Diastereoselective Preparation and Characterization of Ruthenium Bis(bipyridine) Sulfoxide Complexes

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Received September 1, 1999

A new concept in the synthesis of optically active octahedral ruthenium complexes was realized for the first time when *cis*- or *trans*-Ru(bpy)$_2$Cl, (*cis*- or *trans*-**1**) was reacted with either (*R*)-(+)- or (*S*)-(−)-methyl *p*-tolyl sulfoxide (**2** or **3**); this novel asymmetric synthesis leads to the diastereoselective formation of the ruthenium bis(bipyridine) complex *cis*-Δ-[Ru(bpy)$_2$(**2**)Cl]Cl (**4**) (49.6% de) or *cis*-Λ-[Ru(bpy)$_2$(**3**)Cl]Cl (**5**) (48.4% de), respectively. *cis*- or *trans*-Ru(dmbpy)$_2$Cl$_2$ (*cis*- or *trans*-**6**) (dmbpy = 4,4′-dimethyl-2,2′-bipyridine) also reacts with **2** or **3**, leading to the diastereoselective formation of *cis*-Δ-[Ru(dmbpy)$_2$(**2**)Cl]Cl (**7**) (59.5% de) or *cis*-Λ-[Ru(dmbpy)$_2$(**3**)Cl]Cl (**8**) (57.2% de), respectively. The diastereoselectivity of these reactions is governed solely by the chirality of the sulfoxide nucleophile. This represents the first process by which a σ-bonded ligand occupying only a single coordination site has had such an important influence on the stereochemical outcome of a ruthenium bis(bipyridine) complex formation. These novel complexes were fully characterized by elemental analysis and IR, UV/vis, and ^{1}H, ^{13}C, and 2D NMR spectroscopy. An investigation into the chiroptical properties of these novel ruthenium bis(bipyridine) sulfoxide complexes has been carried out, and circular dichroism spectra are used to assign absolute stereochemistry.

Introduction

Ruthenium bis(bipyridine) complexes have been the subject of extensive investigation over many years, as they have a unique combination of chemical, electrochemical, and photochemical properties that make them attractive candidates for photochemical devices,[1−3] and as photocatalysts for redox[4] and stereoselective[5−8] reactions. The majority of the literature describing a preparation of optically pure ruthenium bis- and tris(bipyridine) complexes involves an initial racemic synthesis, followed by a resolution process when chiral ruthenium bipyridine complexes are required. The separation of the optical products of these reactions has been achieved by various methods[9,10] including chromatographic techniques[11−13] although resolutions through crystallization with chiral anions have also been reported.[14] Pure enantiomers of ligand-bridged diruthenium polypyridyl species have also been prepared, either through resolution or through reaction with enantiomerically pure chiral building blocks.[15−17] Keene et al. have prepared the chiral reagent *cis*-[Ru(bpy)$_2$(CO)$_2$]$^{2+}$, which can be used to prepare chiral ruthenium tris(bipyridine) complexes.[17,18] However, it should be stressed that this reagent must be resolved to achieve optically active products. Even after many decades of research, it is only recently that stereoselective syntheses have been realized, and to date the number of successful preparations of enantiomerically enriched ruthenium bipyridine complexes via an asymmetric synthesis is still very small. Using the tetradentate "chiragen" ligand, which contains no less than six chiral centers, von Zelewsky et al. reported a highly diastereoselective synthesis of ruthenium bis(bipyridine) complexes.[19,20]

Below, we describe our attempts to achieve the asymmetric synthesis of simple ruthenium bis(bipyridine) complexes, a feat which has not been reported previously. This work was attempted in three ways, as follows: (i) through the addition

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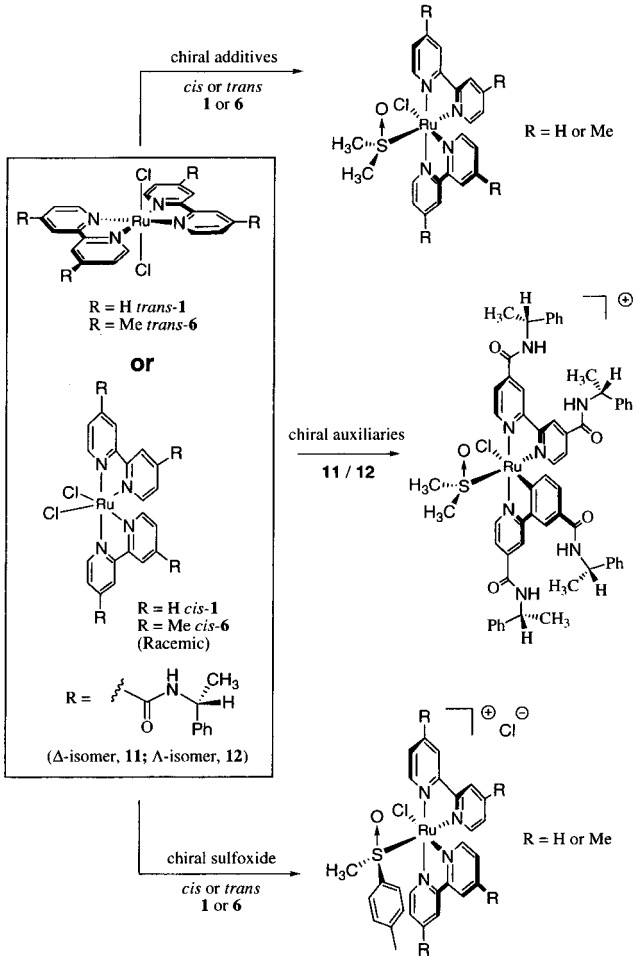
10.1021/ic991059d CCC: $19.00
Published on Web 12/28/1999

Scheme 1. An Outline of the Three Different Methods Employed in an Attempt To Achieve the Asymmetric Synthesis of Ruthenium Bis(bipyridine) Sulfoxide Complexes



of a chiral complexing agent into the reaction media of a normally racemic process, (ii) via the reaction of a bipyridine derivative bearing large, chiral substituents (*cis*-Ru(4,4′-bis((*R*)-(+)-α-phenylethylamido)-2,2′-bipyridine)$_2$Cl$_2$) with an achiral sulfoxide nucleophile, and (iii) by using a chiral sulfoxide nucleophile in an effort to prepare a chiral ruthenium bis(bipyridine) complex (see Scheme 1). Only the last of these three approaches proved successful, and by reacting racemic *cis*- or *trans*-Ru(bpy)$_2$Cl$_2$ (*cis*- or *trans*-**1**) with (*R*)-(+)- or (*S*)-(−)-methyl *p*-tolyl sulfoxide (**2** or **3**), the asymmetric synthesis of *cis*-Δ-[Ru(bpy)$_2$(**2**)Cl]Cl (**4**) (48.4% de) or *cis*-Λ-[Ru(bpy)$_2$(**3**)Cl]Cl (**5**) (49.6% de) was achieved. Using a different starting material, *cis*- or *trans*-Ru(dmbpy)$_2$Cl$_2$ (dmbpy = 4,4′-dimethyl-2,2′-bipyridine) (*cis*- or *trans*-**6**) reaction with **2** or **3** gave products with improved diastereoselectivity, affording *cis*-Δ-[Ru(dmbpy)$_2$(**2**)Cl]Cl (**7**) (59.5% de) or *cis*-Λ-[Ru(dmbpy)$_2$(**3**)-Cl]Cl (**8**) (57.2% de). Thus, through the use of a simple chiral sulfoxide starting material, the first preparation of enantiomerically enriched ruthenium bis(bipyridine) sulfoxide complexes has been accomplished.

Experimental Section

Materials. The reagents used in these studies were reagent grade or better, and were used without further purification. Solvents were purified according to published methods. Dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) were dried overnight over 4 Å molecular sieves, distilled, and stored under argon. Acetonitrile used in the preparation of ruthenium complexes was distilled from calcium hydride, and stored over 4 Å molecular sieves.

