Stereoselective Synthesis of Octahedral Complexes with Predetermined Helical Chirality

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Abstract: Facile stereoselective synthesis of an enantiomerically pure Δ-Ru-trisbipyridine type complex is accomplished by using a new chiral and conformationally rigid ligand, which completely predetermines the helical chirality of the metal, yielding exclusively Δ-configuration in the present case. The ligand, abbreviated chiragen[6] is a bisbipyridine compound, where two pinene substituted bipyridine units are linked through an aliphatic C_6-chain. The two remaining coordination sites of the complex are occupied by 4,4′-dimethylbipyridine. The structure of the Δ-[Ru(chiragen-[6])(4,4′-dimethylbipyridine)]$(CF_3SO_3)_2$ complex has been determined by X-ray crystallography. Metal complexes formed by chiragen ligands have potential applications in enantioselective catalysis and as chiral building blocks for polynuclear species.

Introduction

Octahedral metal complexes with bipyridine derivatives as ligands are widely used and studied: (i) In *homogeneous catalysis*, where, e.g., Ru(II)–bisbipyridine complexes catalyze the epoxidation of olefins,[2] and Ni(II)–bpy complexes catalyze the 1,4-addition of nucleophiles to α,β-unsaturated carbonyl compounds[3] etc. (ii) In *photochemistry*, many mono- and dinuclear Ru(II)–bipyridine complexes have been described as photosensitizers.[4-6] (iii) Ru(II)–trisbipyridine complexes have also been used as *probes for biomolecular structures* (oligonucleotides).[7,8] (iv) *Electrode coating films* have been prepared by electroreductive polymerization of racemic [Ru(bipyridine)$_2$(vinylpyridine)$_2$]$^{2+}$ complexes on PtAu, and glassy carbon electrodes.[9]

Mononuclear complexes containing more than one bipyridine unit in cis configuration are helical and hence chiral (Figure 1).

Unfortunately, in most of the investigations, racemic mixtures of such metal complexes are used. The racemates of the considered metal complexes have been resolved only in rare cases, firstly because of the problem of separation of the enantiomers, and secondly because the metal–bipyridine complexes may racemize after resolution. Using enantiomerically pure and stable bipyridine complexes could improve or simplify many of the above mentioned applications:

There is some evidence, that the *helicity* of a metal–bipyridine catalyst has an effect on the enantioselectivity of the catalyzed reactions, as shown, e.g., in the case of transfer hydrogenation reactions with a Rh(I)–bisphenanthroline complex as catalyst.[10] It would be interesting to test enantiomerically pure metal–bisbipyridine complexes in such asymmetric syntheses.

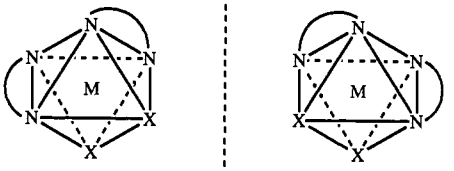

Figure 1. Enantiomeric pair of cis-metal–bisbipyridine complexes: Δ and Λ configuration. X are monodentate ligands.

To our knowledge, no X-ray structure determination has yet been carried out of any of the numerous polynuclear bipyridine complexes used in photophysical investigations. In our experience this lack of full characterization is due to the difficulty of crystallizing the isomeric mixtures obtained by using racemic building blocks. E.g., the simple dinuclear complex [(bpy)$_2$Ru-(bipyrimidine)Ru(bpy)$_2$]$(PF_6)_4$ with two racemic metal centers gives an isomeric mixture of Δ,Δ; Δ,Λ; and Λ,Λ-complexes.

Binding and subsequent photolytic scission of DNA strands, which has been reported in many publications[7,8] is more selective by using enantiomerically pure Ru(II)–trisbipyridine-type complexes.

Electrode coatings, made from enantiomerically pure Ru(II)–bisbipyridine monomers could lead to enantioselective redox reactions at the electrodes.

These prospects prompted us to look for new optically active bipyridine ligands, which, on diastereoselective complexation, lead directly to enantiomerically pure helical bisbipyridine-type complexes. A judicious design of such ligands could avoid the need for separation of enantiomers and, at the same time, make racemization at the metal center virtually impossible.

