4′-di-*tert*-butyl-2,2′-bipyridine. [c]Determined by chiral HPLC with a Chiralpak IA or IB column and a gradient of MeCN:TFA (0.1% in H_2O). [d]Complex is very light-sensitive. [e]Only partial resolution of Λ- and Δ-enantiomers by chiral HPLC.

readily available racemic starting material [Ru(pp)(pp′)Cl$_2$] together with the natural amino acid L-proline. According to our experience, this method is superior to previously disclosed auxiliaries and can be applied to the large-scale synthesis of enantiomerically pure ruthenium(II) polypyridyl complexes.

EXPERIMENTAL SECTION

Materials and Methods. All reactions were carried out under nitrogen or argon atmosphere, and coordination chemistry was additionally executed in the dark to prevent photoisomerizations. Solvents were distilled under nitrogen from calcium hydride (CH_3CN,

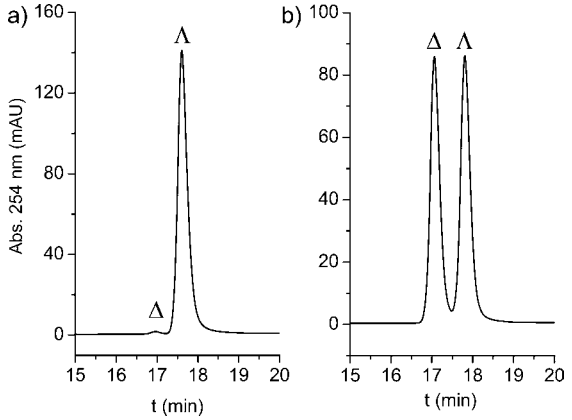


Figure 6. HPLC traces of nonracemic and racemic [Ru(bpy)$_3$](PF$_6$)$_2$. (a) Λ-[Ru(bpy)$_3$](PF$_6$)$_2$ with 99:1 e.r. synthesized from Λ-(*S*)-**2a** (Table 2, entry 1). (b) Racemic [Ru(bpy)$_3$](PF$_6$)$_2$ as a reference. HPLC conditions: Daicel Chiralpak IA column, 250 × 4.6 mm, flow rate = 0.5 mL/min, TFA (0.1% in H_2O) and MeCN as eluent (15→30% in 20 min).

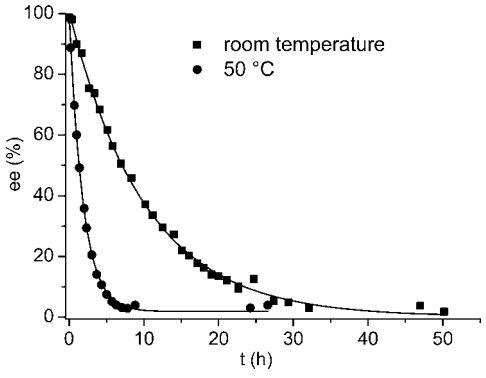


Figure 7. Investigation of the light-induced racemization of Λ-[Ru(bpy)$_3$](PF$_6$)$_2$ in DMF at room temperature and at 50 °C. The samples were irradiated with a 7 W LED reflector lamp and the enantiomeric excess (ee) values were determined by chiral HPLC analysis.

dx.doi.org/10.1021/ic3015157 | *Inorg. Chem.* 2012, 51, 10004−10011

DMF). Racemic *cis*-$[Ru(bpy)_2Cl_2]$, *cis*-$[Ru(phen)_2Cl_2]$, *cis*-$[Ru(biq)_2Cl_2]$, *cis*-$[Ru(dmb)_2Cl_2]$, and *cis*-$[Ru(bpy)(dmb)Cl_2]$ were prepared according to published procedures.[18] Column chromatography was performed with silica gel (230−400 mesh). ^{1}H- and ^{13}C NMR spectra were recorded on a Bruker AVANCE (300 or 500 MHz) spectrometer at ambient temperature. NMR standards used were as follows: (^{1}H NMR) CD_3CN = 1.94 ppm, $CDCl_3$ = 7.26 ppm. (^{13}C NMR) CD_3CN = 1.32 ppm, $CDCl_3$ = 77.00 ppm. IR spectra were obtained on a Bruker Alpha-P series FT-IR spectrometer. CD spectra were recorded on a JASCO J-810 CD spectropolarimeter (1 nm bandwidth, scanning speed of 50 nm/min, accumulation of 5 scans). High-resolution mass spectra were recorded on a Finnigan LTQ-FT instrument using the ESI technique. Chiral HPLC chromatograms were obtained from an Agilent 1200 Series HPLC system with a Chiralpak (250 × 4.6 mm) IA or IB column (flow rate 0.5 mL/min, column temperature 40 °C, UV-absorption detected at 254 nm, solvent A = 0.1% TFA in H_2O, solvent B = MeCN; **3a**: IA column, 15−30% B in 20 min; **3b**: IB column, 15−50% B in 20 min; **3c**: IB column, 20−24% B in 25 min; **3d**: IA column, 22−30% B in 20 min; **3e**: IB column, 10−25% B in 20 min; **3f**: IB column, 30−35% B in 20 min).