Instruments. IR spectra were obtained from the KBr disk using a JEOL JIR 6500 instrument. Circular dichroism spectroscopy was performed on a JASCO J-720WI spectropolarimeter at 25 °C in acetonitrile, or in the HPLC eluent ($NaPF_6$(aq)/CH_3CN mixed solvent). The concentrations of the solutions were determined by UV/vis measurements. Resolution of enantiomers or diastereomers was performed on the preparative scale using a recycling liquid chromatograph JAI LC-908 equipped with a preparative chiral column, Daicel Chiralcel OD-R (20 mm Φ × 250 mm). An aqueous solution of $NaPF_6$ (0.1 M) and acetonitrile was used as eluent, with a flow rate of 3 mL min^{-1}. The chromatograph was monitored at 292 nm with a UV detector. Monitoring the products of the synthetic reactions and the optical purity of the separated fractions was performed using an analytical HPLC system (JASCO GULLIVER series) equipped with an analytical chiral column, Daicel Chiralcel OD-R (4.6 mm Φ × 250 mm), an HPLC pump, PU-980, a three-line degasser, DG-980-50, a UV/vis detector, UV-970, and a column oven, 60-CO. The eluent flow rate was 0.4 mL min^{-1}, and the chromatograph was monitored at 425 nm and recorded with a JASCO integrator, 807-IT. Optical rotations were measured with a Perkin-Elmer model 341 polarimeter using HPLC eluent as solvent. Analytical thin-layer chromatography was performed with plastic-backed silica sheets (Merck Kieselgel 60 F_{254}). All new compounds were characterized by ^{1}H and ^{13}C NMR spectroscopy, and elemental analysis. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-EX 400 spectrometer, operating at 399.65 and 100.40 MHz, respectively. Chemical shifts are reported relative to either the solvent reference or the internal standard tetramethylsilane (TMS; 0.00 ppm) for ^{1}H NMR and the solvent reference for ^{13}C NMR. Pulsed field gradient experiments were used for H−H and C−H correlations (VCOSYNH and VCHSHF pulse sequences, respectively).

Molecular mechanics calculations were performed using the CHARMm/QUANTA program (version 4.0 from Molecular Simulation Inc., 1994) implemented on a Silicon Graphics O2 System (R10000SC). In the CHARMm program, the total energy is expressed as a sum of the bonded and nonbonded terms (eq 1). The bonded terms contain

$$E_{\text{total}} = (1/2)\sum k_b(l - l_0)^2 + (1/2)\sum k_\theta(\theta - \theta_0)^2 + \sum k_\phi/2[1 + \cos(n\phi - \delta)] + (1/2)\sum k_\omega(\omega - \omega_0)^2 + \sum \epsilon_{ij}^*[(r_{ij}^*/r_{ij})^{12} - 2(r_{ij}^*/r_{ij})^6] + \sum (q_i q_j/4\pi\epsilon_0 r_{ij}^2) \quad (1)$$

the parameters for bond, bond angle, dihedral angle, and improper angle energies, and the nonbonded terms contain the van der Waals and electrostatic energies. It should be noted that the electrostatic energy was calculated using a distance-dependent dielectric constant (RDIE) term (see the Results).

All atom types have been taken from the CHARMm parameters except for the bipyridyl nitrogens, the parameters for which have been applied utilizing reported values.[21] These parameters have two kinds of nitrogen atoms, NSR (coordinated N, trans to S) and NIR (coordinated N, not trans to S). Although NSR has been used without change, the name of NIR has been changed to N6R and N6RA, thereby avoiding confusion between the dihedral angles (see the Supporting Information). Moreover, the force constants of the dihedral angles for the coordinated atoms have been set to zero so as not to influence barriers around coordination bonds. The atomic charges which are necessary for calculation of the electrostatic term were calculated using the ZINDO semiempirical quantum mechanics program within the Cerius2 software.[22] The initial structure of the ruthenium complex was prepared from the X-ray structure of the closely related complex [Ru(bpy)$_2$(Cl)(DMSO)]PF_6,[11] which was ligand modified, and then treated with a full Newton−Raphson minimization method. A grid scan around the Ru−S bond, with rotations of 5° from −180° to +180°, was carried out, and each conformation was minimized with an adopted basis

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Newton−Raphson method (ABNR) (1000 steps), with an energy gradient tolerance of 0.001 kcal mol^{-1} $Å^{-1}$.

Synthesis. Δ-*cis*-Ru(4,4′-bis((*R*)-(+)-α-phenylethylamido)-2,2′-bipyridine)$_2$Cl$_2$ (11) and Λ-*cis*-Ru(4,4′-bis((*R*)-(+)-α-phenylethylamido)-2,2′-bipyridine)$_2$Cl$_2$ (12). Ruthenium(III) chloride hydrate (20 mmol) dissolved in dry DMF (80 mL) was treated with an excess of anhydrous LiCl (100 mmol) to give a suspension which was stirred for 5 min at 70 °C. 4,4′-Bis((*R*)-(+)-α-phenylethylamido)-2,2′-bipyridine (0.042 mmol) was added to this solution, and the mixture was stirred at 120 °C for 3 h, under a nitrogen atmosphere. The slurry was allowed to cool and then poured into rapidly stirred ether (100 mL). The precipitate was isolated by vacuum filtration and washed with water. The black solid residue was redissolved in a minimum amount of hot acetone. Addition of ether precipitated a black microcrystalline powder, which was dried in vacuo at 40 °C overnight, giving a mixture of **11** and **12** in 55% yield. Anal. Calcd for $C_{56}H_{52}Cl_2N_8O_4Ru_1{\cdot}4H_2O$ (1145.2): C, 58.73; H, 5.28; N, 9.78. Found: C, 58.66; H, 5.01; N, 9.88. ^{1}H NMR (CD_3CN): δ 10.03 (m, 2H, NH), 9.50 (m, 2H, NH), 9.27 (d, J = 5.6 Hz, 2H, H-6), 9.22 (s, 2H, H-3), 9.05 (s, 2H, H-3), 8.21 (d, J = 6 Hz, 2H, H-6), 7.67 (d, J = 6 Hz, 2H, H-5), 7.48 (d, J = 6.8 Hz, 4H, Ar-H), 7.53 (d, J = 5.6 Hz, 2H, H-5), 7.40 (t, J= 6.8 Hz, 8H, Ar-H), 7.28 (m, 8H, Ar-H), 5.32 (m, 2H, CH), 5.13 (m, 2H, CH), 1.60 (d, J = 6.8 Hz, 6H, CH_3), 1.51 (d, J = 6.8 Hz, 6H, CH_3). ^{13}C NMR (CD_3CN): δ 163.0 (s, CO), 162.7 (s, CO), 159.9, 158.1, 153.3, 152.5, 144.3, 144.2, 144.1, 138.6, 138.4, 128.3, 128.1, 126.7, 126.6, 126.1, 125.9, 123.3, 123.2, 120.4, 120.3, 49.0, 48.8, 22.1, 22.0.

***cis*-[Ru(4,4′-bis((*R*)-(+)-α-phenylethylamido)-2,2′-bipyridine)$_2$-(DMSO)Cl]Cl (13).** A 1:1 mixture of **11** and **12** (1.1 g, 1 mmol) was heated in DMSO at 75 °C under nitrogen for 12 h. Removal of solvent under reduced pressure to dryness gave a red residue, which was redissolved in acetone and rapidly filtered through a Celite bed before the filtrate was evaporated to dryness. To remove unreacted DMSO, the crude residue was treated with ether and dried in vacuo, giving the desired product in 63% yield (0.77 g). ^{1}H NMR (CD_3CN): δ 10.17 (m, 2H), 9.19 (s, 1H), 9.82 (d, J = 5.6 Hz, 1H), 9.72 (s, 1H), 9.70 (d, J = 5.6 Hz, 1H), 9.60 (m, 3H), 9.49 (m, 2H), 9.41 (d, J = 5.6 Hz, 1H), 8.36 (d, J = 6.0 Hz, 1H), 8.24 (d, J = 6.0 Hz, 1H), 7.97 (dd, 2H), 7.70−7.05 (m, 20H), 5.12 and 5.25 (2 × m, 4H), 3.12 (s, 3H), 2.19 (s, 3H), 1.67−1.49 (6 × d, 12H). ^{13}C NMR (CD_3COCD_3): δ 162.9, 162.8, 162.6, 161.9, 159.8, 159.2, 158.6, 157.7, 156.7, 154.5, 153.1, 151.1, 145.4, 145.3, 143.8, 143.4, 142.9, 142.4, 129.0−125 (m), 123.5, 123.4, 122.5, 122.1, 51.2, 51.1, 51.0, 50.9, 44.1, 42.3, 22.6, 22.5. The sample was converted to the perchlorate salt and analyzed. Anal. Calcd for $C_{58}H_{58}ClN_8O_5RuS{\cdot}2H_2O{\cdot}ClO_4$ (1250.27): C, 55.68; H, 4.99; N, 8.96. Found: C, 55.38; H, 5.12; N, 8.88.

