Novel Synthetic Routes to Several New, Differentially Substituted Ruthenium Tris(4,4′-disubstituted-2,2-bipyridine) Complexes

Dusan Hesek,[†] Yoshihisa Inoue,*[,†] Simon R. L. Everitt,[†] Hitoshi Ishida,[†] Mieko Kunieda,[†] and Michael G. B. Drew[‡]

Inoue Photochirogenesis Project, ERATO, JST, 4-6-3 Kamishinden, Toyonaka 560-0085, Japan, and Department of Chemistry, The University of Reading, Whiteknights, Reading RG6 6AD, U.K.

Received July 15, 1999

The stepwise synthesis of several novel Ru(tris(pp)) complexes (pp = 4,4′-disubstituted-2,2′-bipyridine; substituent = H, Me, chiral ester, or chiral amide) is described, where the pp ligands may be the same, or different, in each complex. All of the complexes detailed have been resolved into their pure Δ- and Λ-enantiomers or diastereomers. The complexes, which are prepared starting from $RuCl_3$, contain novel ligand architectures, with a range of chiral esters and amides attached to the 4,4′-positions of the bpy ligands. It was postulated that these chiral groups would be capable of inducing chirality at the metal center, but our investigations have shown this not to be the case, and in all reactions completely racemic products were formed. Resolution by chiral HPLC, and the subsequent characterization of the products through NMR, UV−vis, and circular dichroism (CD) spectroscopy, has been carried out; the characteristics of the CD spectra have been discussed with respect to the electron-donating/withdrawing ability of the groups at the 4,4′-positions. The X-ray crystal structure of the optically pure complex Λ-[Ru(dmbpy)$_2$(4,4′-bis((*R*)-(+)-α-phenylethylamido)-2,2′-bipyridine)]·2PF_6·2$CHCl_3$ was obtained and solved using direct methods. This result, in conjunction with the CD spectra, enabled the complete and unambiguous assignment of the stereocenters of all of the novel Ru(tris(bpy)) complexes prepared in this investigation.

Introduction

Ruthenium tris(polypyridyl) complexes represent interesting possibilities as components in photochemical and electrochemical molecular devices[1−3] and potential chemotherapeutics,[4] and the preparations of a great number of racemic complexes have been reported in the literature.[5−7] More and more frequently, enantio- or diastereomerically pure complexes are prepared, usually through resolution techniques, such as cocrystallization[8,9] or chromatography procedures.[8,10] In more special circumstances diastereomerically enhanced or pure complexes can also be prepared in a diastereoselective manner through the use of chiral reagents, such as Keene's optically resolved *cis*-[Ru(bpy)$_2$(CO)$_2$]$^{2+}$ complex (bpy = 2,2′-bipyridine),[5,8,11] Hua and von Zelewsky's *cis*-[Ru(bpy)$_2$(py)$_2$]$^{2+}$,[12,13] and our recently described *cis*-[Ru(bpy)$_2$(dmso)Cl]$^+$ reagent,[14−16] all of which react with bpy nucleophiles with excellent levels of stereoretention.

The sequential synthesis of complexes which contain nonidentical bipyridyl-derived architectures has been reported by several groups,[17−21] and a range of interesting complexes has been prepared. However, in all of these examples, only relatively simple ligands were employed without attaching chiral auxiliary substituents in the bipyridine rings. Our interest in studying these reactions was stimulated by Ohkubo and co-workers, who reported ligand-bearing chiral groups symmetrically attached to the ruthenium tris(4,4′-disubstituted-2,2′-bipyridine) position.[22−25] When complexes with chiral ligands are prepared, it is essential that these are prepared and handled in a controlled

* To whom correspondence should be addressed. Phone: +81-6-879-7920. Fax: +81-6-879-7923. E-mail: inoue@chem.eng.osaka-u.ac.jp.
† ERATO, JST.
‡ The University of Reading.

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10.1021/ic990840i CCC: $19.00
Published on Web 01/04/2000

manner, as (partial) racemization of each chiral center will result in a large increase in the number of products formed, rendering them very difficult, if not impossible, to separate using current resolution methods.

In this paper we describe a new set of reaction conditions that can be applied to the efficient, "potentially one-pot" synthesis of several novel Ru[(pp)(pp′)(pp″)]·2X complexes (pp, pp′, and pp″ = 4,4′-disubstituted-2,2′-bipyridine, with H, methyl, and chiral ester or amide substituents; X = Cl, PF_6), where all of the chiral centers in the 4,4′-positions maintain their integrity throughout the course of the synthesis. The isolated products are thus a 1:1 mixture of the two Δ- and Λ-isomers of the complex with chloride counterions (see the Experimental Section), which are readily resolved into their enantio- or diastereopure forms using chiral HPLC, during which counterion exchange for the PF_6 anion occurred. The separated diastereomerically pure complexes were also characterized by ^{1}H and ^{13}C NMR spectroscopy. It was also possible to isolate some of the intermediate Ru(bis(pp)) complexes prepared using this synthetic strategy. The selectivity of the new method is such that we have been able to produce complexes where all of the ligands are the same, i.e., pp = pp′ = pp″ (through the use of previously developed methods),[7] where one ligand is different (i.e., pp = pp′ ≠ pp″) and where all ligands are different (i.e., pp ≠ pp′ ≠ pp″). These represent processes of increasing synthetic complexity.

The groups that have been attached in the 4,4′-positions are derived from chiral alcohols or chiral amines, and thus we have been able to investigate the effect of multiple chiral centers on the chirality of the metal center as it forms, and their effect upon the chiroptical properties of the complexes. All of the compounds described in the study have been completely resolved into their enantiomer/diastereomer pairs using chiral HPLC techniques, and the circular dichroism (CD) spectra of the corresponding PF_6 salts have been recorded. The types of complexes produced by us have been demonstrated to have interesting spectroscopic properties, and we have observed that by a careful choice of ligand architecture it will be possible to tune these properties, thus permitting the development of specific wavelength photoexcitable complexes, which will be vital for the development of molecular electronic devices, among other things. We have used this exceptional number of resolved complexes to carefully describe the CD spectra, and to develop an empirical rule to aid assignment of the ligand stereochemistry. This understanding is essential if there is to be a development of further synthetic methodology that will allow the stereoselective synthesis of these types of complexes. The X-ray crystal structure has also been obtained for one of the complexes, and the presence of an auxiliary of known chirality has enabled the unambiguous determination of the chirality at the metal center. This information, in conjunction with CD data, permitted the complete stereochemical assignment of all of the complexes in this study.

Experimental Section

Physical Measurements. 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. Optical resolution 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 mmi.d. × 250 mm). A CH_3CN/0.1 M $NaPF_6$(aq) eluent, with a flow rate of 3 mL min^{-1}, was used. 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 mmi.d. × 250 mm), an HPLC pump, PU-980, a three-line Degasser, DG-980-50, a UV−vis detector, UV-970, and a column oven, 860-CO. The eluent (CH_3CN0.1 M $NaPF_6$(aq)) flow rate was 0.4 mL min^{-1}, and the chromatograph was monitored at 292 nm and recorded with a JASCO integrator, 807-IT. 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 spectrometry and elemental analysis.

NMR Spectroscopy. ^{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 internal standard tetramethylsilane (TMS, 0.00 ppm) for ^{1}H NMR and the solvent reference for ^{13}C NMR.

Crystallographic Measurements. Data collection for X-ray analysis was carried out on compound **Λ-17** using a Rigaku AFC7R diffractometer with filtered Mo Kα radiation and a rotating anode generator. A total of 7405 independent reflections were collected using the ω scan technique, and the structure was solved using direct methods. The non-hydrogen atoms in the cation were refined with anisotropic thermal parameters. Hydrogen atoms were added in geometric positions on the cation and given thermal parameters equivalent to 1.2 times those of the atom to which they were bonded. One of the two PF_6^- anions was disordered. Two sets of octahedral fluorine atoms were refined with occupation factors x and $1 - x$, and x refined to 0.46(1). In the disordered anion the phosphorus atoms were refined anisotropically and the fluorine atoms isotropically. In the ordered anion all atoms were refined anisotropically. Two $CHCl_3$ solvent molecules were located, and the chlorine atoms were refined anisotropically. The dimensions of the disordered anion and the solvent molecules were constrained during the refinement. The absolute stereochemistry of the structure in the noncentrosymmetric $P2_1$ space group was assigned from the known chirality of the substituents. The structure was refined on F^2 to convergence using the Shelxl program.[26] The final R indices [$I > 2\sigma(I)$] were, for 5160 reflections, R1 = 0.0627 and wR2 = 0.1696 and, for all data, R1 = 0.1092 and wR2 = 0.2007. The largest peak and hole in the final difference Fourier map were 1.122 and −0.631 e·Å^{-3}.