Results and Discussion

Modelling of suitable ligands for the stereoselective formation of enantiomerically pure *cis*-bisbipyridine–metal complexes revealed several possible strategies. The most promising structures turned out to be chirally bridged bisbipyridine ligands, which wrap in a predetermined helicity around the metal centers to give C_2-symmetrical complexes (Figure 2). Due to the rigid geometry of such ligands, complete induction of only one of the two cis diastereomers should occur.

We have therefore designed and synthesized bridged chiral bisbipyridine ligands for the diastereoselective preparation of enantiomerically pure metal complexes. We call these ligands *chiragen* (from chirality generator). In an easily performed

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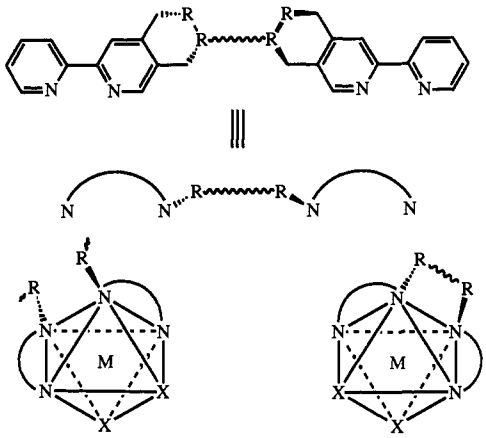


Figure 2. Complexation of a chirally bridged C_2-symmetrical bisbipyridine ligand. Unless the bridge is very long, the Δ-isomer cannot be formed. Only the Λ-configurated diastereomer is possible. R stands for substituents out of the aromatic plane of the bipyridines.

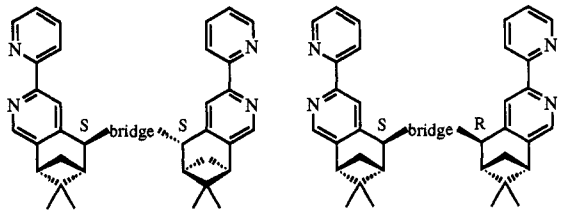
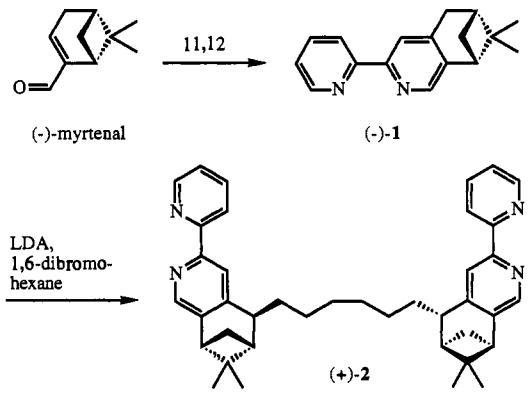


Figure 3. Left: optically active form of chiragen. Right: inactive meso form of chiragen.

Scheme I. Synthesis of (+)-chiragen[6] **2** from (-)-myrtenal via the (-)-[4,5]-pinenebipyridine **1**. [6] indicates the six methylene groups in the bridge.



synthesis, starting from naturally occurring (-)-myrtenal, such chiragen ligands are available in two-step reactions and with high enantiomeric purity (Scheme I). (-)-[4,5]-Pinenebipyridine (**1**) has a known absolute configuration (from precursor (-)-myrtenal) and a determined ee value >90%.[13] The rigid and chiral pinene-type framework of **1** is deprotonated completely regioselectively by LDA. The anion is then alkylated 100% stereoselectively at the less hindered side with 1,6-dibromohexane to give the ligand (+)-chiragen[6] (**2**).[13] Due to the known stereoselectivity of the alkylation reaction,[13] also the absolute configuration of **2** is determined. If **1** has 90% ee, a statistical mixture of chiragen isomers is obtained with calculated amounts of 90.25% (*S,S*), 9.50% (meso *S,R*) and 0.25% (*R,R*), where *S*/*R* indicate the absolute configurations of the bridge substituted stereogenic centers of the pinenebipyridine fragments (Figure 3). This equals a mixture containing 90.5% of optically active (+)-chiragen with >99% ee and 9.5% of the optically inactive meso form of **2**.