***cis*-[Ru(4,4′-bis((*R*)-(+)-α-phenylethylamido)-2,2′-bipyridine)$_2$-(TMSO)Cl]Cl (14).** Anal. Calcd for $C_{60}H_{60}Cl_2N_8O_5RuS{\cdot}2H_2O$ (1213.3): C, 59.39; H, 5.32; N, 9.24. Found: C, 59.46; H, 5.29; N, 9.08. ^{1}H NMR (CD_3COCD_3): δ 10.42 (s, 1H), 10.22 (d, J = 6 Hz, 1H), 9.80 (d, 1H), 9.75 (d, J = 5.6 Hz, 1H), 9.60 (m, 2H), 9.33 (m, 1H), 9. 08 (m, 1H), 8.38 (m, 1H), 8.23 (m, 1H), 8.17 (dd, J = 6 Hz, 2H), 7.70−7.05 (m, 24H), 5.20 and 5.40 (2 × m, 4H), 4.04 (m, 1H), 3.34 (m, 1H), 2.47 (m, 1H), 2.30 (m, 1H), 2.13 (m, 2H), 1.80 (m, 2H), 1.78 (d, J = 6.2 Hz, 3H), 1.69 (m, 6H), 1.60 (d, 3H). ^{13}C NMR (CD_3-$COCD_3$): δ 162.2, 162.0, 161.5, 161.3, 158.9, 158.8, 158.3, 157.0, 156.1, 153.8, 153.5, 150.6, 144.7, 144.4, 143.4, 142.5, 141.8, 128.0−121.2 (m), 56.4, 53.4, 50.3, 50.1, 49.9, 49.8, 21.7, 21.6, 21.5, 21.4.

Optimum Conditions for the Preparation of the Ruthenium Bis-(bipyridine) Sulfoxides. Reaction conditions that afford the greatest de were found to be as follows: a suspension of **6** (1.0 g, 2 mmol) and **3** (0.5 g, 3 mmol) in DMF (50 mL) was heated to 120 °C under a nitrogen atmosphere for 24 h. Unreacted **6** was separated by filtration and the solvent removed in vacuo. The red residue was then redissolved in acetone and rapidly filtered through a Celite pad. The filtrate was evaporated to dryness, rinsed with ether, and dried in vacuo, giving crude **8** in almost quantitative yield with a de of 57.2%, as confirmed by chiral HPLC analysis. The reaction mixture obtained could not be further purified because the ruthenium bis(bipyridine) sulfoxide complexes proved to be slightly photochemically unstable, undergoing a slow photodegradation over a period of several hours. The crude sample was subjected to preparative HPLC, and fractions containing the individual products were collected. To obtain diastereomerically pure samples, the HPLC eluent was then reduced to a minimum volume in vacuo and the residue taken up in CH_2Cl_2 and subsequently washed with distilled water, affording the dark red products as their PF_6 salts. The organic solvent was evaporated to dryness. All of the above operations were carried out in light-free conditions.

***cis*-Δ-[Ru(bpy)$_2$(2)Cl]Cl (4) and *cis*-Λ-[Ru(bpy)$_2$(3)Cl]Cl (5).** ^{1}H NMR ((CD_3)$_2$CO): δ 10.48 (d, J = 5.6 Hz, 1H, H-6), 9.70 (d, J = 5.6 Hz, 1H, H-6), 8.71 (d, J = 8.3 Hz, 1H, H-3), 8.65 (d, J = 8.3 Hz, 1H, H-3), 8.28 (m, 2H, H-3), 8.20 (d, J = 8.3 Hz, 1H, H-3), 8.15 (t, J = 8.3 Hz, 1H, H-3), 8.07 (t, J = 7.8 Hz, 1H, H-4), 7.98 (d, J = 5.6 Hz, 1H, H-6), 7.89 (m, 3H, H-4, H-5), 7.36 (d, J = 5.6 Hz, 1H, H-6), 7.32 (m, 2H, H-5), 6.85 (d, J = 8.0 Hz, 2H, Ar-H), 6.59 (d, J = 8.0 Hz, 2H, Ar-H), 3.60 (s, 3H, S(O)CH_3), 2.22 (s, 3H, Ar-CH_3). ^{13}C MNR (CD_3COCD_3): δ 158.1, 158.0, 157.9, 156.7, 155.9, 153.3, 153.2, 149.7, 141.0, 138.6, 138.6, 138.3, 137.9, 137.7, 136.9, 129.2, 127.5, 126.8, 123.8, 123.4, 123.0, 43.0, 20.1.

***cis*-Λ-[Ru(bpy)$_2$(2)Cl]Cl and *cis*-Δ-[Ru(bpy)$_2$(3)Cl]Cl (Minor Diastereomeric Products).** ^{1}H NMR ((CD_3)$_2$CO)): δ 9.65 (d, J = 5.6 Hz, 1H, H-6), 9.40 (d, J = 5.6 Hz, 1H, H-6), 8.77 (d, J = 8.3 Hz, 1H, H-3), 8.66 (d, J = 8.3 Hz, 1H, H-3), 8.64 (d, J = 8.3 Hz, 1H, H-3), 8.61 (d, J = 8.3 Hz, 1H, H-3), 8.35 (t, J = 7.8 Hz, 1H, H-4), 8.19 (t, J = 7.8 Hz, 1H, H-4), 8.13 (d, J = 5.6 Hz, 1H, H-6), 8.06 (m, 2H, H-4), 7.76 (t, J = 5.8 Hz, 1H, H-5), 7.65 (t, J = 5.8 Hz, 1H, H-5), 7.50 (d, J = 7.8 Hz, 2H, Ar-H), 7.44 (d, J = 5.8 Hz, 1H, H-3), 7.38 (m, 2H, H-5), 7.25 (d, J = 7.8 Hz, 2H, Ar-H), 2.75 (s, 3H, S(O)CH_3), 2.39 (s, 3H, Ar-CH_3). ^{13}C NMR (CD_3COCD_3): δ 158.5, 158.1, 157.8, 156.7, 155.7 (2×), 153.6 (2×), 153.1, 149.8, 141.8, 141.5, 138.4, 138.2, 137.6, 137.4, 129.6, 127.6, 126.4, 125.3, 124.2, 124.1, 123.6, 123.2, 43.4, 20.4.

***cis*-Δ-[Ru(dmbpy)$_2$(3)Cl]Cl (7) and *cis*-Λ-[Ru(dmbpy)$_2$(2)Cl]Cl (8).** ^{1}H NMR ($CDCl_3$): δ 10.15 (d, J = 5.6 Hz, 1H, H-6), 9.36 (d, J = 6.0 Hz, 1H, H-6), 8.10 (d, J = 1.2 Hz, 1H, H-3), 8.00 (d, J = 1.2 Hz, 1H, H-3), 7.96 (d, J = 1.2 Hz, 1H, H-3), 7.87 (d, J = 1.2 Hz, 1H, H-3), 7.51 (dd, J = 6.0 Hz, J = 1.2 Hz, 1H, H-5), 7.46 (d, J = 6.0 Hz, 1H, H-6), 7.33 (dd, J = 6.0 Hz, J = 1.2 Hz, 1H, H-5), 7.05 (dd, J = 6.0 Hz, J = 1.2 Hz, 1H, H-5), 7.01 (d, J = 6.0 Hz, 1H, H-6), 6.87 (dd, J = 6.0 Hz, J = 1.2 Hz, 1H, H-5), 6.80 (d, J = 7.6 Hz, 2H, Ar-H), 6.45 (d, J = 7.6 Hz, 2H, Ar-H), 3.59 (s, CH_3), 2.66 (s, CH_3), 2.65 (s, CH_3), 2.43 (s, CH_3), 2.41 (s, CH_3), 2.26 (s, CH_3). ^{13}C NMR ($CDCl_3$): δ 157.3, 155.5, 155.0, 154.9, 151.3, 150.2, 149.3, 149.0, 141.5, 138.0, 129.2, 127.8, 127.6, 127.4, 125.1, 125.0, 124.8, 124.7, 123.9, 123.7, 123.5, 123.3, 122.8, 44.6, 31.5, 30.9, 30.8, 30.2, 21.3.