Data collection for X-ray analysis of Ru(mono(bpy)) intermediate, [Ru(pp)Cl_3·$NCCH_3$], was carried out using a Rigaku AFC7R diffractometer with filtered Mo Kα radiation and a rotating anode generator. A total of 3618 independent reflections were collected using the ω scan technique. The structure was solved using direct methods. The non-hydrogen atoms in the cation were refined with anisotropic thermal parameters. Hydrogen atoms were added in geometric positions on the cation and given thermal parameters equivalent to 1.2 times those of the atom to which they were bonded. The structure was refined on F^2 to convergence using the Shelxl program.[26] The final R indices [$I > 2\sigma(I)$] were, for 2679 reflections R1 = 0.0356 and wR2 = 0.1065 and, for all data, R1 = 0.0447 and wR2 = 0.1185. The largest peak and hole in the final difference Fourier map were 1.113 and −1.053 e·Å^{-3}.

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. The ligands bpy and dmbpy were obtained as reagent grade materials from Aldrich Chemical Co. Ltd. and were used without further purification.

Sambpy (4,4′-bis((*S*)-(+)-α-phenylethylamido)-2,2′-bipyridine) (3) and Rambpy (4,4′-bis((*R*)-(−)-α-phenylethylamido)-2,2′-bipyridine) (4) (see Chart 1) were prepared by quenching 4,4′-bis(carbonyl chloride)-2,2′-bipyridine (prepared from the commercially available

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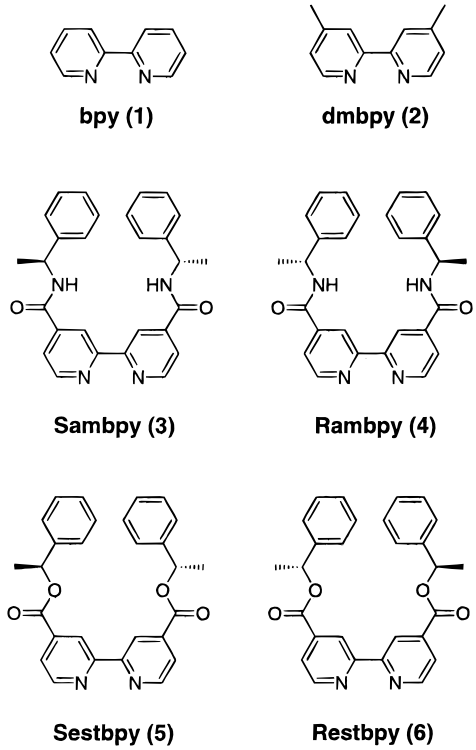
Chart 1



diacid by heating in $SOCl_2$ for 24 h, before removal of the excess $SOCl_2$ under reduced pressure) with the enantiomerically pure α-methylbenzylamine. This led to Sambpy (85% yield from the diacid) and Rambpy (90% yield from the diacid) which were isolated as a white solid. Analytical data for **3** are as follows: ^{1}H NMR ($(CD_3)_2SO$) δ 9.31 (d, J = 8.0 Hz, 1H, NH), 8.86 (d, J = 7.9 Hz, 1H, py-H5), 8.81 (s, 1H, py-H3), 7.88 (d, 1H, py-H6), 7.41 (d, J = 8.0 Hz, 4H, Ph-H2, Ph-H6), 7.34 (t, J = 7.6 Hz, 4H, Ph-H3, Ph-H5), 7.24 (t, J = 7.2 Hz, 2H, Ph-H4), 5.21 (m, 2H, α-H), 1.51 (d, J = 7.2 Hz, 6H, α-CH_3); ^{13}C NMR ($(CD_3)_2SO$) δ 163.9, 155.4, 149.9, 144.3, 142.9, 128.3, 128.3, 126.7, 126.1, 122.1, 118.3, 48.7, 21.9.

Sestbpy (4,4′-bis((*S*)-(+)-α-phenylethyloxycarbonyl)-2,2′-bipyridine) (5) and Restbpy (4,4′-bis((*R*)-(−)-α-phenylethyloxycarbonyl)-2,2′-bipyridine) (6) (see Chart 1) were prepared by quenching 4,4′-bis(carbonyl chloride)-2,2′-bipyridine with the enantiomerically pure α-methylbenzyl alcohol. This led to Sestbpy (75% yield from the diacid) and Restbpy (80% yield from the diacid) which were isolated as colorless oils. Analytical data for **5** are as follows: ^{1}H NMR ($CDCl_3$) δ 8.97 (s, 2H, py-H3), 8.85 (d, 2H, J = 4.1 Hz, py-H5), 7.92 (d, 2H, J = 4.01 Hz, py-H6), 7.48 (d, J = 8.0 Hz, 4H, Ph-H2, Ph-H6), 7.39 (t, J = 7.9 Hz, 4H, Ph-H3, Ph-H5), 7.33 (t, J = 6.1 Hz, 2H, Ph-H4), 6.20 (m, 2H, α-H), 1.731 (d, J = 7.2 Hz, 6H, α-CH_3); ^{13}C NMR ($CDCl_3$) δ 164.4, 156.6, 150.1, 141.0, 138.9, 128.6, 128.2, 126.2, 123.7, 120.6, 74.1, 22.2.

***cis*-Ru(Sambpy)$_2$Cl$_2$ (7).** Ruthenium(III) chloride hydrate (0.5 g, 2.0 mmol) dissolved in dry DMF (35 mL) was treated with an excess of anhydrous LiCl (0.55 g, 13 mmol) to give a suspension which was stirred for 5 min at 70 °C. Sambpy (**3**) (1.8 g, 4.0 mmol) was added to this solution, and the mixture was stirred for 12 h at 70 °C, under a nitrogen atmosphere. The slurry was allowed to cool and then poured into rapidly stirred ether (300 mL). The precipitate was isolated by low-pressure filtration and rinsed with cold 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 **7** in 55% yield: ^{1}H NMR (CD_3CN) δ 10.03 (m, 2H, NH), 9.50 (m, 2H, NH), 9.27 (d, J = 5.6 Hz, 2H, 6-H), 9.22 (s, 2H, 3-H), 9.05 (s, 2H, 3-H), 8.21 (d, J = 6 Hz, 2H, 6-H), 7.67 (d, J = 6 Hz, 2H, 5-H), 7.48 (d, J = 6.8 Hz, 4H, Ar-H), 7.53 (d, J = 5.6 Hz, 2H, 5-H), 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. Anal. Calcd for $C_{56}H_{52}Cl_2N_8O_4Ru\cdot4H_2O$ (1145.2): C, 58.73; H, 5.28; N, 9.78. Found: C, 58.66; H, 5.01; N, 9.88.

General Procedure for the Preparation of [Ru(pp)$_3$](Cl)$_2$. The complexes [Ru(Sambpy)$_3$](Cl)$_2$ (**8**) and [Ru(Rambpy)$_3$](Cl)$_2$ (**9**) were prepared using standard methodology for the preparation of Ru(tris-(pp)) complexes, by dissolving ruthenium(III) chloride hydrate and 3 equiv of the appropriate ligand (i.e., **3** or **4**) in methanol/acetic acid (4:1) for 12 h. Data for **8** and **9** were found to agree with those reproted in the literature.[22] [Ru(Sambpy)$_3$](Cl)$_2$ (**8**) and [Ru(Rambpy)$_3$](Cl)$_2$ (**9**): yield 66−70% and 75−77%, respectively. Data for **9**: ^{1}H NMR ($CDCl_3$) δ 8.96 (s, 6H), 8.86 (d, J = 5.2 Hz, 6H), 7.98 (m, 6H), 7.48−7.25 (m, 36H), 6.20 (q, J = 6.4 Hz, 6H), 1.73 (m, 18H); ^{13}C NMR (CD_3CN) δ 163.1, 158.0, 153.4, 153.3, 144.8, 144.0, 129.5, 129.0, 128.7, 128.5, 128.2, 127.2, 126.4, 126.3, 123.4, 51.3, 51.2, 22.3, 22.2. Anal. Calcd for **9** ($C_{84}H_{78}Cl_2N_{12}O_6Ru\cdot6H_2O$) (1631.7): C, 61.83; H, 5.56; N, 10.30. Found: C, 61.89; H, 5.40; N, 10.19.