The optically active chiragen[*n*] ligands have the following general properties: (i) They can occupy four *nonplanar* coordination sites in an octahedral complex, leaving two equivalent cis positions free for coordination with other ligands. (ii) They comprise a total of six stereogenic carbon atoms (three in each bipyridine moiety). The chirality of the ligand is conformationally rigid, predetermining therewith unambiguously the chirality of the three cis positions (Δ or Λ) of the complex. (iii) The preparation of the ligands from chiral pool precursor (-)-myrtenal yields (+)-chiragen[*n*] with known absolute configuration, which in turn determines the absolute configuration of the octahedral complex. (iv) The bridge of the chiragens can easily be varied by using different alkylating compounds. (v) The absolute configuration of chiragens can be inverted by taking (+)-myrtenal as starting material. (+)-Myrtenal can be obtained in one step from the chiral pool molecule (+)-α-pinene.[14,15] (vi) Complexes of chiragen lead to C_2-symmetrical *cis*-bisbipyridine-type complexes. (vii) Because the bpy units of *meso*-chiragen (optically inactive form) cannot complex on one metal center (sterical reasons), there is a chiral amplification from 90% ee for the (-)-[4,5]-pinenebipyridine to 99% ee for the metal–complex with the optically active chiragen.

The complexation of the ligand chiragen[6] is done in a one-pot synthesis in refluxing ethanol, starting from a $Ru(dmso)_4Cl_2$[16] complex. For a more convenient isolation of the formed Ru(chiragen)Cl_2 complex, the two labile chlorides have been substituted directly by 4,4′-dimethylbipyridine. The obtained trisbipyridine-type complex is precipitated from water with lithium triflate as Ru((chiragen[6])(4,4′-dimethylbipyridine)$(CF_3SO_3)_2$. The crude product has to be purified by column chromatography to remove the polymeric complexes, followed by recrystallization from ethanol/water to give red orange crystals in about 20% overall yield. The characterization of the product by X-ray diffraction proves the expected structure of the complex (Figure 4). The C_6 chain in the ligand spans easily the bridge between the two bpy moieties. All bond lengths and angles are normal compared to $Ru(bpy)_3^{2+}$ and indicate no special structural strain in the metal complex.[17] Model considerations, knowing the absolute configuration of *S,S*-(+)-chiragen[6], predict a Δ-configurated Ru((+)-chiragen[6])(4,4′-dimethylbipyridine)$(CF_3SO_3)_2$ complex. This configuration has been proved by comparison of the CD spectrum and the rotation value of the obtained product with the CD spectrum and the optical rotation of the well-known Δ-$Ru(bpy)_3^{2+}$, obtained by separation of the racemic mixture.[18] The complexation of chiragen[6] is completely diastereoselective as shown by the ^1H NMR spectrum (Figure 5). The spectrum, which has been measured *before recrystallization* of the product, shows no side products. This fact indicate also that the meso form of chiragen does not give a bisbpy-type complex. The ^1H NMR spectrum is relatively simple, owing to the C_2 symmetry of the species.

Most of the other physical properties of Ru(chiragen[6])(4,4′-DMbpy)$^{2+}$ resemble closely those of the $Ru(bpy)_3^{2+}$. E.g., the absorption spectra are very similar for the two complexes and both emit at room temperature at ca. 610 nm.[5]

Because the diastereomeric Λ-configurated product Ru((+)-chiragen[6])(4,4′-dimethylbipyridine)$(CF_3SO_3)_2$ complex is not possible for sterical reasons, these enantiomerically pure chiragen–metal complexes cannot racemize.