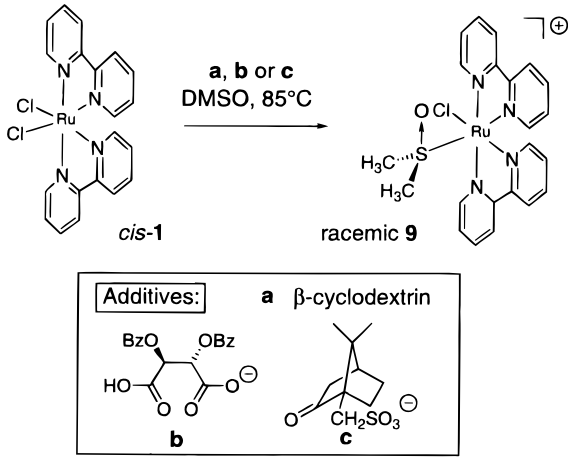
***cis*-Λ-[Ru(dmbpy)$_2$(3)Cl]Cl and *cis*-Δ-[Ru(dmbpy)$_2$(2)Cl]Cl (Minor Diastereomeric Products).** ^{1}H NMR ($CDCl_3$): δ 9.27 (d, J = 5.9 Hz, 1H, H-6), 9.14 (d, J = 5.9 Hz, 1H, H-6), 8.34 (s, 1H, H-3), 8.28 (s, 1H, H-3), 8.15 (s, 1H, H-3), 8.09 (s, 1H, H-3), 7.55 (m, 2H, H-5), 7.42 (d, J = 8.3 Hz, 2H, Ar-H), 7.30 (d, J = 8.3 Hz, 2H, Ar-H), 7.33 (d, J = 5.9 Hz, 1H, H-6), 7.25 (m, 3H, H-5, H-6), 2.70 (s, CH_3), 2.69 (s, CHO_3) 2.56 (s, CH_3), 2.40 (s, CH), 2.40 (s, CH_3), 2.29 (s, CH_3).

Results

Chiral Additives: Ruthenium Bis(bipyridine) Sulfoxide Preparation. It was envisaged that asymmetric induction through the interaction of a chiral complexing agent or counterion might be achieved in the synthesis of ruthenium bis-(bipyridine) sulfoxide complexes. The nucleophilic displacement of one chloride ligand from racemic *cis*- or *trans*-**1** with dimethyl sulfoxide (DMSO) occurs readily in good yield, in both protic and aprotic solvents, and we have shown that this reaction affords racemic products.[23] The mechanism of the displacement of the chloride ligand is reported as being dissociative in nature,[24,25] and a suitable complexing agent might interact with the charged, pentacoordinate species that is formed, hopefully

(23) Hesek, D.; Inoue, Y.; Everitt, S. R. L. *Chem. Lett.* **1999**, 109−110.
(24) Maspero, F.; Ortaggi, *G. Ann. Chim.* **1974**, *64*, 115−117.
(25) Wilkins, R. G. *Kinetics and Mechanism of Reactions of Transition Metal Complexes*; VCH: Weinheim, 1991.

Scheme 2. Chiral Complexing Agents as Additives in the Preparation of *cis*- $[Ru(bpy)_2(DMSO)Cl]^+$

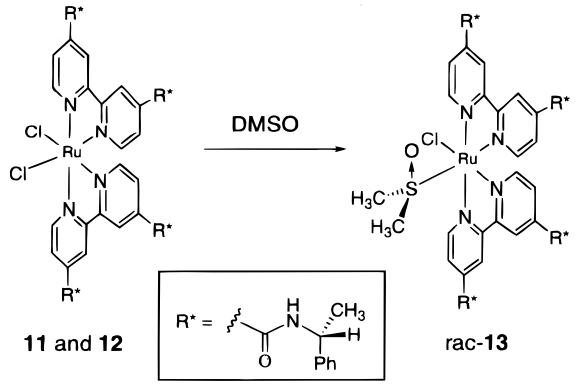


influencing the stereochemistry as the bis(bipyridine) sulfoxide complex forms. Thus, racemic *cis*- or *trans*-$Ru(bpy)_2Cl_2$ (*cis*- or *trans*-**1**) was heated in DMSO containing (*S*)-(+)-camphor-10-sulfonic acid, (−)-*O*,*O*-dibenzoyl-L-tartaric acid, or *β*-cyclodextrin, in a 0.1:1.0 molar ratio with respect to **1**. Although several attempts were made, in each case only racemic mixtures of *cis*-Δ-$[Ru(bpy)_2(DMSO)Cl]Cl$ (**9**) and *cis*-Λ-$[Ru(bpy)_2(DMSO)Cl]Cl$ (**10**) were isolated (Scheme 2). Both **9** and **10** (isolated by chromatographic resolution techniques) were found to be thermally stable under the reaction conditions employed, with no racemization was observed, even upon heating in DMSO at 110 °C for 3−4 h.

Chiral Auxiliaries: Attempts To Prepare Diastereomerically Enriched Bis(bipyridine) Sulfoxides from $Ru(bis(R^*_2$-bipyridine))Cl_2 (R* = 4,4′-bis((*R*)-(+)-α-phenylethylamido)-2,2′-bipyridine). The absolute stereochemistry of ruthenium bis(bipyridine) complexes might be influenced through the introduction of one or several chiral auxiliaries into the ligand architecture of the reagents.[26,27] Thus, a 1:1 mixture of *cis*-Δ-Ru(4,4′-bis((*R*)-(+)-α-phenylethylamido)-2,2′-bipyridine)$_2Cl_2$ (**11**) and *cis*-Λ-Ru(4,4′-bis((*R*)-(+)-α-phenylethylamido)-2,2′-bipyridine)$_2Cl_2$ (**12**) was synthesized. The addition of the bulky auxiliaries gave **11** and **12** an improved solubility in organic solvents, which might also have improved the chances of a successful diastereoselective process, as the usual harsh reaction conditions (refluxing EtOH/AcOH, which might lead to racemization) were not required. Unfortunately, when the conversion of the mixture of **11** and **12** to *cis*-[Ru(4,4′-bis((*R*)-(+)-α-phenylethylamido)-2,2′-bipyridine)$_2$(DMSO)Cl]Cl (**13**) was carried out in hot DMSO, no diastereoselectivity was observed (Scheme 3). This observation led us to conclude that chiral groups in the 4,4′-positions of the bipyridine ligands could not play a part in the steric processes that occur during the formation of **13**. During the course of these investigations the novel complex *cis*-[Ru(4,4′-bis((*R*)-(+)-α-phenylethylamido)-2,2′-bipyridine)$_2$(TMSO)Cl]Cl (**14**) was also synthesized, again with no observed diastereoselectivity.