Diastereoselective Synthesis of Complexes Λ-(*S*)-2a−e. *General Procedures.* In a sealed glass vial fitted with a septum, a solution of racemic ruthenium complexes **1a−e** (1.0 equiv), L-proline (2.0 equiv), and K_2CO_3 (0.5 equiv) in ethylene glycol was degassed with argon for 5 min and then heated in an oil bath at a constant temperature. [Note that the optimal reaction time is a function of the used reaction vessel and scale.] The reaction mixture was cooled to room temperature, and the crude material was purified by silica gel chromatography with first MeCN, then switched to MeCN:H_2O = 10:1, and finally the product was eluted with CH_3CN:H_2O:KNO_3(sat) = 100:3:1 and CH_3CN:H_2O:KNO_3(sat) = 50:3:1. The product eluents were concentrated to dryness, the resulting material was dissolved in nearly 20 mL of water, and the product was precipitated by the addition of excess solid NH_4PF_6. Then, CH_2Cl_2 (15 mL) was added, and the layers were separated. The aqueous phase was extracted with CH_2Cl_2 (2 × 10 mL), and the combined organic extracts were dried over Na_2SO_4, filtered, concentrated, and dried under high vacuum to afford the product as a single diastereomer which was stored under argon at −20 °C.

Λ-*(S)*-***2a***. According to the general procedure for diastereoselective synthesis, a solution of racemic *cis*-$[Ru(bpy)_2Cl_2]$ (**1a**) (260 mg, 0.5 mmol), L-proline (115 mg, 1.0 mmol), and K_2CO_3 (34.5 mg, 0.25 mmol) in ethylene glycol (2.5 mL) was heated at 190 °C for 3.5 min to afford Λ-(*S*)-**2a** as the major diastereomer (250 mg, 74%). ^{1}H NMR (300.1 MHz, CD_3CN): δ (ppm) 9.16 (ddd, J = 5.7, 1.3, 0.8 Hz, 1H), 9.06 (ddd, J = 5.6, 1.5, 0.8 Hz, 1H), 8.49 (ddd, J = 8.2, 1.3, 0.7 Hz, 1H), 8.46 (d, J = 8.0 Hz, 1H), 8.33 (ddd, J = 3.2, 1.2, 0.8 Hz, 1H), 8.31 (ddd, J = 3.3, 1.2, 0.8 Hz, 1H), 8.14 (ddd, J = 8.8, 7.6, 1.7 Hz, 1H), 8.09 (ddd, J = 8.8, 7.5, 1.5 Hz, 1H), 7.97 (ddd, J = 5.8, 1.5, 0.9 Hz, 1H), 7.78 (ddd, J = 7.6, 5.6, 1.3 Hz, 1H), 7.75 (m, 3H), 7.36 (ddd, J = 5.9, 1.5, 0.7 Hz, 1H), 7.12 (m, 2H), 4.96 (dd, J = 14.5, 8.0 Hz, 1H), 3.90 (td, J = 13.4, 7.1 Hz, 1H), 2.21 (m, 1H), 2.08 (m, 1H), 1.80 (m, 1H), 1.43 (m, 3H). ^{13}C NMR (75.5 MHz, CD_3CN): δ (ppm) 182.9, 160.3, 159.66, 159.65, 159.1, 155.0, 152.9, 152.8, 151.5, 137.14, 137.12, 136.0, 135.4, 128.3, 127.6, 126.7, 126.5, 124.6, 124.5, 124.4, 124.2, 64.3, 50.3, 30.6, 27.2. IR (thin film): ν (cm^{-1}) 3645, 2961, 2922, 1597, 1462, 1444, 1420, 1368, 1318, 1262, 1160, 1104, 1064, 1019, 929, 830, 759, 729, 657, 555, 423. CD ($\Delta\varepsilon/M^{-1}$ cm^{-1}, MeCN): 282.5 nm (−72), 297 nm (+203). HRMS calcd for $C_{25}H_{24}N_5O_2Ru$ (M-PF_6)$^+$: 528.0975, found: 528.0963.