Other chiragen[*n*] complexes containing various metals are under investigation. Such optically active metal–bisbipyridine-type complexes will be tested as catalysts in asymmetric

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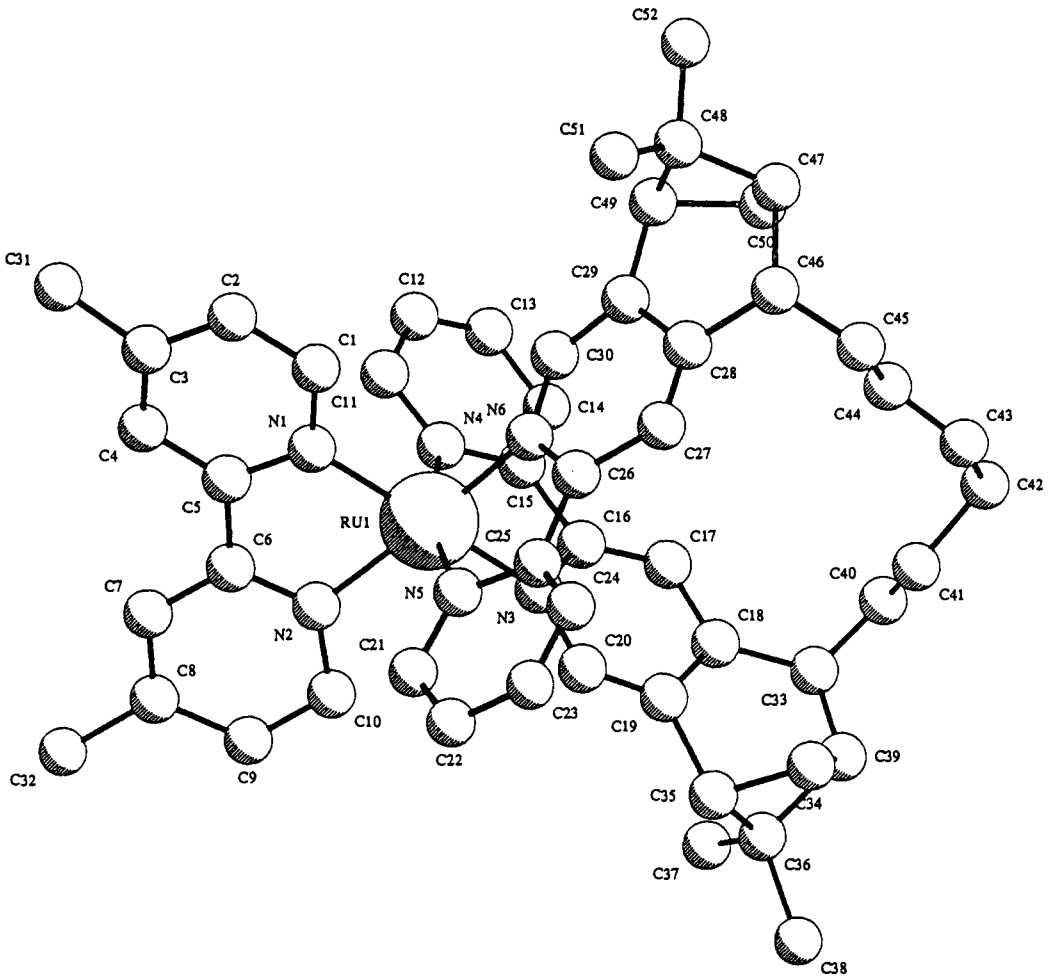

Figure 4. X-ray structure of the Δ-[Ru((+)-chiragen[6])(4,4′-dimethylbipyridine)]$(CF_3SO_3)_2$ complex. Hydrogen atoms have been removed for clarity.

syntheses.[2,10,19] Chiragen[n] with n = 4,5 have also been synthesized and complexed with ruthenium in the same way as for n = 6.

Conclusion

For the first time, an *enantiomerically pure* octahedral metal–bipyridine complex with *known absolute configuration* has been synthesized *without the need of separation of enantiomers*. It was fully characterized by X-ray crystallography. The rather low yield of the complexation step is due to the formation of polynuclear species. Alternation of the methylene chain to more rigid bridges could improve the situation.