General Procedure for the Preparation of [Ru(pp)(pp′)$_2$](Cl)$_2$. The complexes [Ru(Sambpy)$_2$(bpy)](Cl)$_2$ (**10**), [Ru(Rambpy)$_2$(bpy)](Cl)$_2$ (**11**), [Ru(bpy)$_2$(Sambpy)](Cl)$_2$ (**12**), [Ru(bpy)$_2$(Rambpy)](Cl)$_2$ (**13**), [Ru(Sambpy)$_2$(dmbpy)](Cl)$_2$ (**14**), [Ru(Rambpy)$_2$(dmbpy)](Cl)$_2$ (**15**), [Ru(dmbpy)$_2$(Sambpy)](Cl)$_2$ (**16**), [Ru(dmbpy)$_2$(Rambpy)](Cl)$_2$ (**17**), [Ru(Sambpy)$_2$(Sestbpy)](Cl)$_2$ (**18**), [Ru(Rambpy)$_2$(Restbpy)](Cl)$_2$ (**19**), [Ru(Sestbpy)$_2$(Sambpy)](Cl)$_2$ (**20**), [Ru(Restbpy)$_2$(Rambpy)](Cl)$_2$ (**21**), [Ru(Sestbpy)$_2$(Rambpy)](Cl)$_2$ (**22**), and [Ru(dmbpy)$_2$(Sestbpy)](Cl)$_2$ (**23**) were prepared according to the following procedure, described for **10**. Ru(Sambpy)$_2$Cl$_2$ (**7**), prepared according to the method described above, was not isolated from the crude reaction mixture, but used directly after the DMF was removed in vacuo. A solution of bpy (**1**) (1 equiv) was dissolved in methanol and added to the residue of **7** and the mixture heated to reflux for 12 h, before being cooled to room temperature. The solvent was then removed in vacuo, and the residual red oil redissolved in hot acetone and precipitated out of solution by the slow addition of diethyl ether. The solid was gathered by vacuum filtration, and purified by column chromatography (Sephadex-LH-20-100, CH_3CN), giving the desired product in 85% yield for the racemic mixture. If the final ligand to be added was bpy or dmbpy (**1** or **2**) or either of the diester ligands **5** or **6**, the final stage of the reaction was carried out in refluxing methanol over 3−12 h, as described above for **1**. However, insolubility problems led to the use of refluxing methanol/acetic acid (4:1) for the addition of either of the diester ligands **3** or **4**, over 12 h. The workup procedure employed was identical thereafter.

***rac*-[Ru(Sambpy)$_2$(bpy)](Cl)$_2$ (10) and *rac*-[Ru(Rambpy)$_2$(bpy)](Cl)$_2$ (11)**: yield 85% and 91%, respectively. Data for **10**: ^{1}H NMR (CD_3CN) δ 10.75 (s, 4H), 10.04 (m, 4H), 8.42 (m, 2H), 8.00 (m, 2H), 7.87−7.16 (m, 32H), 5.31 (m, 4H), 1.74 (m, 12H); ^{13}C NMR (CD_3CN) δ 162.3, 158.9, 158.8, 157.5, 157.4, 153.2, 152.8, 146.1, 146.0, 145.9, 142.9, 139.0, 129.2, 128.9, 128.7, 128.6, 128.5, 127.7, 127.5, 127.1, 125.1, 123.5, 123.4, 51.3, 22.8. Anal. Calcd for **10** ($C_{66}H_{60}Cl_2N_{10}O_4Ru\cdot6H_2O$) (1337.4): C, 59.27; H, 5.43; N, 10.47. Found: C, 59.70; H, 5.20; N, 10.40.

***rac*-[Ru(bpy)$_2$(Sambpy)](Cl)$_2$ (12) and *rac*-[Ru(bpy)$_2$(Rambpy)](Cl)$_2$ (13)**: yield 82% and 80%, respectively. Data for **12**: ^{1}H NMR ($CDCl_3$) δ 10.84 (s, 2H), 9.35 (m, 2H), 8.97 (m, 4H), 8.05 (m, 6H), 7.60−7.21 (m, 20H), 5.30 (m, 2H), 1.84 (dd, J = 6.5 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ 160.9, 157.6, 156.8, 156.5, 150.7, 150.6, 150.5, 144.2, 144.1, 142.8, 138.9, 138.8, 138.7, 128.3, 127.9, 127.1, 127.0, 126.9, 126.8, 126.7, 125.7, 125.5, 123.6, 51.2, 51.1, 22.4. Anal. Calcd for **12** ($C_{48}H_{42}Cl_2N_8O_2Ru\cdot3H_2O$) (935.0): C, 54.80; H, 4.69; N, 10.43. Found: C, 54.60; H, 4.88; N, 10.55.

***rac*-[Ru(Sambpy)$_2$(dmbpy)](Cl)$_2$ (14) and *rac*-[Ru(Rambpy)$_2$(dmbpy)](Cl)$_2$ (15)**: yield 76% and 79%, respectively. Data for **15**: ^{1}H NMR (CD_3CN) δ 10.52 (m, 4H), 9.69 (m, 4H), 8.31 (s, 2H), 7.90−7.11 (m, 24H), 5.29 (m, 4H), 2.50 (s, 3H), 2.48 (s, 3H), 1.69 (m, 12H); ^{13}C NMR (CD_3CN) δ 162.5, 158.8, 157.0, 153.2, 152.7, 125.6, 151.8, 145.9, 145.8, 145.7, 142.8, 129.4, 129.2, 129.0, 128.7, 128.6, 127.9, 127.8, 127.5, 126.9, 125.9, 123.4, 51.3, 51.2, 22.9, 21.3. Anal. Calcd

for **15** ($C_{68}H_{64}Cl_2N_{10}O_4Ru\cdot 3H_2O\cdot CH_2Cl_2$) (1396.3): C, 59.35; H, 5.20; N, 10.03. Found: C, 59.15; H, 5.19; N, 10.20.

***rac*-[Ru(dmbpy)$_2$(Sambpy)](Cl)$_2$ (16) and *rac*-[Ru(dmbpy)$_2$(Rambpy)](Cl)$_2$ (17)**: yield 77% and 80%, respectively. Data for **16**: ^{1}H NMR ($CDCl_3$) δ 10.76 (d, $J = 6$ Hz, 2H), 9.90 (s, 2H, NH), 8.58 (s, 2H), 8.55 (d, $J = 6.4$ Hz, 2H), 8.00 (d, $J = 5.6$ Hz, 2H), 7.60 (m, 6H), 7.54 (d, $J = 6.4$ Hz, 1H), 7.50 (d, $J = 6.4$ Hz, 1H), 7.28 (m, 8H), 7.19 (d, $J = 8.9$ Hz, 2H), 7.10 (m, 2H), 5.32 (m, 2H), 2.59 (m, 6 H), 1.86, 1.85, 1.84 and 1.83 (4 $\times$ s, CH_3); ^{13}C NMR (CD_3CN) δ 163.3, 158.6, 157.3, 157.2, 153.2, 153.1, 153.0, 151.8, 151.7, 151.6, 151.4, 151.3, 144.9, 143.0, 129.5, 129.3, 129.2, 129.0, 128.9, 128.7, 128.6, 128.5, 128.3, 128.2, 127.2, 125.9, 125.8, 123.0, 51.2, 51.1, 22.3, 22.2, 21.3, 21.2, 21.1. Anal. Calcd for **16** ($C_{52}H_{50}Cl_2N_8O_2Ru\cdot H_2O\cdot CHCl_3$) (991.1): C, 56.41; H, 4.73; N, 9.93. Found: C, 56.69; H, 5.32; N, 9.57.

***rac*-[Ru(Sambpy)$_2$(Sestbpy)](Cl)$_2$ (18) and *rac*-[Ru(Rambpy)$_2$(Restbpy)](Cl)$_2$ (19)**: yield 55% and 60%, respectively. Data for **18**: ^{1}H NMR ($CDCl_3$) δ 10.90 (s, 4H), 9.96 (brs, 2H), 9.81 (brs, 2H), 8.83 (s, 2H), 7.95 (d, $J = 5.6$ Hz, 2H), 7.93 d, $J = 5.7$ Hz, 4H), 7.65 (d, $J = 6.4$H, 2H), 7.57−7.11 (m, 34 H), 6.15 (q, $J = 6.4$ Hz, 2H), 5.28 (m, 4H), 1.83 (m, 12H), 1.71 (d, $J = 6.8$ Hz, 6H); ^{13}C NMR ($CDCl_3$) δ 162.9, 162.8, 162.0, 156.6. 156.5, 156.2, 144.7, 144.4, 142.7, 142.6, 140.0, 139.7, 128.7, 128.6, 127.4, 126.3, 123.3, 122.7, 122.5, 75.9, 50.5, 30.2, 21.8, 21.5. Anal. Calcd for **18** ($C_{84}H_{76}Cl_2N_{10}O_8Ru\cdot 4H_2O$) (1599.7): C, 63.07; H, 5.47; N, 8.76. Found: C, 62.62; H, 5.42; N, 8.50.