Reference data of the minor diastereomer Δ-(*S*)-**2a**, which was isolated from a mixture of diastereomers synthesized at a lower temperature: ^{1}H NMR (300.1 MHz, CD_3CN): δ (ppm) 9.17 (d, J = 5.3 Hz, 1H), 8.97 (ddd, J = 5.6, 1.4, 0.7 Hz, 1H), 8.50 (dt, J = 8.1, 1.2 Hz, 1H), 8.45 (d, J = 7.7 Hz, 1H), 8.31 (m, 2H), 8.16 (ddd, J = 8.1, 7.6, 1.5 Hz, 1H), 8.09 (ddd, J = 8.1, 7.6, 1.4 Hz, 1H), 7.99 (ddd, J = 5.7, 1.3, 0.7 Hz, 1H), 7.75 (m, 4H), 7.37 (ddd, J = 5.7, 1.3, 0.7 Hz, 1H), 7.09 (m, 2H), 4.15 (dd, J = 16.4, 8.0 Hz, 1H), 3.56 (m, 1H), 3.00 (m, 1H), 2.78 (m, 1H), 2.05 (m, 3H), 1.69 (m, 1H). ^{13}C NMR (75.5 MHz, CD_3CN): δ (ppm) 182.8, 160.7, 160.2, 159.8, 159.6, 154.9, 153.8, 153.0, 152.2, 137.8, 136.1, 135.5, 128.3, 127.5, 126.9, 126.4, 124.8, 124.4, 124.1, 65.1, 52.3, 31.0, 27.2. IR (thin film): ν (cm^{-1}) 3645, 3192, 1596, 1462, 1444, 1420, 1368, 1318, 1262, 1160, 1105, 1064, 1019, 929, 830, 759, 729, 657, 555, 423. CD ($\Delta\varepsilon/M^{-1}$ cm^{-1}, MeCN): 282 nm (+54), 296.5 nm (−143). HRMS calcd for $C_{25}H_{24}N_5O_2Ru$ (M-PF_6)$^+$: 528.0975, found: 528.0973.

Λ-*(S)*-***2b***. According to the general procedure for diastereoselective synthesis, a solution of racemic *cis*-$[Ru(dmb)_2Cl_2]$ (**1b**) (200 mg, 0.347 mmol), L-proline (80 mg, 0.694 mmol), and K_2CO_3 (24 mg, 0.173 mmol) in ethylene glycol (1.7 mL) was heated at 190 °C for 3 min to afford Λ-(*S*)-**2b** as the major diastereomer (177 mg, 70%). ^{1}H NMR (300.1 MHz, CD_3CN): δ (ppm) 8.95 (t, J = 0.8 Hz, 1H), 8.82 (t, J = 0.8 Hz, 1H), 8.30 (dd, J = 10.4, 8.3 Hz, 2H), 8.14 (dd, J = 8.3, 3.1 Hz, 2H), 7.92 (dd, J = 8.3, 1.3 Hz, 1H), 7.87 (dd, J = 8.3, 1.0 Hz, 1H), 7.75 (t, J = 0.8 Hz, 1H), 7.55 (m, 2H), 7.11 (t, J = 0.8 Hz, 1H), 4.91 (dd, J = 14.5, 7.2 Hz, 1H), 3.93 (dt, J = 8.9, 7.2 Hz, 1H), 2.57 (d, J = 11.3 Hz, 6H), 2.15 (m, 2H), 2.09 (d, J = 18.8 Hz, 6H), 1.80 (m, 1H), 1.45 (m, 3H). ^{13}C NMR (75.5 MHz, CD_3CN): δ (ppm) 183.1, 157.8, 157.3, 157.1, 156.7, 154.5, 152.7, 152.3, 151.1, 138.7, 138.3, 137.7, 137.6, 136.94, 136.90, 136.6, 136.0, 123.6, 123.5, 123.3, 123.1, 64.3, 50.3, 30.7, 27.3, 19.0, 18.8, 18.4, 18.2. IR (thin film): ν (cm^{-1}) 2962, 2924, 2852, 1603, 1475, 1452, 1388, 1259, 1087, 1014, 836, 794, 738, 697, 652, 557, 504, 436. CD ($\Delta\varepsilon/M^{-1}$ cm^{-1}, MeCN): 290.5 nm (−90), 305 nm (+214). HRMS calcd for $C_{29}H_{32}N_5O_2Ru$ (M-PF_6)$^+$: 584.1602, found: 584.1599.

