New Configurationally Stable Chiral Building Blocks for Polynuclear Coordination Compounds: Ru(chiragen[X])Cl_2

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Abstract: The two enantiomers (Δ and Λ) of Ru(chiragen[X])Cl_2, where "chiragen" is a tetradentate ligand with a chiral bridging unit between two bipyridine moieties, have been prepared in high yields. X is *m*-xylyl (*m*-xyl); other bridging groups (e.g., $-(CH_2)_5-$ or $-(CH_2)_6-$) behave similarly. This complex can be used as an enantiomerically pure building block for the synthesis of stereochemically well defined polynuclear species. As an example, all three isomers (ΔΔ, ΛΛ, and ΔΛ) of [(chiragen[*m*-xyl])Ru(bpym)Ru(chiragen[*m*-xyl])]$(PF_6)_4$ were prepared and fully characterized by NMR and various other spectroscopic methods.

Introduction

Predetermination of chirality at an octrahedrally coordinated metal center (OC-6) has been achieved through various methods. For example, in the *hexadentate* ligand "mepenten" the configuration at the stereogenic center determines unambiguously the helical chirality at the metal center.[1,2] An *R* configuration at C(2) induces the configuration $\Delta_2\Lambda$ in the octahedral coordination sphere. In the case of several *pentadentate* ligands, the chirality at the metal center is predetermined by the configuration of the ligand too.[3,4] We were interested to achieve chiral predetermination with *tetradendate* ligands in OC-6 complexes, so that the remaining two sites can be occupied by either two monodentate ligands or one bidentate ligand. Such complexes can be used for example as enantiomerically pure chiral building blocks[5,6] for the synthesis of polynuclear metal complexes containing many metal centers with helical chirality.

The ligand family designed for the purpose of chiral predisposition around the central metal are the so-called chiragens[7] (Figure 1). The synthesis of the first complex with such a ligand was described by us earlier.[8] Until now, however, only tris(diimine) complexes with the new ligand family could be prepared. These were charged species comprised of chelate ligands only, where substitution of a single ligand is difficult to achieve. It was therefore a primary goal to develop methods for obtaining complexes that have easily substitutable ligands. Such species would be useful as universally applicable chiral building blocks. A first example of an enantiomerically pure chiral block, $[Ru(bpy)_2(py)_2]^{2+}$, with two relatively labile unidentate pyridine ligands was prepared by us several years ago.[5,6] Subsequently, the preparation of the enantiomerically pure bis(bidentate) complexes Δ-$[Ru(bpy)_2Cl_2]$[9] and Δ- or Λ-$[Ru(bpy)_2(CO)_2]^{2+}$ [10] have been described. Since Cl^- and CO are labile ligands, both types of complexes can serve as enantiomerically pure chiral building blocks. All these complexes have two drawbacks however: (i) A separation of the two enantiomers is necessary at at least one step during the synthesis and (ii) they are configurationally not very stable, e.g., under irradiation by visible light.[9]

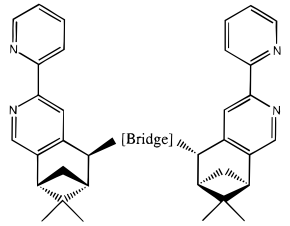

Figure 1. Tetradentate chiragen ligand family. Each molecule consists of two stereoselectively linked 4,5-pinene-2,2′-bipyridine subunits. The ligands are systematized according to the nature of the bridge and abbreviated as CG[X].

In the present paper we describe a method to prepare complexes of the type [Ru(chiragen[bridge])Cl_2]. The helical configuration at the metal center is here completely predetermined through the chirality of the ligand.[8,11] In addition, through sterical constraints in the ligand backbone, no racemization of the complex can take place. Thus, this type of complex represents the first *configurationally inert* chiral building block suitable for forming stereochemically well defined polynuclear coordination species. This type of application is demonstrated with the synthesis of homo- and heterochiral dinuclear Ru(II) complexes.