***rac*-[Ru(Sestbpy)$_2$(Sambpy)](Cl)$_2$ (20) and *rac*-[Ru(Restbpy)$_2$(Rambpy)](Cl)$_2$ (21)**: yield 56% and 54%, respectively. Data for **21**: ^{1}H NMR ($CDCl_3$) δ 8.85 (s, 2H), 8.69 (s, 4H), 8.03 (m, 2H), 7.84 (d, $J = 5.6$ Hz, 2H), 7.62 (m, 6H), 7.56 (d, $J = 5.6$ Hz, 4H), 7.50−7.15 (m, 30H), 6.12 (q, $J = 6.4$ Hz, 2H), 5.14 (m, 4H), 1.70 (d, $J = 6.8$ Hz, 6H), 1.55 (m, 12H); ^{13}C NMR ($CDCl_3$) δ 161.4, 160.5, 160.4, 157.4, 157.1, 157.0, 156.9, 151.5, 150.2, 149.7, 144.1, 144.0, 143.8, 143.7, 139.8, 139.7, 139.5, 128.9, 128.8, 128.4, 127.7, 127.1, 126.9, 126.7, 126.2, 124.3, 123.6, 76.2, 51.3, 51.2, 29.2, 22.2, 21.7, 21.6. Anal. Calcd for **21** ($C_{84}H_{74}Cl_2N_8O_{10}Ru\cdot 5H_2O$) (1617.7): C, 62.37; H, 5.23; N, 6.93. Found: C, 62.35; H, 5.14; N, 7.23.

***rac*-[Ru(Sestbpy)$_2$(Rambpy)](Cl)$_2$ (22)**: yield 66%; ^{1}H NMR (CD_3CN) δ 9.06 (s, 2H), 8.96 (s, 2H), 7.88−7.71 (m, 15H), 7.51 (dd, $J = 6.8$ Hz, $J = 0.8$ Hz, 2H), 7.51−7.25 (m, 25H), 6.15 (q, 2H, $J = 6.8$ Hz), 5.20 (m, 4H), 1.68 (d, $J = 6.8$ Hz, 4H); ^{13}C NMR (CD_3CN) δ 163.6, 163.1, 158.3, 158.0, 157.9, 153.5, 144.8, 144.2, 142.1, 140.2, 129.6, 129.5, 129.3, 128.2, 127.7, 127.6, 126.3, 125.0, 124.9, 123.4, 76.2, 51.2, 51.1, 22.4, 22.3, 22.2, 22.1. Anal. Calcd for $C_{66}H_{60}Cl_2N_{10}O_4Ru\cdot 4H_2O\cdot 2CH_3CN$ (1681.8): C, 62.85; H, 5.27; N, 8.33. Found: C, 62.21; H, 5.27; N, 8.51.

***rac*-[Ru(dmbpy)$_2$(Sestbpy)](Cl)$_2$ (23)**: yield 73%; ^{1}H NMR (CD_3CN) δ 8.82 (s, 2H), 8.72 (s, 2H), 8.66 (s, 2H), 8.21 (m, 2H), 8.04 (m, 2H), 7.67−7.52 (app ddd, 4H), 7.44−7.25 (m, 16H), 6.14 (q, 2H, $J = 4.1$ Hz), 2.61 and 2.57 (app dd, 12H), 1.69 (d, $J = 4.0$ Hz, 6H); ^{13}C NMR (CD_3CN) δ 162.4, 157.1, 156.0, 155.6, 153.3, 151.3, 151.2, 151.1, 150.6, 150.4, 139.9, 137.9, 129.3, 129.1, 129.1, 128.5, 127.3, 127.2, 126.3, 125.9, 122.7, 116.3, 75.6, 75.3, 21.7, 21.4, 14.5. Anal. Calcd for $C_{52}H_{48}Cl_2N_6O_4Ru\cdot 4H_2O\cdot CH_2Cl_2$ (1150.0): C, 55.35; H, 5.08; N, 7.31. Found: C, 55.17; H, 5.08; N, 7.69.

***rac*-[Ru(bpy)$_2$(dmbpy)](Cl)$_2$ (24).** This compound was prepared following the procedure described above, and the product isolated in 80% yield. The compound was found to be in good agreement with the literature.[14]

General Procedure for the Preparation and HPLC Separation of [Ru(pp)(pp′)(pp″)](X)$_2$ (X = Cl, PF$_6$). The complexes [Ru(dmbpy)(Sestbpy)(Rambpy)]$^{2+}$ (**25**) and [Ru(dmbpy)(Restbpy)(Rambpy)]$^{2+}$ (**26**) were prepared according to the following procedure.

***rac*-[Ru(dmbpy)(Sestbpy)(Rambpy)](Cl)$_2$ (25).** Ruthenium(III) chloride hydrate (0.5 g, 2 mmol), dissolved in dry DMF (35 mL), was treated with an excess of anhydrous LiCl (0.2 g, 4.7 mmol) to give a suspension which was stirred for 5 min at 90 °C. Rambpy (**4**) (1 g, 2.2 mmol), dissolved in DMF (20 mL), was added to this solution, and the mixture was then stirred for 6 h under a nitrogen atmosphere. The solution was then gradually warmed to 110 °C before Sestbpy (**5**) (0.37 g, 2.4 mmol) was added, and the resulting mixture was stirred under nitrogen for an additional 10 h. After being cooled to room temperature, the solution was filtered to remove a small amount of unreacted ruthenium(III) chloride and other insoluble components. The filtrate was reduced to dryness by removal of the solvent in vacuo, and the solid washed with ether (2 $\times$ 100 mL). The residue was then dissolved in methanol (100 mL), dmbpy (**2**) (0.5 g, 2.7 mmol) was added, and the mixture was heated to reflux for 4 h, during which time the solution became deep red in color. The solution was allowed to cool to room temperature, and the solvent was then evaporated to dryness in vacuo. The resulting red oil was redissolved in a small amount of hot acetone, and diethyl ether was slowly added. After the solution was stirred at room temperature for 1 h, the precipitate formed was collected by vacuum filtration. This solid was redissolved in a minimum amount of acetonitrile and purified by column chromatography (Sephadex-LH-20-100, CH_3CN), which affords the crude racemic product as a glassy red solid in 44% yield. A sample was recrystallized from $CHCl_3$−ether mixed solvent for elemental analysis. The racemic mixture was finally separated into the Δ/Λ-diastereomers using preparative chiral stationary-phase HPLC, during which process counterion exchange for the PF_6^- anion occurred.

***rac*-[Ru(dmbpy)(Sestbpy)(Rambpy)](Cl)$_2$ (25) and *rac*-[Ru(dmbpy)(Restbpy)(Rambpy)](Cl)$_2$ (26)**: yield 44−46%; ^{1}H NMR (CD_3CN) δ 9.04 (m, 2H), 8.96 (m, 2H), 8.36 (s, 2H), 7.95−7.63 (m, 8H), 7.50−7.18 (m, 24H), 6.18 (m, 2H), 5.22 (m, 2H), 1.71 (m, 6H), 1.58 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 173.7, 162.1, 161.8, 160.9, 160.8, 157.5, 157.3, 157.2, 156.6, 155.8, 152.0, 151.9, 144.1, 144.0, 143.1, 143.0, 139.8, 139.7, 138.8, 128.7, 127.2, 127.1, 126.8, 126.6, 126.3, 123.6, 75.7, 51.2, 51.1, 22.2, 21.7, 21.2. Anal. Calcd for $C_{62}H_{62}Cl_2N_8O_6Ru\cdot 7H_2O$: C, 58.95; H, 5.53; N, 8.09. Found: C, 58.74; H, 5.20; N, 8.16.