Experimental Section

General Data. ^{1}H NMR (300 MHz) and ^{13}C NMR (75.4 MHz) spectra were recorded with a Varian Gemini 300 instrument using solvent as the internal standard. Chemical shifts are reported in ppm on the δ scale. Infrared spectral data were collected using a Perkin Elmer IR spectrometer, and mass spectral data were obtained with a VG Instruments 7070E mass spectrometer equipped with a FAB inlet system. UV–vis spectral data were collected using a Perkin-Elmer Lambda 5 spectrophotometer. CD spectra were measured on a Jobin Yvon auto dichrograph Mark V. The emission spectra were measured on a Perkin-Elmer MPF-4 spectrometer. Rotation values have been obtained with a Perkin-Elmer MC 241 polarimeter. Unless otherwise stated, commercial chemicals were used as supplied. THF was distilled under N_2 from sodium. $RuCl_3 \cdot 3H_2O$ is obtained from Johnson Matthey, (1*R*)-(−)-myrtenal from Aldrich; all other starting materials are from Fluka. All bipyridine compounds can be detected with diluted $FeSO_4$ solution as red spots on TLC.

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(−)-[4,5]-Pinenebipyridine (1). Ten grams (66.7 mmol) of (1*R*)-(−)-myrtenal (Aldrich), 21.7 g (66.7 mmol) of 1-(2-acetylpyridine)pyridinium iodide,[11,12] and 10.27 g (133.4 mmol) of ammonium acetate are suspended in 100 mL of formamide and heated at 75 °C for 6 h. The dark viscous solution is immediately diluted with 100 mL of water and extracted 10 times with 100-mL portions of *n*-hexane. The combined organic layers are washed with water and dried over $MgSO_4$. The solvent is evaporated. The product is pure enough at this stage for the next synthesis step, but it can be obtained more pure by filtering over silica gel with *n*-hexane/ethyl acetate 1:1 with 10% triethylamine: yield 80%; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.62 (dxd, 1H, ^3J = 4.0 Hz, ^4J = 1.8 Hz), 8.31 (dxd, 1H, ^3J = 8.0 Hz, ^4J = 1.1 Hz), 8.17 (s, 1H), 8.15 (s, 1H), 7.75 (dxdxd, 1H, ^3J = 7.5 Hz, ^3J = 8.0 Hz, ^4J = 1.8 Hz), 7.23 (dxdxd, 1H, ^3J = 7.5 Hz, ^3J = 4.0 Hz, ^4J = 1.1 Hz), 3.01 (m, 2H), 2.83 (dxd, 1H, ^3J = 5.5 Hz, ^4J = 5.5 Hz), 2.67 (dxdxd, 1H, ^2J = 9.5 Hz, ^3J = 5.5 Hz, ^3J = 5.5 Hz), 2.27 (m, 1H), 1.37 (s, 3H), 1.20 (d, 1H, ^2J = 9.5 Hz), 0.61 (s, 3H); ^{13}C NMR ($CDCl_3$, 75.44 MHz) δ 156.76, 154.50, 148.99, 145.56, 145.43, 143.00, 136.83, 123.23, 120.86, 120.47, 44.57, 40.14, 39.29, 32.94, 31.86, 26.06, 21.38; MS (EI) m/z 250 (8, M^+), 235 (8, $M^+ - CH_3$), 207 (100, M^+ – isopropyl), 180 (13), 167 (2), 152 (2), 128 (3), 78 (6 pyridine$^+$); $[\alpha]_D$ = −85°, 20 °C, 20 mg in 10 mL of CH_2Cl_2. Anal. Calcd for $C_{17}H_{18}N_2$: C, 81.56; H, 7.25; N, 11.19. Found: C, 81.34; H, 7.21; N, 10.93.

(+)-Chiragen[6] (2). In a three-necked, 100-mL flask, fitted with a septum, low-temperature thermometer, and N_2 supply are placed 50 mL of dry THF. At −40 °C, 2.3 mL (16 mmol) of diisopropylamine and 9.4 mL (15 mmol) of 1.6 M butyllithium in hexane are injected. The temperature is raised to 0 °C for 15 min and dropped again at −40 °C, where a solution of 2.5 g (10 mmol) of (−)-[4,5]-pinenebipyridine in 10 mL of dry THF are injected. The solution is stirred for 2 h (maximum temperature −10 °C). At −40 °C, 5.1 mmol of 1,6-dibromohexane are then added to the dark mixture. After 30 min, the temperature is raised to about 20 °C, and the solution is stirred for 48 h. One milliliter of water is added to quench the reaction. The solvent is removed under reduced pressure, and the residue is dissolved in 80 mL of 6 M hydrochloric acid.