Asymmetric Synthesis and Characterization of the Novel Bis(bipyridine) Sulfoxides $[Ru(bpy)_2Cl(X)]PF_6$ and $[Ru(dmbpy)_2Cl(X)]PF_6$ (X = (*R*)-(+)- or (*S*)-(−)-Methyl *p*-Tolyl Sulfoxide (2 or 3)). Recently we have described the preparation

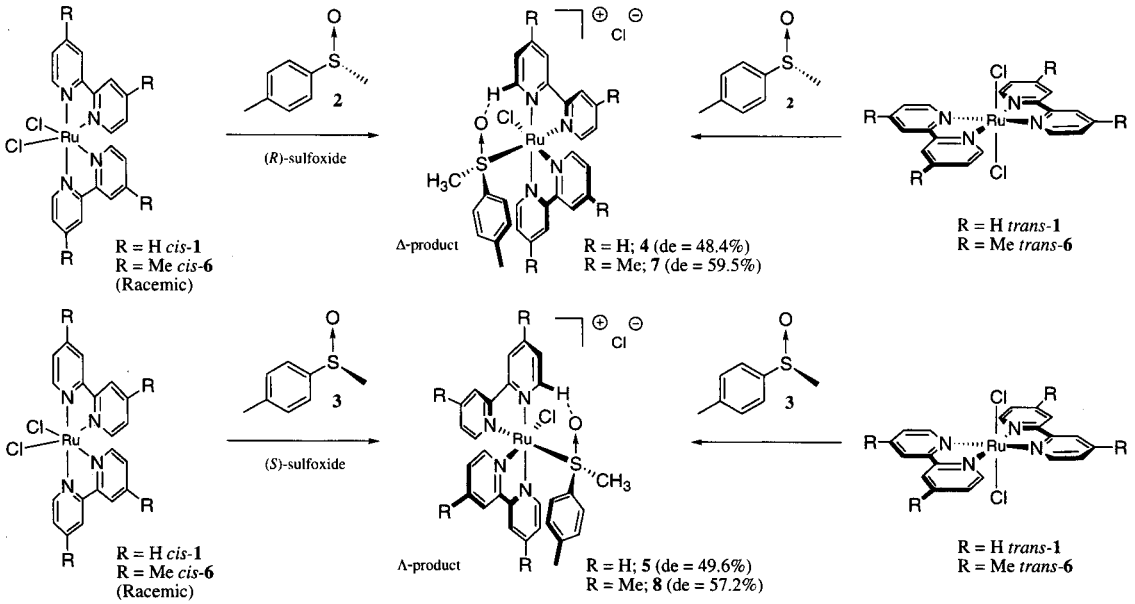
Scheme 3. Chiral Auxiliaries on the bpy Ligands, Used in Attempts To Influence the Approach of a DMSO Nucleophile



and characterization of the novel ruthenium sulfoxide complexes *cis*-$[Ru(bpy)_2(DMSO)Cl]Y$ (**9**) and *cis*-$[Ru(bpy)_2(TMSO)Cl]Y$ (**15**) (where Y = Cl^-, I^-, PF_6^-, or ClO_4^-) using a racemic synthesis.[11] We have proposed that an intramolecular hydrogen bond between the sulfoxide oxygen and the pyridyl α-proton contributes to the high stability of these complexes. Indeed, the stability of these complexes was sufficient to permit the measurement of their circular dichroism (CD) spectra, and the complexes could be stored in dark conditions for periods of several months with no loss of chirality. Evidence for the intramolecular stabilization network was taken from the strong resistance to rotation about the Ru−S bond, as registered in the ^1H NMR spectrum, and DIFNOE experiments, which showed the methyl groups to be in well-defined chemical environments with a difference of 1.1 ppm between the two sharp singlets observed. Support for our proposed structure was also taken from quantum mechanics calculations, and solid-state interatomic distances, which showed a hydrogen bond of ca. 2.3 Å in length.[11] Following from this work, it seemed likely that sulfoxides bearing other substituents (e.g., aryl sulfoxides) would be able to interact with a pyridyl α-proton, [S−O···H] hydrogen bonding, and there is also the possibility of [C−H···π] or [π···π] interactions which could enhance complex stabilty. We perceived that the use of chiral sulfoxides, which could interact in such a way with the bipyridine ligands, would lead to diastereoselectivity in the ruthenium bis(bipyridine) sulfoxides formed. On the basis of the observed properties and reactivity of the achiral sulfoxide complexes, we also expected that optically pure ruthenium bis(bipyridine) sulfoxides could be used as a starting point for the synthesis of a wide variety of enatiomerically enriched ruthenium complexes, and indeed, we have recently described the synthesis of Δ-$[Ru(bpy)_2(dmbpy)]PF_6$ starting from chromatographically resolved Δ-$[Ru(bpy)_2(DMSO)Cl]Cl$ (98.6% ee) which proceeded with almost complete retention of absolute configuration.[28] This synthesis was subsequently applied to the preparation of a tetrakis$[Ru(bpy)_2(bpy)^*]$calix[6]arene derivative, which was formed in excellent yield, with an ee of *ca*. 90%.[29] Clearly the most economical syntheses of Δ- or Λ-ruthenium bis(bipyridine) sulfoxide complexes should not employ a resolution procedure, although to date such methodology has not been reported in the literature. We considered that two possible courses of action were feasible at this stage. The first involved the resolution of the racemic

(26) Ohkubo, K.; Hamada, T.; Ishida, H.; Fukushima, M.; Watanabe, M. *J. Mol. Catal.* **1994**, *89*, L5−L10.
(27) Ohkubo, K.; Hamada, T.; Ishida, H. *J. Chem. Soc., Chem. Commun.* **1993**, 1423−1425.
(28) Hesek, D.; Inoue, Y.; Everitt, S. R. L.; Ishida, H.; Kunieda, M.; Drew, M. G. B. *Chem. Commun.* **1999**, 403−404.
(29) Hesek, D.; Inoue, Y.; Everitt, S. R. L.; Ishida, H.; Kunieda, M.; Drew, M. G. B. *Tetraherdon: Asymmetry* **1998**, *9*, 4089−4097.

Scheme 4. Diastereoselective Synthesis of Ruthenium Bis(bipyridine) Chiral Sulfoxide Complexes and Ruthenium Bis(4,4′-dimethyl-2,2′-bipyridine) Chiral Sulfoxide Complexes



cis-Ru(bpy)$_2$Cl$_2$ (*cis*-**1**) precursor into its Δ- and Λ-isomers, which could then be reacted with an achiral nucleophile to give an enantiomerically enriched product. However, only partial resolution of *cis*-**1** has been reported.[30,33] Thus, a second approach was to react racemic *cis*- or *trans*-**1** with an enantiomerically pure nucleophile to form an enantiomerically enriched ruthenium bis(bipyridine) complex, using the nucleophile as the source of chiral information during the displacement of one of the two chloride ligands. The chiral product should be readily modified to give other ruthenium complexes, preferably affording these with retention of optical activity. On the basis of our work concerning the preparation and resolution of complexes containing achiral sulfoxide ligands,[11,23] and the knowledge that the optically resolved sulfoxide precursor reacts with bipyridine nucleophiles with a conservation of optical activity,[28,29] we decided to investigate the thermal reactions of racemic *cis*- and *trans*-**1** and related compounds with enantiomerically pure sulfoxides.[31] Thus, racemic *cis*- or *trans*-Ru(dmbpy)$_2$Cl$_2$ (**6**) was heated with (*R*)-(+)- or (*S*)-(−)-methyl *p*-tolyl sulfoxide (**2** or **3**) to afford a diastereomerically enhanced product, consisting principally of *cis*-Δ-[Ru(dmbpy)$_2$(**2**)Cl]Cl (**7**) or *cis*-Λ-[Ru(dmbpy)$_2$(**3**)Cl]Cl (**8**), respectively (see Scheme 4). In these reactions, optimization of reaction conditions led to Δ:Λ ratios of *ca*. 79.7:20.3 (59.5% de) for reaction with **2** and of *ca*. 21.4:78.6 (57.2% de) for reaction with **3**, as determined by chiral phase HPLC (see the Experimental Section for details). For both sulfoxide enantiomers, the choice of cis or trans starting material proved irrelevant, as nearly identical yields and de's were observed in each case. This evidence suggests that a common, pentacoordinate ruthenium intermediate is formed during the course of the nucleophilic reaction between sulfoxides and *cis*- or *trans*-**6**, presumably after the dissociation of one of the chloride ligands, although it is also possible that a solvent molecule is weakly bound in the sixth coordination site, following the dissociation process. Minor rearrangements, followed by attack of the chiral sulfoxide, will then lead to the products. However, no further evidence to substantiate these mechanistic claims is currently available.