Λ-*(S)*-***2c***. According to the general procedure for diastereoselective synthesis, a solution of racemic *cis*-$[Ru(phen)_2Cl_2]$ (**1c**) (200 mg, 0.352 mmol), L-proline (82 mg, 0.704 mmol), and K_2CO_3 (24 mg, 0.176 mmol) in ethylene glycol (1.7 mL) was heated at 190 °C for 4 min to afford Λ-(*S*)-**2c** as the major diastereomer (170 mg, 67%). ^{1}H NMR (300.1 MHz, CD_3CN): δ (ppm) 9.62 (dd, J = 5.3, 1.1 Hz, 1H), 9.47 (dd, J = 5.3, 1.2 Hz, 1H), 8.72 (dd, J = 8.2, 1.2 Hz, 1H), 8.64 (dd, J = 8.2, 1.0 Hz, 1H), 8.14 (m, 9H), 7.57 (dd, J = 5.4, 1.3 Hz, 1H), 7.34 (dd, J = 8.1, 5.4 Hz, 1H), 7.30 (dd, J = 8.1, 5.4 Hz, 1H), 5.31 (dd, J = 13.7, 8.0 Hz, 1H), 4.07 (dt, J = 8.9, 7.1 Hz, 1H), 2.10 (m, 1H), 1.83 (m, 1H), 1.32 (m, 4H). ^{13}C NMR (75.5 MHz, CD_3CN): δ (ppm) 183.2, 155.8, 153.91, 153.88, 152.7, 151.3, 150.6, 150.4, 149.8, 136.4, 136.1, 135.0, 134.4, 131.7, 131.6, 131.5, 131.4, 129.0, 128.6, 128.5, 127.1, 126.4, 125.5, 125.4, 64.6, 50.6, 30.8, 27.3. IR (thin film): ν (cm^{-1}) 1604, 1425, 1367, 1262, 1201, 1096, 1054, 1020, 930, 828, 768, 719, 555. CD ($\Delta\varepsilon/M^{-1}$ cm^{-1}, MeCN): 260.5 nm (−120), 269.5 nm (+213). HRMS calcd for $C_{29}H_{24}N_5O_2Ru$ (M-PF_6)$^+$: 576.0976, found: 576.0960.

Λ-*(S)*-***2d***. According to the general procedure for diastereoselective synthesis, a solution of racemic *cis*-$[Ru(biq)_2Cl_2]$ (**1d**) (200 mg, 0.278 mmol), L-proline (64 mg, 0.555 mmol), and K_2CO_3 (19.2 mg, 0.139 mmol) in ethylene glycol (1.4 mL) was heated at 180 °C for 3 min to afford Λ-(*S*)-**2d** as the major diastereomer (175 mg, 72%). ^{1}H NMR (300.1 MHz, CD_3CN): δ (ppm) 8.78 (m, 6H), 8.58 (d, J = 8.8 Hz, 1H), 8.53 (d, J = 8.8 Hz, 1H), 8.16 (d, J = 8.1 Hz, 1H), 8.03 (ddd, J = 7.0, 2.6, 1.2 Hz, 2H), 7.85 (dd, J = 8.1, 0.8 Hz, 1H), 7.64 (ddd, J = 8.1, 5.0, 3.0 Hz, 1H), 7.54 (m, 2H), 7.40 (ddd, J = 8.0, 7.0, 0.9 Hz, 1H), 7.32 (m, 2H), 7.20 (m, 2H), 7.04 (d, J = 8.8 Hz, 1H), 6.82 (ddd, J = 8.8, 7.0, 1.4 Hz, 1H), 6.66 (ddd, J = 8.8, 6.9, 1.4 Hz, 1H), 6.05 (d, J = 8.8 Hz, 1H), 4.13 (m, 1H), 2.32 (m, 2H), 1.34 (m, 1H), 1.17 (m, 2H), 1.00 (m, 1H), 0.43 (dq, J = 11.5, 5.3 Hz, 1H). ^{13}C NMR (75.5 MHz, CD_3CN): δ (ppm) 180.7, 163.8, 163.2, 163.0, 161.7, 153.2, 153.0, 151.9, 151.5 139.0, 138.9, 137.1, 136.4, 133.2, 131.91, 131.85, 131.4, 131.2, 129.8, 129.73, 129.67, 129.63, 129.61, 129.4, 129.1, 128.7, 128.5, 128.2, 127.9, 126.1, 125.2, 122.4, 122.0, 121.84, 121.75, 64.2, 49.5, 28.4, 25.2. IR (thin film): ν (cm^{-1}) 3640, 3322, 1595, 1509, 1429, 1367, 1302, 1247, 1147, 1098, 964, 812, 748, 635, 555, 488, 431. CD ($\Delta\varepsilon/M^{-1}$ cm^{-1}, MeCN): 256 nm (−81), 270 nm (+104), 324 nm (−48), 349 nm (+127). HRMS calcd for $C_{41}H_{32}N_5O_2Ru$ (M-PF_6)$^+$: 728.1605, found: 728.1588.