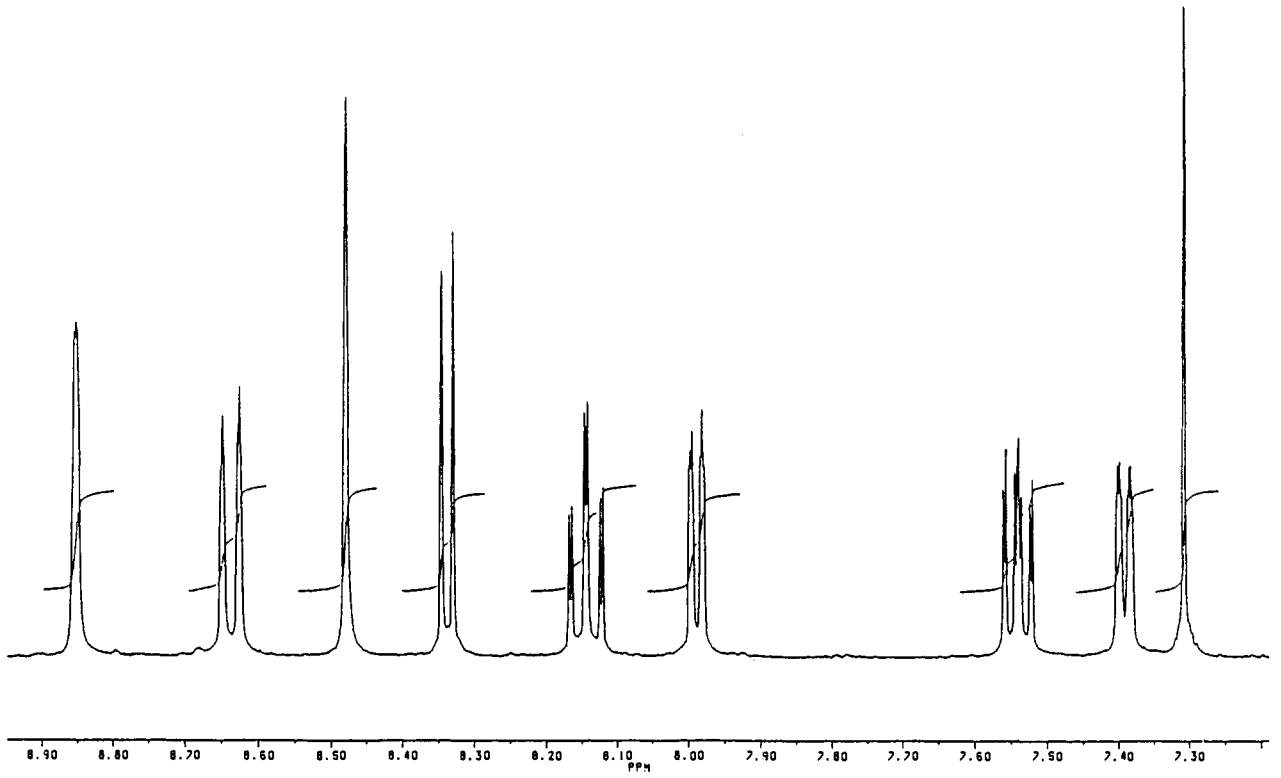

Figure 5. Aromatic region of the ^1H NMR spectrum of the Δ-[Ru((+)-chiragen[6])(4,4′-dimethylbipyridine)]$(CF_3SO_3)_2$ complex, measured in acetone-d_6.