Results and Discussion

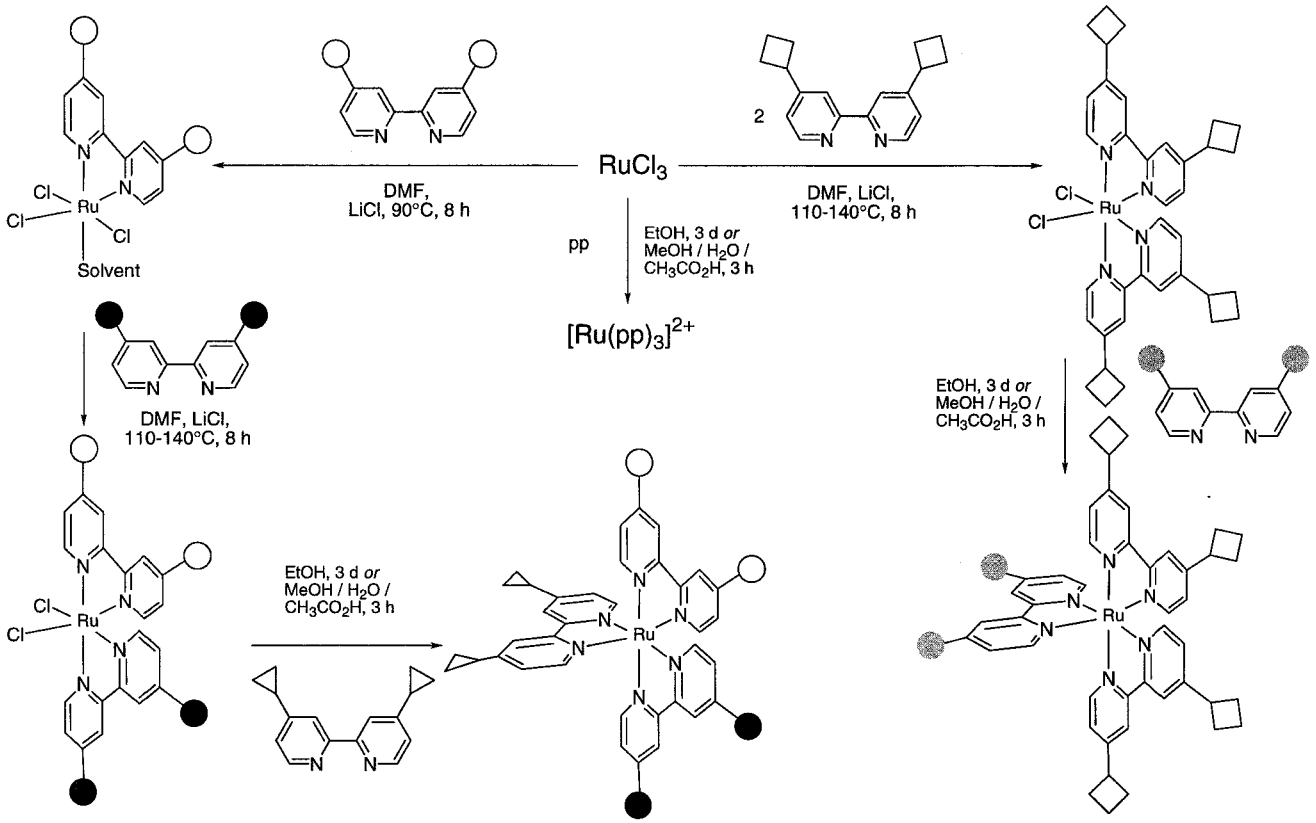
Although a large number of ruthenium(II) tris(polypyridyl) complexes have been prepared, the routes to these compounds have thus far been limited, especially if enantio- or diastereomerically pure forms are required. Indeed, approaches toward complexes that contain three different pp ligands have been restricted to just a few different methods.[17−20] Because of the interest that octahedral ruthenium complexes have generated, perhaps because of their potential as molecular electronics components,[1,27] we decided to try to develop a new, easily applicable synthesis of such compounds.

A new set of reaction conditions should ideally require a minimum of separation/purification steps, as these serve to increase the complexity of the synthesis, as well as increase the number of situations where yield losses can occur. Thus, an efficient, easily applicable synthesis of Ru(pp)(pp′)(pp″) complexes was our objective. This was achieved, and a series of novel Ru[(pp)(pp′)(pp″)]$^{2+}$(X$^-$)$_2$ complexes (where pp, pp′, and pp″ = 4,4′-disubstituted-2,2′-bipyridine, with H, methyl, or chiral ester or amide substituents at the 4,4′-positions, and X = Cl or PF_6) have been prepared. The versatility of this method is such that it is possible to produce complexes where all of the ligands are the same (using existing methodology), where one ligand is different (i.e., pp = pp′ $\neq$ pp″), and where all ligands are different (i.e., pp $\neq$ pp′ $\neq$ pp″). The reaction conditions used to achieve this goal are shown for all three of the above situations in Scheme 1.

The selectivity of the new method is based upon the use of reaction temperature and controlled stoichiometries of the reagents, as seen in Scheme 1. Thus, the preparation of complexes containing three identical ligands (which requires no selectivity) is carried out using existing methods,[22] which are very forceful. This methodology was used to prepare [Ru(Sambpy)$_3$]$^{2+}$ (**8**) and [Ru(Rambpy)$_3$]$^{2+}$ (**9**). Increased selectivity

(27) von Zelewsky, A.; Belser, P.; Hayoz, P.; Dux, R.; Hua, X.; Suckling, A.; Stoeckli-Evans, H. *Coord. Chem. Rev.* **1994**, *132*, 75−85.

Scheme 1. Three Different Methods for the Formation of Octahedral Ruthenium Tris(polypyridyl) Complexes[a]



[a] In the three-step synthesis, the structure of the mono-derivative [Ru(bpy)Cl_3·solvent] was confirmed from the X-ray crystal structure of the isolated compound.

is required to prevent the reaction from proceeding beyond the second ligation of a pp ligand, i.e., at the bis(pp) stage, and this could be achieved by "turning down" the forcefulness of the ligation process through the use of a different, milder set of conditions, these being DMF/LiCl/110−140 °C/8 h. If 2 equiv of the pp ligand was added to the reaction mixture, only the *cis*-Ru(pp)$_2$$Cl_2$ product was observed, with none of the possible tris(pp) complex formed. To achieve this goal, more forcing conditions were required, and the DMF was evaporated before a more standard set of conditions (i.e., MeOH/H_2O/CH_3CO_2H/reflux/3−12 h/pp′ for the diamide ligands (**3** and **4**), or MeOH/reflux/12 h/pp′ for bpy, dmbpy, or the diester ligands (**1**, **2**, **5**, or **6**)) were applied. This resulted in the formation of the desired [Ru(pp)$_2$(pp′)]$^{2+}$ in high yield. The most difficult synthesis, that of [Ru(pp)(pp′)(pp″)]$^{2+}$, was achieved by again reducing the forcefulness of the reaction conditions. Thus, monoligation was achieved by reacting 1 equiv of pp with $RuCl_3$ in DMF/LiCl/90 °C/8 h, which afforded [Ru(pp)Cl_3·solvent]. This compound was isolated from the crude reaction mixture, and the novel structure confirmed by X-ray diffraction analysis of the solid-state structure, which is shown in Figure 1, together with the atomic numbering scheme. The metal ion is in a distorted octahedral environment, bonded to two nitrogen atoms of a bipy ligand at 2.047(3) and 2.054(3) Å, one nitrogen of a acetonitrile (2.057(3) Å) and three chlorine atoms in a mer arrangement (2.317(1), 2.356(1), and 2.371(1) Å). The unique chlorine atom trans to a pyridine nitrogen atom has the longest bond. As before, none of the undesired, bis(pp) or tris(pp) products were observed, and the isolated compound was in good agreement with previously reported Ru(mono(bpy)) complexes.[28−31]

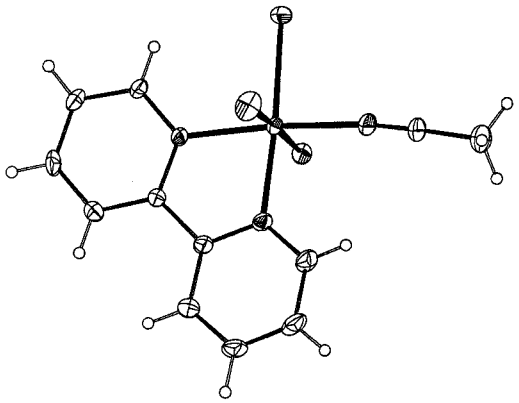


Figure 1. ORTEP view of the intermediate [Ru(bpy)Cl_3(NCMe)], $C_{12}H_{11}Cl_3N_3Ru$, M = 404.67, triclinic, space group $P1$, a = 8.093(1) Å, b = 12.975(1) Å, c = 6.914(1) Å, α = 87.64(1)°, β = 88.38(1)°, γ = 86.39(1)°, V = 723.72(15) Å^3, Z = 2, d_c = 1.857 Mg/m^3, μ = 1.624 mm^{-1}, F(000) = 398.

The addition of exactly 1 equiv of pp′, and an increase in temperature, led to the formation of the bis product *cis*-Ru(pp)(pp′)Cl_2 before the solvent was removed, and the third ligand added under the harshest set of conditions, affording the desired product in good yield. It should also be noted that this three-step, one-pot process can be used to prepare [Ru(pp)$_2$(pp′)]$^{2+}$ and [Ru(pp)$_3$]$^{2+}$ complexes as well, although this is not of practical importance.