The reaction of dmbpy-liganded complex **6** with the enantiomerically pure (*R*)-sulfoxide **2** affords *cis*-Δ-[Ru(dmbpy)$_2$(**2**)Cl]Cl (**7**; de = 59.5%) as the major product, and reaction of the same complex with the enantiomerically pure (*S*)-sulfoxide **3** predominantly affords *cis*-Λ-[Ru(dmbpy)$_2$(**3**)Cl]Cl (**8**; de = 57.2%). When Ru(bpy)$_2$Cl$_2$ (**1**) was used as the starting material, the observed de's fell by *ca*. 10% for the reaction with both sulfoxides (**2** afforded *cis*-Δ-[Ru(bpy)$_2$(**2**)Cl]Cl (**4**) as the major product with a de of 48.4%, and **3** afforded *cis*-Λ-[Ru(bpy)$_2$(**3**)Cl]Cl (**5**) with a de of 49.6%). This fall in diastereoselectivity only relates to a difference of 207 cal mol^{-1} (at 120 °C), which is not too significant, although it is possible that the electron-donating ability of the methyl groups in dmbpy might serve to stabilize the intermediate species postulated above. Another factor might be the steric effects of the methyl groups in dmbpy. It is also interesting to note that a change in the reaction temperature and/or prolonged reaction times did not appear to have any effect on the ratio of diastereomers formed in DMF, although the chemical yield of the reaction increased slightly as the reaction time was extended. This may be the result of the low solubility of **1** in DMF. In contrast, if more polar solvents are used (e.g., acetic acid/alcohol mixtures), undesired *O*-bonded products are observed. Even though the diastereoselectivity of the reaction is acceptable in polar/protic solvents (although *ca*. 10% lower de is observed than in cases where polar aprotics are employed), as the reaction proceeds, decomposition of the desired product is observed, ultimately leading to a decrease in the observed de.

NMR Spectroscopy. All pyridine protons in the ruthenium sulfoxide complexes **4**, **5**, **6**, and **8** are nonequivalent on the NMR time scale, confirming that the structures are all C_1-symmetric, thus excluding any possible trans-isomers.[32,33] The

(30) Grover, N.; Gupta, N.; Thorp, H. H. *J. Am. Chem. Soc.* **1992**, *114*, 3390.

(31) The reaction of sulfoxide nucleophiles with both *cis*- and *trans*-Ru(bpy)$_2$Cl$_2$ leads to an identical product, namely, [Ru(dmbpy)$_2$(DMSO)Cl]Cl, and it is probable that the mechanism for the nucleophilic displacement involves a common intermediate for both of these reactions, on the basis of this evidence. Photochemical transformations of both *cis*- and *trans*-**2** and -**7** have been investigated by us, and described in a separate report (see ref 22).

(32) Coe, B. J.; Meyer, T. J.; White, P. S. *Inorg. Chem.* **1993**, *32*, 4012−4020.

(33) Arce Sagüés, J. A.; Gillard, R. D.; Smalley, D. H.; Williams, P. A. *Inorg. Chim. Acta* **1980**, *43*, 211−216.

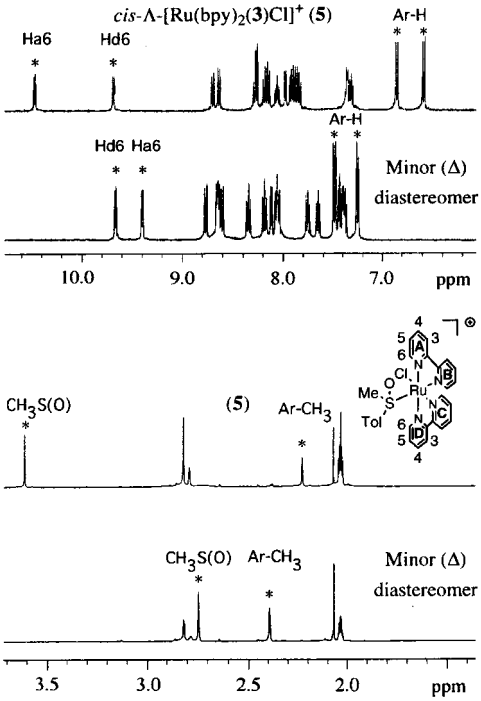


Figure 1. ^{1}H NMR of *cis*-Λ-[Ru(bpy)$_2$(**3**)Cl]$^+$ (**5**) and *cis*-Δ-[Ru(bpy)$_2$(**3**)Cl]$^+$ (minor diastereomer) in $CDCl_3$.

^{1}H NMR spectrum of the diastereomeric pair shown in Figure 1, which also includes a representation of the general labeling used throughout this paper, *cis*-Λ-[Ru(bpy)$_2$(**3**)Cl]PF_6 (**5**) and *cis*-Δ-[Ru(bpy)$_2$(**3**)Cl]PF_6 (minor isomer), shows an 18-signal pattern in the low-field region from $\delta = 6.5$ ppm to δ 10.6 ppm, a feature that is characteristic of diastereotopic bpy protons. For both major and minor products, the Ha6 protons are observed at similar chemical shifts, these being 9.65 and 9.70 ppm, respectively, suggesting that both protons experience a similar chemical environment, which is most likely to be a [C−H···O] hydrogen bond with the sulfoxide ligand. However, larger differences are observed in the chemical shifts of the Hd6 protons. For the major diastereomer, Hd6 is observed at 10.48 ppm. In the minor product, the tolyl moiety does not $\pi-\pi$ stack with the C and D rings, but instead projects into the space on the opposite side of the A/B ring plane. This places the Hd6 proton into the shielding cone of the tolyl moiety, thus shifting it strongly upfield to 9.40 ppm. In this diastereomer, the two doublet resonances of the tolyl protons ($\delta = 7.50$ and 7.25) appear somewhat closer to the resonances of the starting (*S*)-sulfoxide **3** at $\delta = 7.57$ and 7.32 ppm. Conversely, the ^{1}H NMR spectrum of the major diastereomer **5** shows an upfield shift of the two doublet resonances corresponding to aromatic protons ($\delta = 6.85$ and 6.59 ppm), which are attributed to the tolyl group in a $\pi-\pi$ stacking environment (see Figure 1).

Additionally, comparison of the methyl group's singlet resonances in the aliphatic region serves to highlight differences in configuration of the Λ- and Δ-isomers. Thus, the sulfoxide methyl group of the Δ-isomer has its resonance shifted significantly upfield ($\delta = 2.75$) with respect to the corresponding methyl resonance in the Λ-isomer **5** ($\delta = 3.60$), while smaller shift differences are observed for the tolyl methyl singlets ($\delta = 2.39$) and in the Δ-isomer ($\delta = 2.22$). These chemical shift changes imply that the preferred conformation of the Λ-isomer **5** places the tolyl moiety in close proximity to one of the bipyridine units, overlapping with the bpy D-ring, giving rise to $\pi-\pi$ interactions, which may stabilize this arrangement, and it appears that a combination of [C−H···O] hydrogen bonding and $\pi-\pi$ interactions are responsible for the diastereomeric excess observed in this system.

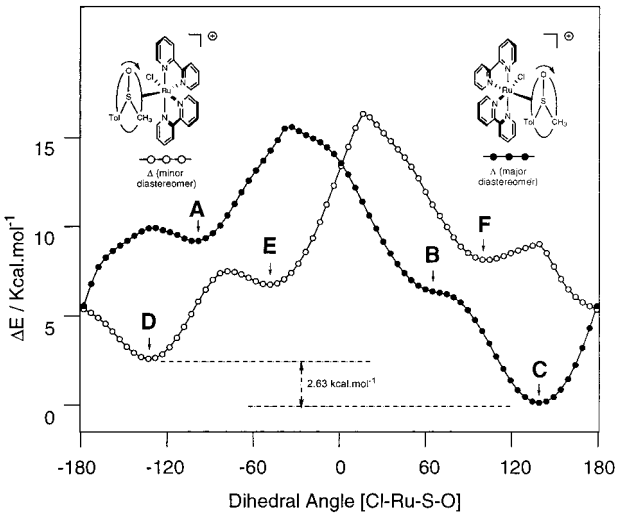


Figure 2. Energy profiles for the molecular mechanics calculations for *cis*-Λ-[Ru(bpy)$_2$(**3**)Cl]$^+$ (**5**) and *cis*-Δ-[Ru(bpy)$_2$(**3**)Cl]$^+$. For atom types and numbering, see the Supporting Information.