The aqueous solution is washed once with 50 mL of dichloromethane to remove bromohexylated side product. The water layer is carefully neutralized with saturated sodium hydroxide solution and then extracted three times with 50-mL portions of dichloromethane. The organic phase is dried over $MgSO_4$ and concentrated. The residue is purified by silica gel column chromatography (hexane 3/ethyl acetate 1 with 10% triethylamine): yield 70%; ^1H NMR ($CDCl_3$, 300 MHz) δ 8.62 (d, 2H, ^3J = 4.6 Hz), 8.31 (d, 2H, ^3J = 8.0 Hz), 8.26 (s, 2H), 8.16 (s, 2H), 7.74 (dxdxd, 2H, ^3J = 7.8 Hz, ^3J = 8.0 Hz, ^4J = 1.6 Hz), 7.21 (dxd, 2H, ^3J = 7.8 Hz, ^3J = 4.6 Hz), 2.95 (d, 2H, ^3J = 9.2 Hz), 2.82 (dxd, 2H, ^3J = 5.4 Hz, ^4J = 5.4 Hz), 2.52 (dxdxd, 2H, ^3J = 5.9 Hz, ^3J = 5.4 Hz, ^2J = 9.8 Hz), 2.26–2.23 (m, 2H), 2.01–1.95 (m, 2H), 1.54–1.21 (m, 10H), 1.40 (s, 6H), 1.24 (d, 2H, ^2J = 9.8 Hz), 0.59 (s, 6H); ^{13}C NMR ($CDCl_3$, 75.44 MHz) δ 156.81, 154.64, 150.12, 149.02, 145.42, 142.76, 136.90, 123.26, 120.91, 119.68, 45.12, 43.15, 41.20, 40.97, 33.53, 29.89, 28.27, 27.85, 26.43, 21.05; IR (KBr) 2980 (m), 2930 (s), 2860 (m), 1590 (s), 1545 (m), 1465 (s), 1440 (m), 1385 (m), 1255 (m), 1090 (w), 1060 (w), 995 (w), 800 (m), 755 (m), 745 (m) cm^{-1}; MS (EI) m/z 582 (42, M^+), 539 (23, M^+-isopropyl), 333 (42, M^+-**1**), 263 (71, $\mathbf{1}^+$ + methyl), 249 (100, $\mathbf{1}^+$), 233 (45), 221 (40), 207 (90, $\mathbf{1}^+$ – isopropyl), 78 (11, pyridine$^+$); $[\alpha]_D$ = +30°, 20 °C, 20 mg in 10 mL of CH_2Cl_2.

Δ-[Ru((+)-chiragen[6])(4,4′-dimethylbipyridine)]$(CF_3SO_3)_2$ (3). One hundred mg (0.21 mmol) of $Ru(dmso)_4Cl_2$[15] is refluxed in 5 mL of acetonitrile for 2 h. $Ru(NCCH_3)_4Cl_2$ is precipitated with about 70 mL of diethyl ether. The ether solution is then decanted. The freshly prepared $Ru(NCCH_3)_4Cl_2$ and 122 mg (0.21 mmol) of (+)-chiragen[6] are dissolved each in 250 mL of ethanol, mixed, and refluxed for 10 h. After removal of the solvent, the brownish residue is redissolved in 5 mL of ethylene glycol and 0.5 mL of water. 4,4′-Dimethylbipyridine (1.5 equiv) is added, and the mixture is heated for ca. 30 min to 120 °C. The fluorescent complex is precipitated by the addition of 70 mL of water and 1 g of $LiCF_3SO_3$ and then purified by column chromatography over basic Al_2O_3 with acetone as eluent: yield 25%. Some remaining [Ru(4,4′-dimethylbipyridine)$_3$]$(CF_3SO_3)_2$ side product may be eliminated by preparative thin-layer chromatography on silica gel with ethanol/water/NaCl 10:10:1 as eluent. Recrystallization from ethanol/water afforded red-orange crystals: ^1H NMR (acetone-d_6, 300 MHz) δ 8.85 (s, 2H), 8.64 (d, 2H, ^3J = 8.0 Hz), 8.48 (s, 2H), 8.34 (d, 2H, ^3J = 5.7 Hz), 8.14 (dxdxd, 2H, ^3J = 8.0 Hz, ^3J = 8.0 Hz, ^4J = 1.4 Hz), 7.99 (d, 2H, ^3J = 5.5 Hz), 7.54 (dxdxd, 2H, ^3J = 5.5 Hz, ^3J = 8.0 Hz, ^4J = 1.3 Hz), 7.39 (d, 2H, ^3J = 5.7 Hz), 7.31 (s, 2H), 3.42–3.36 (m, 2H), 2.62 (s, 6H), 2.59 (dxd, 2H, ^3J = 5.5 Hz, ^4J = 5.5 Hz), 2.54 (dxdxd, 2H, ^3J = 5.5 Hz, ^3J = 5.5 Hz, ^2J = 9.9 Hz), 2.21–2.16 (m, 2H), 2.15–2.05 (m, 2H), 1.72–1.58 (m, 2H), 1.39–1.25 (m, 2H), 1.34 (s, 6H), 1.25 (d, 2H, ^2J = 9.9 Hz), 1.06–0.90 (m, 6H), 0.64 (s, 6H); MS (FAB) 1017 (54, $M^+ - CF_3SO_3^-$), 869 (68, $M^+ - 2CF_3SO_3^-$), 434 (100), 329 (34); UV–vis (acetonitrile, 1.744E-5M) 454 (13 300), 427 (sh, 11 400), 289 (69 800), 237 (32 800); CD (acetonitrile) c 3.306E-5 (700–350 nm), 485 (–10), 425 (13); c 1.061E-5 (350 nm – 200 nm), 305 (–165), 285 (110); $[\alpha]_{365}$ = –4516°, 20 °C, 0.62 mg in 50 mL of acetonitrile; emission (acetonitrile, 1.744E-5M) excitation 454 nm, emission 608 nm.