Λ-*(S)*-***2e***. According to the general procedure for diastereoselective synthesis, a solution of racemic *cis*-$[Ru(bpy)(dmb)Cl_2]$ (**1e**) (205 mg, 0.4 mmol), L-proline (92 mg, 0.8 mmol), and K_2CO_3 (27.6 mg, 0.2 mmol) in ethylene glycol (2.5 mL) was heated at 190 °C for 3 min to

dx.doi.org/10.1021/ic3015157 | *Inorg. Chem.* 2012, 51, 10004−10011

afford Λ-(*S*)-**2e** (210 mg, 75%) as a mixture of two diastereomers with Λ-configuration at the ruthenium. CD ($\Delta\varepsilon/M^{-1}$ cm^{-1}, MeCN): 287 nm (−80), 300.5 nm (+166). HRMS calcd for $C_{27}H_{28}N_5O_2Ru$ (M-PF_6)$^+$: 556.1288, found: 556.1283. Elemental analysis calcd for Λ-(*S*)-**2e**·H_2O, $C_{27}H_{30}F_6N_5O_3PRu$: N 9.75, C 45.13, H 4.21; found: N 9.32, C 45.45, H 4.31.

Stereospecific Proline Substitution. *General Procedures.* The reaction was executed in the dark, while workup and purification were performed under reduced light. In a sealed brown-glass vial fitted with a septum, a solution of freshly synthesized ruthenium complex Λ-(*S*)-**2a**−**e** (1.0 equiv), bipyridyl ligand (15.0 equiv), and trifluoroacetic acid (8.0 equiv) in CH_3CN (100 mM) was heated at 110 °C (oil bath temperature) under an argon atmosphere. The reaction mixture was cooled to room temperature, and the crude material was purified by silica gel chromatography with first MeCN, then switched to CH_3CN:H_2O:KNO_3(sat) = 100:3:1, and CH_3CN:H_2O:KNO_3(sat) = 50:3:1. The product eluents were concentrated to dryness, the resulting material dissolved in minimal amounts of water or ethanol/water, and the product was precipitated by the addition of excess solid NH_4PF_6. The precipitate was centrifuged, washed twice with water, and dried under high vacuum to afford the nonracemic ruthenium complexes Λ-**3a**−**e**.

Λ-***3a***. According to the general procedure for proline removal, a solution of complex Λ-(*S*)-**2a** (50 mg, 0.075 mmol), 2,2′-bipyridine (175 mg, 1.12 mmol), and trifluoroacetic acid (0.044 mL, 0.595 mmol) in CH_3CN (0.8 mL) was heated at 110 °C for 2.5 h to afford Λ-[Ru(bpy)$_3$](PF_6)$_2$ (51 mg, 79%) with 99:1 e.r. as determined by chiral HPLC analysis.

Λ-***3b***. According to the general procedure for proline removal, a solution of complex Λ-(*S*)-**2b** (50 mg, 0.069 mmol), 5,5′-dimethyl-2,2′-bipyridine (189 mg, 1.03 mmol), and trifluoroacetic acid (0.041 mL, 0.552 mmol) in CH_3CN (0.7 mL) was heated at 110 °C for 2.5 h to afford Λ-[Ru(dmb)$_3$](PF_6)$_2$ (54 mg, 83%) with 97:3 e.r. as determined by chiral HPLC analysis. ^{1}H NMR (300.1 MHz, CD_3CN): δ (ppm) 8.31 (d, J = 8.4 Hz, 6H), 7.84 (ddd, J = 8.4, 1.8, 0.6 Hz, 6H), 7.44 (dd, J = 1.8, 1.0 Hz, 6H), 2.19 (s, 18H). ^{13}C NMR (75.5 MHz, CD_3CN): δ (ppm) 155.6, 152.3, 139.06, 139.01, 124.2, 18.6. IR (thin film): ν (cm^{-1}) 1606, 1475, 1241, 822, 727, 556, 520, 433. CD ($\Delta\varepsilon/M^{-1}$ cm^{-1}, MeCN): 284 nm (−149), 298.5 nm (+324). HRMS calcd for $C_{36}H_{36}F_6N_6PRu$ (M-PF_6)$^+$: 799.1691, found: 799.1666.