(28) Haire, G. R.; Leadbeater, N. E.; Lewis, J.; Raithby, P. R.; Edwards, A. J.; Constable, E. C. *J. Chem. Soc., Dalton Trans.* **1997**, 2997.

(29) Haukka, M.; Venalainen, T.; Ahlgren, M.; Pakkanen, T. A. *Inorg. Chem.* **1997**, *36*, 3794.

(30) Haukka, M.; Venalainen, T.; Ahlgren, M.; Pakkanen, T. A. *Inorg. Chem.* **1995**, *34*, 2931.

(31) Constable, E. C.; Henney, R. P. G.; Tocher, D. A. *J. Chem. Soc., Dalton Trans.* **1991**, 2335.

Although this methodology is apparently simple, we found that the order in which the ligands were attached to the ruthenium was of prime importance. The substituents on the 4,4′-positions can be classified as activating (for 4,4′-dimethyl), neutral (for 4,4′-diH), or deactivating (for 4,4′-diester or 4,4′-diamide), on the basis of their electron-donating/withdrawing properties. When the mildest set of conditions is applied (for the single ligation), the reaction time is strongly dependent upon the activation/deactivation properties of the pp ligand. Thus, whereas the activating dmbpy ligand reacts to completion in just 3 h, bpy requires 6 h and diester/diamide ligands require 12 h to react. Thus, it is clear that we should add the least reactive ligand to the ruthenium center at the earliest opportunity, as the difficulty of attaching sterically demanding/deactivating ligands; i.e., the diester/diamide ligands will become progressively more difficult as the ligand architecture around the metal center increases in complexity. Ideally, the most activating ligand is added in the final step, leading to a very short reaction time under the harshest set of conditions. This selection process will reduce the number of byproducts arising from undesired reactions, side chain racemizations, etc. Indeed, after solving the problem of the order in which the ligands should be attached, we observed no racemization of the chiral auxiliaries, and yields were good to excellent for the overall process. It should be noted that Keene and co-workers have also recently reported a method for preparing ruthenium(II) species containing carboxylate-functionalized 2,2′-bipyridine ligands.[32] This method involves the preparation of a complex containing ester groups, which are then subjected to base hydrolysis.

X-ray Crystallography. Λ-17: The Key to Understanding the Absolute Stereochemistry of the Octahedral Complexes. The crystal structures of many octahedral Ru(tris(pp)) complexes have been reported, but in the majority of cases, these complexes have been racemic; i.e., there is no external control over the stereochemical information at the metal center. Even when the complex is resolved prior to crystallization, the methods for determining absolute stereochemistry are not simple, and the absolute configuration cannot always be obtained directly and unequivocally from the X-ray structure determination. However, when ligands which contain known chiral centers are used to form complexes, all of the remaining stereocenters in the complex can be defined with reference to these centers. We were able to demonstrate the importance of this procedure by preparing and determining the structure of the enantiopure complex Λ-[Ru(dmbpy)$_2$(4,4′-bis((*R*)-(+)-α-phenylethylamido)-2,2′-bipyridine)]2PF_6·2$CHCl_3$, **Λ-17**.

The asymmetric unit contains a discrete cation, shown in Figure 2, together with the atomic numbering scheme, two anions (of which one is disordered), and two solvent chloroform molecules. In the cation, the metal atom occupies the expected slightly distorted octahedral site (dimensions are shown in the Supporting Information). It is interesting that the bond lengths to the 4,4′-bis((*R*)-(+)-α-phenylethylamido)-2,2′-bipyridine ligand, Ru−N(1) and Ru−N(12), are slightly shorter at 2.033(7) and 2.049(7) Å than the bonds to the dmbpy ligands, 2.052(7)−2.089(8) Å. The two amide groups on this unique ligand show the same conformation with the N−H groups directed inward to form a potentially hydrogen-bonding planar cavity.[25] This cavity is occupied by one of the PF_6^- anions, and two mutually *cis*-fluorine atoms form intermolecular hydrogen bonds with dimensions N(23)···F(31) = 2.94 Å and N(23)···F(36) = 3.08 Å. The N−H···F angles are 158° and 167°, respectively.

(32) Patterson, B. T.; Keene, F. R. *Aust. J. Chem.* **1998**, *51*, 999−1002.

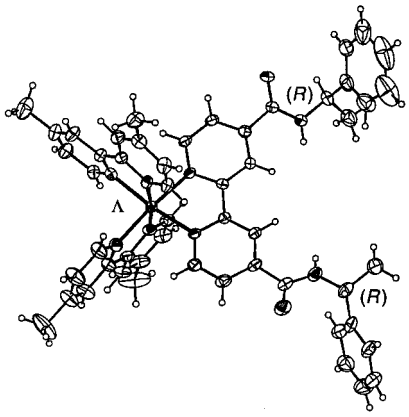


Figure 2. ORTEP view of **Λ-17**, Λ-[Ru(dmbpy)$_2$(4,4′-bis((*R*)-(+)-α-phenylethylamido)-2,2′-bipyridine)] from the 2PF_6^- salt, with thermal ellipsoids at 30% probability. The ruthenium is in a distorted octahedral environment with Ru−N distances ranging from 2.038(7) to 2.079(7) Å.

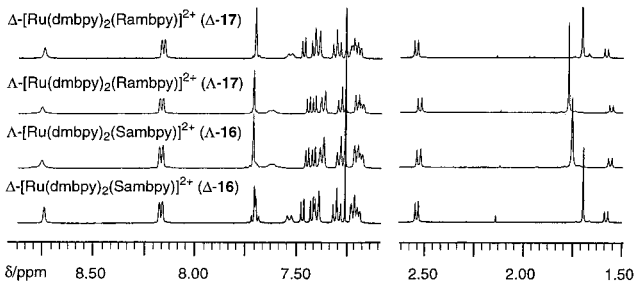


Figure 3. ^{1}H NMR of the resolved diastereomers of **16** and **17**, run in $CDCl_3$.

Using the same crystal as that employed for the structure determination, the chiral HPLC retention time of the Λ-diastereomer was confirmed, and from this information, the CD spectrum of this fraction (see Figure 5) could be unambiguously assigned. This result was in good agreement with the stereochemistry determined from the circular dichroism spectra; it was now possible to assign all of the other chromatographically resolved complexes in this study on the basis of their CD spectra with complete confidence. This crystal structure is therefore of fundamental importance to the work, as it is this result that enables us to decode unambiguously all of the stereochemical information contained in the set of novel complexes prepared.

NMR Spectroscopy. The ^{1}H and ^{13}C NMR data for the complexes prepared in this study are readily assigned. Complete listings of the chemical shifts of the racemic complexes are given in the Experimental Section, and the ^{1}H NMR spectra are also displayed in the Supporting Information. We shall consider only one set of separated four diastereomeric complexes, these being the Δ- and Λ-isomers of [Ru(dmbpy)$_2$(Sambpy)]$^{2+}$(PF_6^-)$_2$ (**16**) and [Ru(dmbpy)$_2$(Rambpy)]$^{2+}$(PF_6^-)$_2$ (**17**), the ^{1}H NMR spectra of which are shown in Figure 3. The ^{1}H NMR spectra of the remaining separated pure Δ- and Λ-diastereomers together with their CD spectra are also displayed in the Supporting Information.

The spectra for the pairs **Δ-16** and **Λ-17**, and **Λ-16** and **Δ-17**, have the same chemical shifts, because these are enantiomeric pairings. However, there are small, but observable, differences in the spectra of the diastereomeric pairs, which are most pronounced for the 4- and 4′-methyl groups, that resonate at 1.77 and 1.70 ppm for **Λ-17** and **Λ-16**, respectively. There is also a moderate shift in the position of the NH doublet (7.64 and 7.55 ppm, respectively). However, even for the completely

resolved complexes, the differences in the remainder of the ^{1}H NMR spectra are not overly significant, with small shift changes observed for the dmbpy and Rambpy or Sambpy H-5 and H-6 protons around 7.30−7.45 ppm, respectively. It should also be noted that simply by changing the counterion we can cause large chemical shift changes, as observed for the bpy H-3 protons in the symmetrically substituted $[Ru(Rambpy)_3](PF_6)_2$ (**9**) when the counterion is switched from PF_6^- (δ = 10.18 ppm in CD_3CN) to I^- (δ = 10.38 ppm) and to AcO^- (δ = 10.24 ppm). Even larger chemical shift changes are observed for the amide NH proton in this complex, which moves from 9.25 ppm (PF_6 counterion) through 9.64 ppm (I^-) to 11.40 ppm (AcO^-), which is a change in shift of over 2 ppm! These observations, in conjunction with the spectra for the resolved complexes that we have prepared in this study, lead us to conclude that the determination of the configuration of the complex is not possible through an inspection of the NMR chemical shift data, which may be subject to large changes, depending upon the conditions under which the spectrum is obtained. It is also important to note that, in cases where the metal center is racemic, there is only a limited amount of information that can be gained from the ^{1}H NMR, as the overlapping peaks serve to confuse the issue, often beyond an interpretable level, and it is therefore essential in many cases to obtain samples of resolved material for accurate chemical shift determination and assignment.