X-ray Structure Determination. Single crystals were grown from ethanol/water at room temperature. Data were collected on a Stoe AED2 4-circle diffractometer, using the $\omega/2\theta$ scan mode and Mo Kα graphite monochromated radiation (λ 0.71073 Å). The crystals are monoclinic, space group $P2_1$. Cell dimensions: a = 10.680(2), b = 22.958(5), c = 11.874(3) Å, β = 101.44(2)°, V = 2853.6(11) Å^3, Z = 2, D_{calc} = 1.357 g cm^{-3}, R = 0.10. Some selected interatomic distances (Å): Ru–N1 2.087, Ru–N2 2.094, Ru–N3 2.048, Ru–N4 2.078, Ru–N5 2.072, Ru–N6 2.033, N1–C5 1.36, C5–C6 1.45, N5–C21 1.35, C21–C22 1.37, C22–C23 1.47, C23–C24 1.33, C24–C25 1.39, C25–N5 1.36, C25–C26 1.46, C26–N6 1.38, C26–C27 1.49, C27–C28 1.32, C28–C29 1.42, C29–C30 1.42, C30–N6 1.30, C29–C49 1.51, C49–C48 1.52, C49–C50 1.58, C48–C51 1.46, C48–C52 1.52, C48–C47 1.51, C47–C50 1.50, C47–C46 1.65, C46–C28 1.56, C46–C45 1.45, C45–C44 1.52, C44–C43 1.36, C43–C42 1.61; some selected angles (deg) are as follows: N1–Ru–N2 78.6, N1–Ru–N3 174.2, N1–Ru–N4 96.4, N1–Ru–N5 95.4, N1–Ru–N6 96.7, N2–Ru–N3 99.3, N2–Ru–N4 95.2, N2–Ru–N5 97.8, N2–Ru–N6 174.2, N3–Ru–N4 78.5, N3–Ru–N5 90.4, N3–Ru–N6 86.1, N4–Ru–N5 164.3, N4–Ru–N6 88.9, N5–Ru–N6 79.3.

Other chiragen ligands with n = 4, 5 and their complexes have been synthesized by the same procedures as given above. The physical data are almost identical with the samples of chiragen[6] and its Ru complex. The yield of the complex Δ-[Ru((+)-chiragen[4])(4,4′-dimethylbipyridine)]-$(CF_3SO_3)_2$ reaches only 12% due to a too short aliphatic chain. Yield of the chiragen[5] complex: 25%.

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Supplementary Material Available: Tables of crystallographic data of **3**, positional and displacement parameters, and bond distances and angles (9 pages); tables of observed and calculated structure factors (16 pages). Ordering information is given on any current masthead page.