Λ-***3c***. According to the general procedure for proline removal, a solution of complex Λ-(*S*)-**2c** (50 mg, 0.070 mmol), 1,10-phenanthroline (188 mg, 1.04 mmol), and trifluoroacetic acid (0.042 mL, 0.555 mmol) in CH_3CN (0.7 mL) was heated at 110 °C for 2.5 h to afford Λ-[Ru(phen)$_3$](PF_6)$_2$ (53 mg, 81%) with 99:1 e.r. as determined by chiral HPLC analysis.

Λ-***3d***. According to the general procedure for proline removal, a solution of complex Λ-(*S*)-**2d** (10.9 mg, 0.0125 mmol), 2,2′-bipyridine (29.3 mg, 0.1875 mmol), and trifluoroacetic acid (0.0074 mL, 0.100 mmol) in CH_3CN (0.25 mL) was heated at 110 °C for 12 h to afford [Ru(biq)$_2$(bpy)](PF_6)$_2$ (2.0 mg, 15%) with 67:33 e.r. as determined by chiral HPLC analysis. This compound is light-sensitive and not very stable and should be stored under argon at −20 °C. ^{1}H NMR (300.1 MHz, CD_3CN): δ (ppm) 9.01 (d, J = 8.9 Hz, 2H), 8.94 (d, J = 8.9 Hz, 2H), 8.82 (d, J = 8.9 Hz, 2H), 8.49 (d, J = 8.8 Hz, 2H), 8.12 (dd, J = 8.1, 1.2 Hz, 2H), 7.91 (d, J = 5.3 Hz, 2H), 7.86 (d, J = 8.1 Hz, 2H),7.73 (dt, J = 7.8, 1.4 Hz, 2H), 7.58 (d, J = 7.9 Hz, 2H), 7.51 (ddd, J = 8.2, 7.0, 0.9 Hz, 2H), 7.44 (ddd, J = 7.6, 6.0, 1.3 Hz, 2H), 7.40 (ddd, J = 8.6, 7.0, 0.9 Hz, 2H), 7.35 (d, J = 9.0 Hz, 2H), 7.10 (m, 4H), 6.93 (ddd, J = 8.9, 6.9, 1.3 Hz, 2H). ^{13}C NMR (75.5 MHz, CD_3CN): δ (ppm) 162.3, 161.7, 157.4, 152.7, 152.6, 151.0, 141.2, 139.9, 139.6, 133.7, 131.6, 130.8, 130.5, 130.3,130.00, 129.97, 129.6, 128.5, 126.7, 126.2, 123.6, 123.5, 122.6. IR (thin film): ν (cm^{-1}) 1595, 1509, 1432, 1369, 1246, 1213, 1146, 1098, 830, 812, 781, 767, 750, 632, 556, 516, 482, 431. CD ($\Delta\varepsilon/M^{-1}$ cm^{-1}, MeCN): 262.5 nm (−35), 270.5 nm (+30). HRMS calcd for $C_{46}H_{32}F_6N_6PRu$ (M-PF_6)$^+$: 915.1381, found: 915.1361.

Λ-***3e***. According to the general procedure for proline removal, a solution of complex Λ-(*S*)-**2e** (45 mg, 0.064 mmol), 1,10-phenanthroline (174 mg, 0.968 mmol), and trifluoroacetic acid (0.039 mL, 0.512 mmol) in CH_3CN (0.6 mL) was heated at 110 °C for 2.5 h to afford Λ-[Ru(bpy)(dmb)(phen)](PF_6)$_2$ (48 mg, 82%) with 98:2 e.r. as determined by chiral HPLC analysis. ^{1}H NMR (300.1 MHz, CD_3CN): δ (ppm) 8.62 (dt, J = 8.4, 1.1 Hz, 2H), 8.54 (d, J = 8.1 Hz, 1H), 8.49 (d, J = 8.2 Hz, 1H), 8.37 (d, J = 8.4 Hz, 1H), 8.33 (d, J = 8.4 Hz, 1H), 8.24 (s, 2H), 8.09 (m, 3H), 7.97 (dt, J = 7.6, 1.3 Hz, 1H), 7.90 (dd, J = 8.4, 1.0 Hz, 1H), 7.86 (dd, J = 5.5, 0.6 Hz, 1H), 7.80 (ddd, J = 8.3, 2.0, 1.0 Hz, 1H), 7.75 (ddd, J = 8.2, 7.5, 5.2 Hz, 2H), 7.61 (s, 1H), 7.47 (m, 2H),7.35 (s, 1H), 7.20 (ddd, J = 7.7, 5.6, 1.0 Hz, 1H), 2.23 (s, 3H), 2.04 (s, 3H). ^{13}C NMR (75.5 MHz, CD_3CN): δ (ppm) 158.5, 158.1, 155.8, 155.5, 153.47, 153.44, 153.0, 152.8, 152.72, 152.66. 148.7, 148.6, 139.4, 139.32, 139.25, 139.21, 138.7, 138.5, 137.7, 132.1, 132.0, 129.12, 129.09, 128.4, 127.1, 127.0, 125.3, 125.2, 124.2, 124.1, 18.6, 18.4. IR (thin film): ν (cm^{-1}) 1596, 1510, 1428, 1211, 1126, 828, 762, 720, 555, 517. CD ($\Delta\varepsilon/M^{-1}$ cm^{-1}, MeCN): 263.5 nm (−108), 292.5 nm (+277). HRMS calcd for $C_{34}H_{28}F_6N_6PRu$ (M-PF_6)$^+$: 767.1064, found: 767.1041.