UV−Vis Spectroscopy. The electron-donating/withdrawing features of groups attached to the 4,4′-positions of the pp ligands in the Ru^{II}(tris(pp)) complexes prepared in this study have an important role to play in the synthesis of the complexes, as it is observed that the more electron-donating ligands are able to react much more rapidly than those with electron-withdrawing ability. Thus, it was necessary to react the electron-withdrawing ligands (i.e., the amide- and ester-bearing ligands, **3** and **4**, and **5** and **6**, respectively) at the earliest stages of the preparation of mixed ligand complexes, as the increasing complexity of the ligand architecture places restrictions such that these slower reacting ligands are much more difficult to attach to the metal during the later stages of the synthesis. This results in longer reaction times under more forceful conditions, which can lead to decomposition, or racemization of the chiral appended groups.

Interestingly, the electron-donating/withdrawing ability of the ligands also has a strong effect in the UV−vis spectra of the complexes. Figure 4 shows the spectra of eight species, which bear ligands of varying degrees of electron-donating/withdrawing ability (in the order **24** > **16** > **12** > **10** > **14** > **8** > **18** > **20** in terms of electron donating ability), recorded at a concentration of 3.5×10^{-5} M. The absorbance scale is identical for all eight spectra. The strongest maximum (287 nm) corresponding to the ligand-centered (LC) band is observed for **24**, which bears one electron-donating ligand, namely, dmbpy. This complex shows the shortest wavelength absorption for the metal-to-ligand charge-transfer (MLCT) band, which appears at 455 nm. As the electron-withdrawing nature of the substituents at the 4,4′-positions increases, there is a significant change in the intensity of the LC band, which is observed to have a maximum at 287 nm for **16** and **12**, with a shoulder at 305 nm for **16**, which increases in intensity for **12**. **10** and **14** bear two electron-withdrawing ligands, and a neutral, or electron-donating ligand, respectively. These two complexes fall into a middle ground, where two LC peaks of roughly equal intensity are observed. For **8**, **18**, and **20**, which bear three electron-withdrawing ligands, the maximum at 287 nm completely disappears, and the peak at 305 nm now becomes the main LC absorption. The MLCT band, centered around 450 nm, is observed to move by a considerable amount as the ligand's substituents are modified. The amount by which this peak moves is apparently not related to the degree of electron-donating/withdrawing ability of the ligands, as the longest wavelengths are attained for **16** and **14** (λ_{max} = 490 and 485 nm), which have one and two electron-withdrawing ligands, respectively. When the symmetry of the complex is lost, through the introduction of different ligands, the dipole moment of the complex is likely to increase, especially as the electron-withdrawing nature of these ligands increases. In these circumstances, the MLCT band is observed to shift to longer wavelengths. Indeed, complexes bearing three similar or identical electron-withdrawing ligands (**8**, **18**, and **20**) have small dipole moments, and their MLCT peaks are observed around 465 nm. These important wavelength difference features for the LC and MLCT bands may enable photochemical devices to be prepared where the absorption wavelength is tuned, not only by altering the metal center,[33] but also through fine-tuning of the substituent on the bipyridyl ligands, as demonstrated by this study.

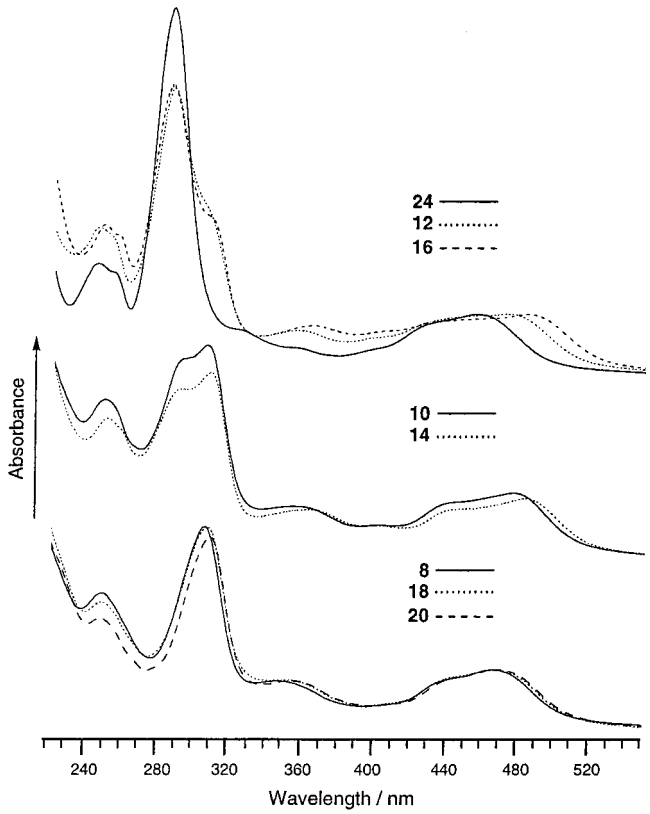


Figure 4. UV−vis spectra, recorded in acetonitrile, all of which were measured at a concentration of 3.5×10^{-5} M.

Circular Dichroism Spectra. All of the complexes in this study have been completely resolved into their Δ- and Λ-isomers using chiral HPLC techniques, as detailed in the Experimental Section and Table 1. The absolute configuration around the metal center can be assigned from the sign of the Cotton effects of the LC bands (at ca. 280 and/or 305 nm) of the CD spectra. This result is in good agreement with the literature, which states that complexes with a large positive/small negative ligand-centered (LC) band (with extrema at 300 and 275 nm, respectively), which arises due to the exciton coupling of the long-axis polarized transitions of the three pp ligands, have a Λ-metal center.[34] With this verification of the stereochemistry

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(34) Bosnich, B. *Inorg. Chem.* **1968**, *7*, 2379−2386.