Molecular Modeling of *cis*-Λ-[Ru(bpy)$_2$(3)Cl]$^+$ (5) and *cis*-Δ-[Ru(bpy)$_2$(3)Cl]$^+$. Molecular mechanics calculations on *cis*-Λ-[Ru(bpy)$_2$(**3**)Cl]$^+$ (**5**) and *cis*-Δ-[Ru(bpy)$_2$(**3**)Cl]$^+$ (minor isomer) using a grid scan for the Cl−Ru−S−O dihedral angle were carried out using the force field described by Gerimia et al.,[21] which included the usual molecular mechanics bonded and nonbonded interaction terms, and used atomic charges generated by the Cerius^2/ZINDO semiempirical quantum mechanics program (see the Experimental Section). The atom types and atomic charges used are given in the Supporting Information, as are the set of $\epsilon = 0-20$ energy profiles. The dielectric constant value (ϵ) was initially set at $\epsilon = 1.0$, which is the vacuum value, and increased in a stepwise fashion to $\epsilon = 20$. At $\epsilon = 1$, the calculation shows a local minimum at −100° (conformer A, relative energy +9.82 kcal mol^{-1}), a shoulder at 55° (conformer B, relative energy +6.69 kcal mol^{-1}), and a strong global minimum at 140° (conformer C) for *cis*-Λ-[Ru(bpy)$_2$(**3**)Cl]$^+$ (**5**) (see Figures 2 and 3). In contrast, *cis*-Δ-[Ru(bpy)$_2$(**3**)Cl]$^+$ is calculated to be significantly higher in energy, with a weak local minimum at 100° (conformer F, relative energy +8.72 kcal mol^{-1}) and minima at −135° (conformer D, relative energy +2.63 kcal mol^{-1}) and −50° (conformer E, relative energy +7.16 kcal mol^{-1}). The global minimum for the major diastereomer **5** represents a conformation where a strong overlap of the tolyl ring and one of the bpy C- or D-rings is possible, as well as the possible formation of an [O···H−C] hydrogen bond between the sulfoxide oxygen and the proton at position 6 of the A-ring (Ha6), highlighting the importance of these intramolecular interactions; this occurs when the oxygen is located in a position where there should not be a high contribution from the repulsion between the sulfoxide oxygen and the chloride. For the Λ-isomer, the barrier to rotation is prohibitively high (16.79 kcal mol^{-1}). When the aromatic groups are in an overlapping conformation (Λ-isomer), the oxygen projects toward Ha6, but in this case, it lies in closer proximity to the chloride, with which there is a repulsive electrostatic interaction. This situation corresponds to the local minimum at −40°. At higher ϵ values ($\epsilon > 5$), the energy profile for the Λ-isomer is similar in shape to the $\epsilon = 1$ curve, although the barrier to rotation becomes considerably lower. However, as the ϵ values increase, conformer E becomes more stable than

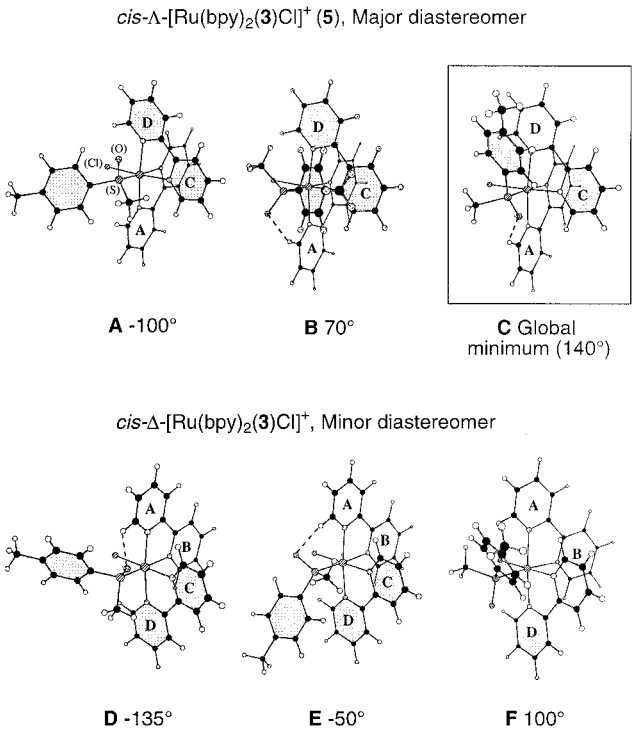


Figure 3. Conformers A−F represent selected positions in the energy profiles obtained from the molecular mechanics calculations for *cis*-Λ-[Ru(bpy)$_2$(**3**)Cl]$^+$ (**5**) and *cis*-Δ-[Ru(bpy)$_2$(**3**)Cl]$^+$.

conformer D (Δ-isomer). The Δ-isomer cannot attain a conformation where both a $\pi-\pi$ overlap and a [S−O···Ha6] hydrogen bond are formed without strong repulsive interactions between the O and Cl atoms (see conformer E), which results in a higher energy profile. These modeling studies are in full agreement with experimental results, which also show that *cis*-Λ-[Ru(bpy)$_2$(**3**)Cl]$^+$ (**5**) is more stable than *cis*-Δ-[Ru(bpy)$_2$(**3**)Cl]$^+$ in low dielectric solvents.

Circular Dichroism Spectral Characterization. The chiral sulfoxide complexes **4**, **5**, **6**, and **8** can be completely resolved using chiral HPLC techniques. The absolute configurations around the metal centers are assigned from the characteristic Cotton effects of the LC bands (at *ca*. 280 nm) of the CD spectra. Previous investigations involving [Ru(bpy)$_2$(DMSO)Cl]PF$_6$ allowed us to compare the X-ray crystal structure with the CD spectra of the resolved material, and thus assign stereochemistry to the CD spectra.[28,29] In these types of complexes, the Cotton effects at *ca*. 440 nm which correspond to the MLCT band have the same sign as the LC band (which arises as a result of the exciton coupling between the two long-axis polarized transitions occurring in the 2,2′-bipyridine ligands). According to exciton theory, we are able to assign Λ- and Δ-configurations to the major and minor isomers from the reaction of (*S*)-(−)-methyl *p*-tolyl sulfoxide (**3**) with racemic Ru(bpy)$_2$Cl$_2$. The minor diastereomer shows a negative Cotton effect for the MLCT band at 420 nm, and for the LC band at 290 nm, and the major diastereomer **5** shows a spectrum with the opposite profile, as shown in Figure 4. The CD spectra of *cis*-Δ-[Ru(dmbpy)$_2$(**2**)Cl]Cl (**7**) and the minor diastereomer *cis*-Λ-[Ru(dmbpy)$_2$(**2**)Cl]Cl are also shown.

Because these isomers have two types of chirality, namely, Δ or Λ at the metal center and *R* or *S* at the chiral sulfoxide, *cis*-Δ-[Ru(bpy)$_2$(**2**)Cl]$^+$ (**4**) (formed from the (*R*)-(+)-sulfoxide starting material) gives a CD spectrum which is a mirror image of *cis*-Λ-[Ru(bpy)$_2$(**3**)Cl]$^+$ (**5**) (formed from the (*S*)-(−)-sulfoxide starting material). A similar relationship is also observed between *cis*-Δ-[Ru(dmbpy)$_2$(**2**)Cl]PF$_6$ (**7**) and *cis*-Λ-[Ru(dmbpy)$_2$(**3**)Cl]PF$_6$ (**8**) which have essentially the same CD spectra as the previous pair, although small differences can be observed, especially around the MC bands. These differences indicate that the LC and MLCT regions of the CD spectra are determined primarily by the metal center configuration (Δ or Λ), whereas the LC band region is determined by the chiral circumstances resulting from a combination of Δ (or Λ) and *R* (or *S*) configuration of the sulfoxide ligand. The CD spectra of the four minor diastereomers are also displayed in Figure 4, along with the UV/vis spectra of a diastereomeric pair of bpy-liganded complexes, *cis*-Δ-[Ru(bpy)$_2$(**2**)Cl]PF$_6$ (**4**) and *cis*-Λ-[Ru(bpy)$_2$(**2**)Cl]PF$_6$, and a diastereomeric pair of dmbpy-liganded complexes, *cis*-Δ-[Ru(dmbpy)$_2$(**2**)Cl]PF$_6$ (**7**) and *cis*-Λ-[Ru(dmbpy)$_2$(**2**)Cl]PF$_6$.