Λ-***3f***. According to the general procedure for proline removal, a solution of complex Λ-(*S*)-**2e** (45 mg, 0.064 mmol), 4,4′-di-*tert*-butyl-2,2′-bipyridine (260 mg, 0.968 mmol), and trifluoroacetic acid (0.039 mL, 0.512 mmol) in CH_3CN (0.6 mL) was heated at 110 °C for 2.5 h to afford Λ-[Ru(bpy)(dmb)(dbb)](PF_6)$_2$ (54 mg, 85%) with 98:2 e.r. as determined by chiral HPLC analysis. ^{1}H NMR (300.1 MHz, CD_3CN): δ (ppm) 8.52 (s, 1H), 8.50 (s, 1H), 8.485 (d, J = 2.0 Hz, 1H), 8.475 (d, J = 2.0 Hz, 1H), 8.345 (d, J = 2.7 Hz, 1H), 8.328 (d, J = 2.7 Hz, 1H), 8.05 (m, 2H), 7.86 (m, 2H), 7.73 (m, 2H), 7.61 (d, J = 6.1 Hz, 1H), 7.59 (d, J = 6.0 Hz, 1H), 7.48 (m, 1H), 7.44 (m, 1H), 7.41 (m, 4H), 2.207 (s, 3H), 2.198 (s, 3H), 1.426 (s, 9H), 1.412 (s, 9H). ^{13}C NMR (75.5 MHz, CD_3CN): δ (ppm) 152.6, 152.52, 152.47, 152.4, 152.2, 151.96, 151.94, 139.28, 139.22, 139.1, 138.67, 138.64, 138.49, 138.46, 128.6, 128.5, 128.4, 125.7, 125.6, 125.5, 125.2, 124.2, 122.61, 122.57, 36.3, 30.52, 30.50, 18.62, 18.56. IR (thin film): ν (cm^{-1}) 2960, 2872, 1615, 1466, 1414, 1244, 828, 762, 606, 555, 419. CD ($\Delta\varepsilon/M^{-1}$ cm^{-1}, MeCN): 279 nm (−138), 293.5 nm (+315). HRMS calcd for $C_{40}H_{44}F_6N_6PRu$ (M-PF_6)$^+$: 855.2318, found: 855.2298.

Single Crystal X-ray Diffraction. Crystals of Λ-(*S*)-**2a** were obtained by slow evaporation from an aqueous solution saturated with KNO_3. Crystals of a 1:1 diastereomeric mixture Λ-(*S*)-**2d**/Δ-(*S*)-**2d** were obtained by slow diffusion from a MeCN solution layered with Et_2O. Data were collected on a STOE-IPDS2T diffractometer employing graphite-monochromated Mo−Kα radiation (λ = 0.71069 Å) at a temperature of 100 K and were corrected for absorption effects using mutiscanned reflections (PLATON program).[19,20] The structures were solved by direct methods using the programs SIR-2011[21] (Λ-(*S*)-**2a**) or SHELXS-97[22] (Λ-(*S*)-**2d**/Δ-(*S*)-**2d**). Refinement was done by full-matrix least-squares based on F^2 data using SHELXL-97.[22] The absolute configurations were determined.[23] Table 3 lists cell information, data collection parameters, and refinement data.