Table 1. HPLC Elution Times/Chirality of the Product

	ligand 1	ligand 2	ligand 3	Δ/Λ	fraction no.	de (%)	elution time, min
8	Sambpy (**3**)	Sambpy (**3**)	Sambpy (**3**)	Λ	F1	100	20.20
8	Sambpy (**3**)	Sambpy (**3**)	Sambpy (**3**)	Δ	F2	100	26.61
9	Rambpy (**4**)	Rambpy (**4**)	Rambpy (**4**)	Δ	F1	100	25.88
9	Rambpy (**4**)	Rambpy (**4**)	Rambpy (**4**)	Λ	F2	100	43.40
10	bpy (**1**)	Sambpy (**3**)	Sambpy (**3**)	Λ	F1	100	12.39
10	bpy (**1**)	Sambpy (**3**)	Sambpy (**3**)	Δ	F2	97.9	15.61
11	bpy (**1**)	Rambpy (**4**)	Rambpy (**4**)	Λ	F1	95.6	14.27
11	bpy (**1**)	Rambpy (**4**)	Rambpy (**4**)	Δ	F2	100	19.78
12	bpy (**1**)	bpy (**1**)	Sambpy (**3**)	Λ	F1	100	8.69
12	bpy (**1**)	bpy (**1**)	Sambpy (**3**)	Δ	F2	97.6	10.03
13	bpy (**1**)	bpy (**1**)	Rambpy (**4**)	Λ	F1	100	9.04
13	bpy (**1**)	bpy (**1**)	Rambpy (**4**)	Δ	F2	93.9	10.34
14	dmbpy (**2**)	Sambpy (**3**)	Sambpy (**3**)	Λ	F1	100	14.82
14	dmbpy (**2**)	Sambpy (**3**)	Sambpy (**3**)	Δ	F2	100	19.69
15	dmbpy (**2**)	Rambpy (**4**)	Rambpy (**4**)	Λ	F1	100	18.44
15	dmbpy (**2**)	Rambpy (**4**)	Rambpy (**4**)	Δ	F2	100	29.41
16	dmbpy (**2**)	dmbpy (**2**)	Sambpy (**3**)	Λ	F1	100	12.15
16	dmbpy (**2**)	dmbpy (**2**)	Sambpy (**3**)	Δ	F2	94.2	14.07
17	dmbpy (**2**)	dmbpy (**2**)	Rambpy (**4**)	Λ	F1	100	13.32
17	dmbpy (**2**)	dmbpy (**2**)	Rambpy (**4**)	Δ	F2	98.9	17.73
18	Sestbpy (**5**)	Sambpy (**3**)	Sambpy (**3**)	Λ	F1	100	14.14
18	Sestbpy (**5**)	Sambpy (**3**)	Sambpy (**3**)	Δ	F2	100	17.60
19	Restbpy (**6**)	Rambpy (**4**)	Rambpy (**4**)	Λ	F1	100	13.91
19	Restbpy (**6**)	Rambpy (**4**)	Rambpy (**4**)	Δ	F2	100	21.29
20	Sestbpy (**5**)	Sestbpy (**5**)	Sambpy (**3**)	Λ	F1	100	24.71
20	Sestbpy (**5**)	Sestbpy (**5**)	Sambpy (**3**)	Δ	F2	100	33.82
21	Restbpy (**6**)	Restbpy (**6**)	Rambpy (**4**)	Λ	F1	100	13.36
21	Restbpy (**6**)	Restbpy (**6**)	Rambpy (**4**)	Δ	F2	100	24.80
22	Sestbpy (**5**)	Sestbpy (**5**)	Rambpy (**4**)	Λ	F1	100	12.77
22	Sestbpy (**5**)	Sestbpy (**5**)	Rambpy (**4**)	Δ	F2	100	18.59
23	dmbpy (**2**)	dmbpy (**2**)	Sestbpy (**5**)	Λ	F1	100	40.66
23	dmbpy (**2**)	dmbpy (**2**)	Sestbpy (**5**)	Δ	F2	98.2	52.54
25	dmbpy (**2**)	Sestbpy (**5**)	Rambpy (**4**)	Λ	F1	100	14.42
25	dmbpy (**2**)	Sestbpy (**5**)	Rambpy (**4**)	Δ	F2	95.7	19.28
26	dmbpy (**2**)	Restbpy (**6**)	Rambpy (**4**)	Λ	F1	100	10.30
26	dmbpy (**2**)	Restbpy (**6**)	Rambpy (**4**)	Δ	F2	98.8	17.40

of the metal center, we were then able to assign all of the other complexes in this study, as shown in Table 1. The spectra generally have a Cotton effect at ca. 440 nm which corresponds to the MLCT band, and this has the same sign as the LC band. It is very important to note that the CD spectra may be active (i.e., indicate that the material under inspection is chiral), even if the complex contains a metal center that is completely racemic. In this instance, the active CD can be assigned to the enantiopure groups bound to the 4,4′-positions, and care must be taken not to confuse this result with the erroneous assumption of some degree of diastereomeric excess.

The CD spectra for the Δ- and Λ-isomers of compounds **10**, **16**, **21**, and **24** are shown in Figure 5. Although the spectra bear many similarities, with the largest extrema always being the LC band (ca. 285−310 nm), the peak intensities, and the shape of the group of small peaks in the 200−300 nm wavelength region, show significant, ligand-dependent differences for the compounds involved in this study. It is observed that, as the electron-withdrawing nature of the ligands increases, the intensity of the larger of the two LC extrema (at longer wavelength) decreases, but after a rapid initial fall, the intensity quickly becomes near constant, at about one-third of the height observed for **24**. The LC band for all investigated complexes is composed of two overlapping peaks, one centered at 287 nm, which arises for long axis transitions in the bpy and dmbpy ligands, and the other centered at ca. 310 nm, which arises from the same transition in the ester- and amide-bearing ligands. The change in composition of the complex's ligand architecture results in a peak at 287 nm for **24**, which broadens (ca. 295 nm) as the ligands become mixed in character (**16**), ultimately sharpening at 307 nm, e.g., **11** and **21**. The broad MLCT band (spanning ca. 200 nm) has the same sign as the LC band, with

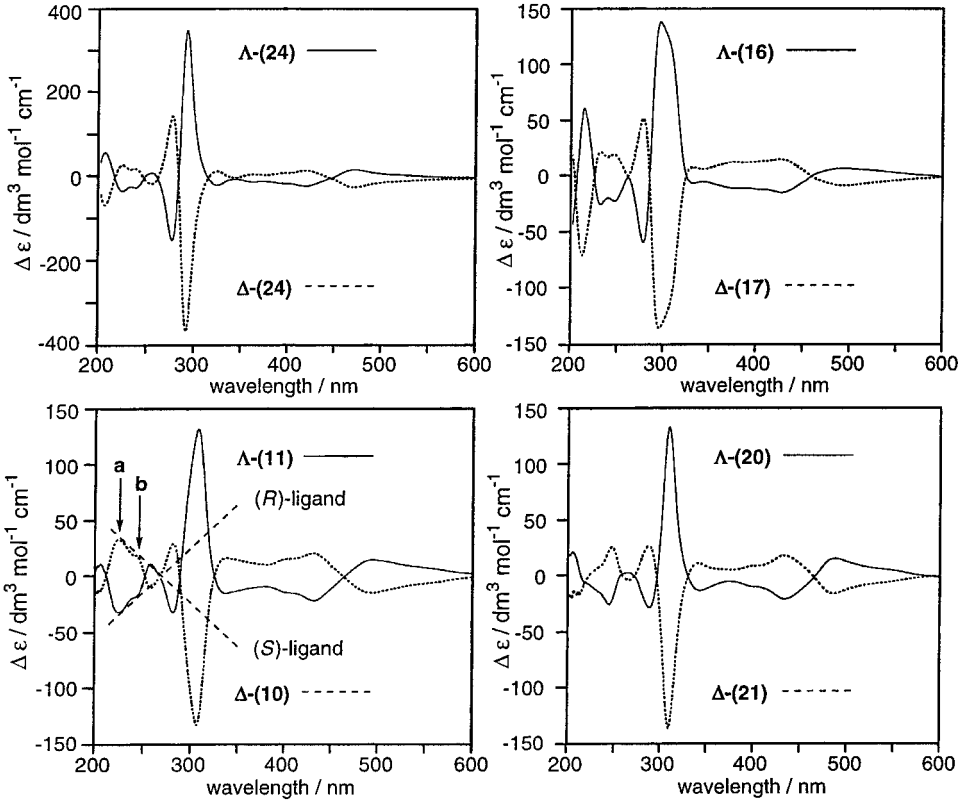

Figure 5. Molar CD spectra for the enantiomers Λ- and Δ-**24**, the enatiomeric pairs Λ-**16** and Δ-**17**, and Λ-**11** and Δ-**10**, and the diastereomers Λ-**20** and Δ-**21**. The symmetry of the spectra is clearly seen for all enantiomeric pairings. The spectra of Λ-**11** and Δ-**10** also show the two peaks (a and b) that can be used for determining the chirality of the attached ligands, by reading the gradient between the two extrema; a positive gradient indicates (*R*)-ligands, and a negative gradient (*S*)-ligands.

a midpoint at ca. 450 nm. This band is observed to red-shift slightly (by 15−20 nm) as the electron-withdrawing nature of the ligands increases, although the intensity of the peak is roughly consistent for all complexes investigated.

The region between 200 and 280 nm is the most ligand-dependent part of the CD spectra in this study, showing between three and five small positive and negative sign peaks, the first of which (centered around ca. 210 nm) always has the same sign as the larger of the two LC band extrema. A useful empirical rule can be derived from this "fingerprint" region of the spectrum that allows us to determine the stereochemistry of the chiral ligands, at least for the more straightforward cases, either where there is only one chiral ligand, i.e., **23**, **17**, **13**, **15**, or **11**, or when all of the chiral ligands are the same, i.e., **9**. The second and third peaks (225−250 nm, marked a and b on the spectra of the enantiomeric pair Δ-**12** and Λ-**13**) have the same sign as one another, and in general, there is only a point of inflection, rather than a minimum, between them. If a line is drawn from the extrema of one peak, through the extrema of the second, a positive gradient indicates *R*-stereocenters on the ligands, and a negative gradient indicates *S*-stereocenters, as indicated in Figure 5. This empirical rule works for all of the complexes listed above, and should be applicable to other, as yet unprepared, complexes. Unfortunately, when there are two different chiral ligands, it is not applicable.

Supporting Information Available: ^{1}H NMR spectra including HH-COSY experiments, CD spectra for all of the resolved complexes described in this study, and X-ray data for the intermediate [Ru(bpy)-Cl_3·solvent] and for Λ-**17**. This material is available free of charge via the Internet at http://pubs.acs.org.

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