Discussion

The reaction of *cis*- or *trans*-Ru(bpy)$_2$Cl$_2$ (*cis*- or *trans*-**1**) with either (*R*)-(+)- or (*S*)-(−)-methyl *p*-tolyl sulfoxide (**2** or **3**) leads to the diastereoselective formation of the novel ruthenium bis(bipyridine) complex *cis*-Δ-[Ru(bpy)$_2$(**2**)Cl]Cl (**4**) (48.4% de) or *cis*-Λ-[Ru(bpy)$_2$(**3**)Cl]Cl (**5**) (49.6% de), respectively. *cis*- or *trans*-Ru(dmbpy)$_2$Cl$_2$ (*cis*- or *trans*-**6**) also reacts with **2** or **3**, leading to the diastereoselective formation of *cis*-Δ-[Ru(dmbpy)$_2$(**2**)Cl]Cl (**7**) (59.5% de) or *cis*-Λ-[Ru(dmbpy)$_2$(**3**)Cl]Cl (**8**) (57.2% de), respectively. The good diastereoselectivity of these reactions is governed solely by the chirality of the sulfoxide nucleophile, and this paper represents the first time that such a diastereoselective synthesis has been reported. We have established that the reaction of DMSO with *cis*- or *trans*-**1** leads to products which are readily separated by chiral HPLC techniques, and are stable upon heating in DMSO for several hours, thus demonstrating the irreversible nature of this reaction. It is likely that the approach of the chiral sulfoxide nucleophile toward a pentacoordinated or solvent-ligated intermediate could theoretically occur with equal probability along either of two pathways, affording a racemic product. However, intermolecular attractions in the transition state, which subsequently go on to become strong intramolecular interactions in the product, appear to influence the preferred direction of approach. One approach will lead to the formation of the Ru−S σ-bond, and *either* a [S−O···Ha6] hydrogen bond *or* a $\pi-\pi$ interaction. However, the other approach gives rise to *all three* bonding interactions, and it is this direction of attack which leads to the major diastereomer. This implies that the cooperative intramolecular interactions that contribute to the stability of this type of ruthenium bis(bipyridine) sulfoxide complex are fundamental to the diastereoselectivity observed. It is likely, therefore, that an alteration of the sulfoxide that improves the strength of the intramolecular interactions should allow us to carry out syntheses with a higher degree of diastereoselectivity.

Conclusions. Several attempts have been made to create a new asymmetric synthetic procedure for the preparation of ruthenium bis(bipyridine) complexes. Such a process has not previously been observed in the literature for *cis*- or *trans*-Ru(bpy)$_2$Cl$_2$, or related derivatives, except von Zelewsky's chiragen ligand work which uses a highly preorganized tetradentate ligand that bears six chiral centers, rendering it significantly different in nature from our work. The introduction of chiral complexing agents into the reaction media of a normally racemic reaction led to products with no optical activity, indicating the absence of any controlling supramolecular interactions at the potentially stereodefining step of sulfoxide ligation. Likewise, the use of a chiral auxiliary on the bpy ligands of the starting material also

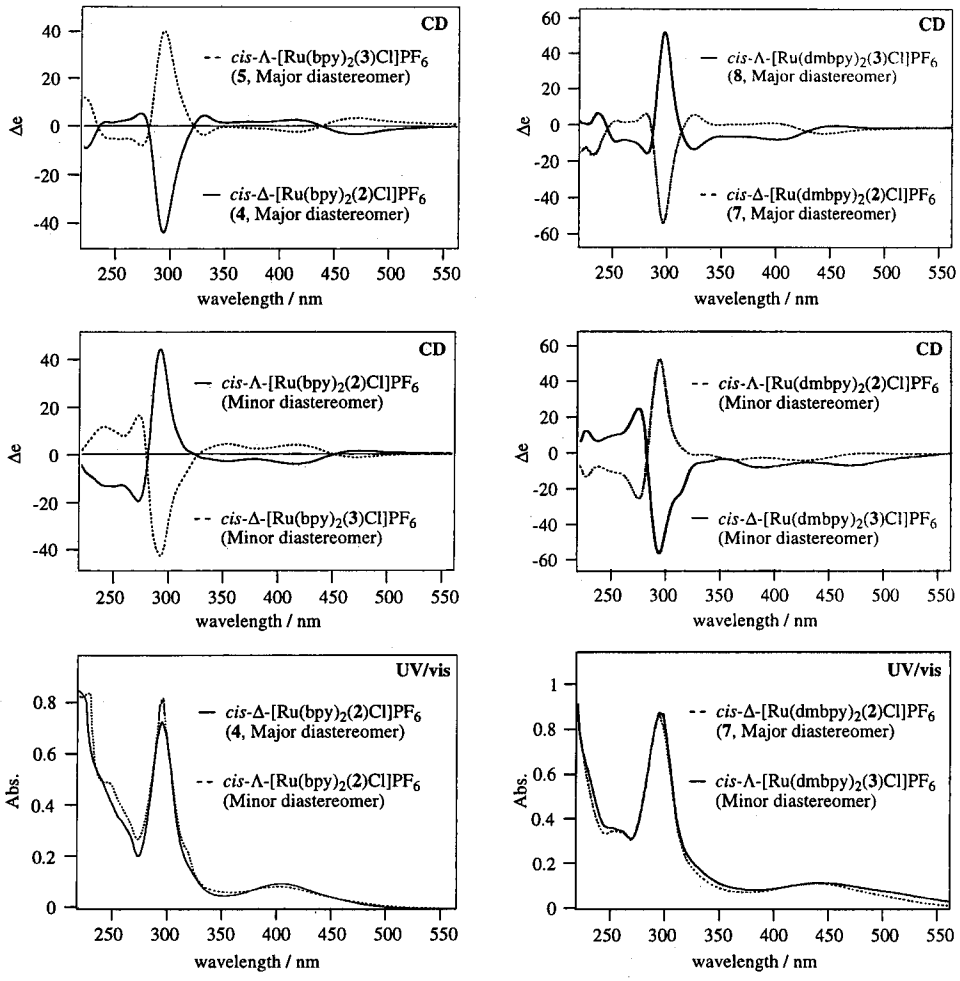


Figure 4. CD and UV/vis spectra of the ruthenium bis(bipyridine) chiral sulfoxide complexes and ruthenium bis(4,4′-dimethyl-2,2′-bipyridine) chiral sulfoxide complexes.

failed to generate any diastereomeric enrichment. However, the reaction of a chiral sulfoxide with racemic *cis*- or *trans*-Ru(bpy)$_2$Cl$_2$ (*cis*- or *trans*-**1**), or with racemic *cis*- or *trans*-Ru(dmbpy)$_2$Cl$_2$ (*cis*- or *trans*-**6**), led to ruthenium bis(bipyridine) sulfoxide complexes and ruthenium bis(4,4′-dimethyl-2,2′-bipyridine) sulfoxide complexes with a high level of asymmetric induction. This new concept in the synthesis of optically active ruthenium bis(bipyridine) complexes uses an asymmetric induction which is found to be based solely on the choice of the chiral sulfoxide starting material, and indeed, de's as high as 59.5% were observed. Although this represents a modest chiral selectivity, this new approach toward the synthesis of optically active octahedral complexes should serve as the basis for a fresh approach to a long established area of research interest and, ideally, challenge inorganic chemists to develope new and exciting methods for the asymmetric synthesis of high optical purity octahedral ruthenium bipyridine complexes. The chiral ruthenium bis(bipyridine) sulfoxide complexes were studied, and their preferred solution-state conformations postulated on the basis of NMR studies, comparison with the X-ray crystal structures of related complexes,[11,28] and molecular modeling experiments. The sulfoxide complexes were found to be stable enough to allow isolation, analysis, and storage, as long as prolonged exposure to light was prevented. Descriptions of the transformation of these chiral sulfoxide complexes into a variety of optically active ruthenium tris(bipyridines), and the diastereoselective, photoinduced replacement of the chiral sulfoxide ligand, will be the subject of further reports from our laboratory.

Acknowledgment. Helpful discussions with Professor N. Harada (Tohoku University, Sendai, Japan) concerning the CD spectra contained in this paper are gratefully acknowledged.

Supporting Information Available: Selected ^{1}H, ^{13}C, and 2D H−H NMR spectra and HPLC data for the chiral sulfoxide-containing complexes **4**, **5**, **6**, and **8**, etc., selected NMR/HPLC data for the chiral complexing agent and chiral auxiliary work, and the atom types and charges used in the molecular modeling studies. This material is available free of charge via the Internet at http://pubs.acs.org.

IC991059D