Thermal Conversion of Δ-(*S*)-2a into Λ-(*S*)-2a. In a sealed glass vial fitted with a septum, a solution of Δ-(*S*)-**2a** (10 mg, 0.015 mmol) and L-proline (17.3 mg, 0.150 mmol) in ethylene glycol (0.15 mL) was degassed with argon for 5 min and then heated at an oil bath temperature of 190 °C for 20 min. The reaction mixture was cooled to room temperature, and the crude material was purified by silica gel chromatography with acetonitrile and later CH_3CN:H_2O:KNO_3(sat) = 40:3:1. The dark-purple eluents were concentrated to dryness, the resulting material was dissolved in water (15 mL), and the product was precipitated by the addition of excess solid NH_4PF_6. CH_2Cl_2 (10 mL) was added, and the layers were separated. The organic extracts were dried over Na_2SO_4, filtered, concentrated, and dried under high vacuum to afford Λ-(*S*)-**2a** as a single diastereomer (8.2 mg, 82%).

Visible Light-Induced Racemization Studies. A solution of Λ-[Ru(bpy)$_3$](PF_6)$_2$ (98.7% ee) in DMF (c = 1 mM) was stirred in a two neck pointed flask under nitrogen atmosphere at a defined temperature (21 or 50 °C; ± 1 °C) and irradiated using a 7 W Megaman LED reflector lamp MM27024 (PAR16 reflector, GU10 LR0707-SP). The distance between light source and sample was 8 cm resulting in an illuminance of $E_v \approx$ 80 klx. Samples of the solution were

Table 3. Crystal Data and Details of Data Collection for Λ-(*S*)-2a and Λ-(*S*)-2d/Δ-(*S*)-2d

	Λ-(*S*)-**2a**	Λ-(*S*)-**2d**/Δ-(*S*)-**2d**
empirical formula	$2(C_{25}H_{24}N_5O_2Ru)$, $2(NO_3)$, $13(H_2O)$	$2(C_{41}H_{32}N_5O_2Ru)$, PF_6)
fw	1411.34	1745.52
space group	$P2_12_12_1$	$P2_1$
a, Å	13.8864 (7),	14.0011 (5)
b, Å	18.8230 (9)	18.2927 (6)
c, Å	23.6930 (16)	14.4932 (5)
β, deg		106.071(3)
V, Å^3	6193.0 (6)	3566.9 (2)
Z	4	2
λ, Å	0.71069	0.71069
μ, mm^{-1}	0.57	0.56
crystal size, mm	0.20 × 0.17 × 0.04	0.23 × 0.23 × 0.21
T_{min}, T_{max}	0.785, 1.090	0.530, 0.709
no. of measured, independent and observed [$I > 2\sigma(I)$] reflections	42032, 11537, 5048	34262, 13276, 9196
R_{int}	0.143	0.059
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S[a]	0.056, 0.117, 0.78	0.030, 0.051, 0.69
no. of reflections	11537	13276
no. of parameters	802	1009
no. of restraints	102	1
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.49, −0.73	0.63, −0.42
Flack parameter	−0.02 (4)	−0.03 (2)
CCDC no.	886122	886121

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$; $S = \{\sum[w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$.

concentrated to dryness under high vacuum, redissolved in acetonitrile, and analyzed by chiral HPLC to determine the enantiomeric ratios. With progressing racemization, the baseline separation for the Δ- and Λ-enantiomer signals diminished so that peak integration was fitted to overlapping exponentially modified Gaussian functions. The applied evolutionary fitting algorithm uses a sum of two exponentially modified Gaussian functions where each individual function (i = Δ, Λ) describes one single peak in the HPLC trace. The general form of the individual function is given by eq 1.

$$S_i(t) = \left[A\cdot\exp\left[-\exp\left[-\frac{(t-t_{ca})}{w_a}\right]\right] - B\cdot\exp\left[-\exp\left[-\frac{(t-t_{cb})}{w_b}\right]\right]\right] \times \exp\left[-\left[\frac{(t-t_{ca})}{\tau_a}\right] - \left[\frac{(t-t_{ca})}{\tau_b}\right] + 1\right] \quad (1)$$

The parameters A and B in eq 1 describe the amplitudes of the two contributing Gaussian functions, t is the retention time, t_{ca} and t_{cb} represent the center of the individual peak, w_a and w_b are the full width at half-maximum (fwhm) values associated with the amplitudes A and B, and τ_a and τ_b are tailing parameters.

■ ASSOCIATED CONTENT

Supporting Information

Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: meggers@chemie.uni-marburg.de.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the German Research Foundation (ME 1805/4-1). We thank Jan Philip Kraack for providing the fitting algorithm applied to the determination of the ee values in the light-induced racemization study.

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