Results and Discussion

Synthesis of [Ru(CG[*m*-xyl)Cl_2]. In the original preparations, solutions of the chiragen-type ligand and the precursor $[Ru(CH_3CN)_4Cl_2]$ were mixed and refluxed.[8] Under these conditions, the formation of polynuclear complexes is predominant, allowing for only 20% of mononuclear compounds isolated. Increasing the rigidity of the bridge in the chiragen ligand by the replacement of the aliphatic chains with *o*-, *m*- and *p*-xylyl bridges did not increase these yields significantly.[11] This lead us to an analysis of the situation in the complexation

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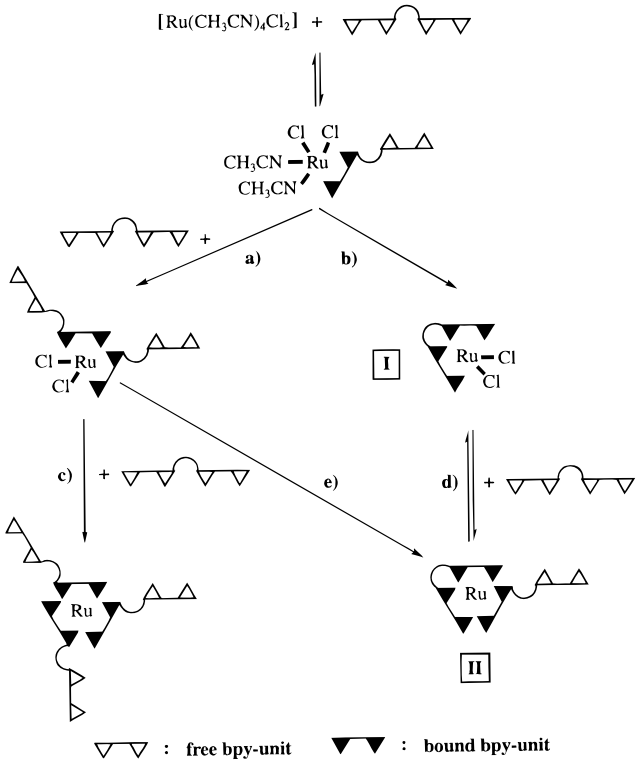
Scheme 1. Formal Reactions Possible in the Complexation of $[Ru(CH_3CN)_4Cl_2]$ with Tetradentate Chiragen-Type Ligands[a]



[a] The chirality of the metal centers (Δ or Λ) in **I** and **II** is predetermined.

step. The reactions depicted in Scheme 1 are all likely to take place in the reaction mixture. To increase the yield of the targeted dichloro complex **I**, the following points have to be considered: (i) High-dilution conditions lower the availability of a second tetradentate ligand and therefore disfavor reaction a. (ii) A large excess of chloride ions in the reaction mixture shifts the equilibria d to the desired dichloro complex **I**. High-dilution conditions in the complexation step were achieved with specially designed glassware.[12] The second point is fulfilled using a large excess of LiCl in the reaction mixture.

Chiragen (CG)-type ligands derived from (−)-α-pinene are predisposed for Δ-octahedral complexes; those from (+)-α-pinene form the Λ-enantiomer.[7,8] Starting from (−)-CG[*m*-xyl], the complex Δ-[Ru-(−)-CG[*m*-xyl]Cl_2] was thus synthesized, and from (+)-CG[*m*-xyl] the complex Λ-[Ru-(+)-CG[*m*-xyl]-Cl_2] was isolated. Yields of up to 90% were obtained. The identity of the products is demonstrated by the full accordance of the isotopic patterns of the M^+ and $M^+ - Cl^-$ peaks measured in FAB-MS with those expected by calculation. The absolute configurations at the metal centers can be determined nonempirically using exciton theory.[13,14] The results are in full agreement with absolute configurations determined by X-ray crystallography in related complexes with similar chiragen ligands.[8,11] Unlike the resolved chiral compounds of the type $Ru(bpy)_2(X)_2$[6,9,10] or $Ru(phen)_2(X)_2$[5,6] these chiral building blocks *cannot* photoracemize upon irradiation with visible or UV light. This is an inherent consequence of the design of the chiragen-type ligands. Steric constraints in the pinene moiety completely inhibit the inversion of the helical configuration at the metal center. Chiral building blocks with other ligands of the chiragen family, e.g., with aliphatic bridging units $-(CH_2)_5-$ or $-(CH_2)_6-$,[7] can also be obtained as described above.

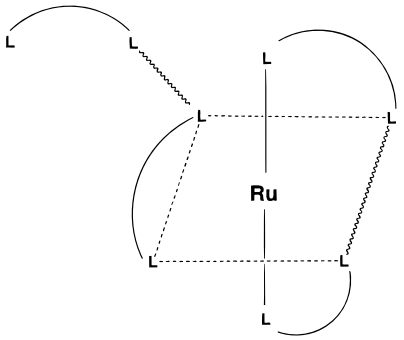
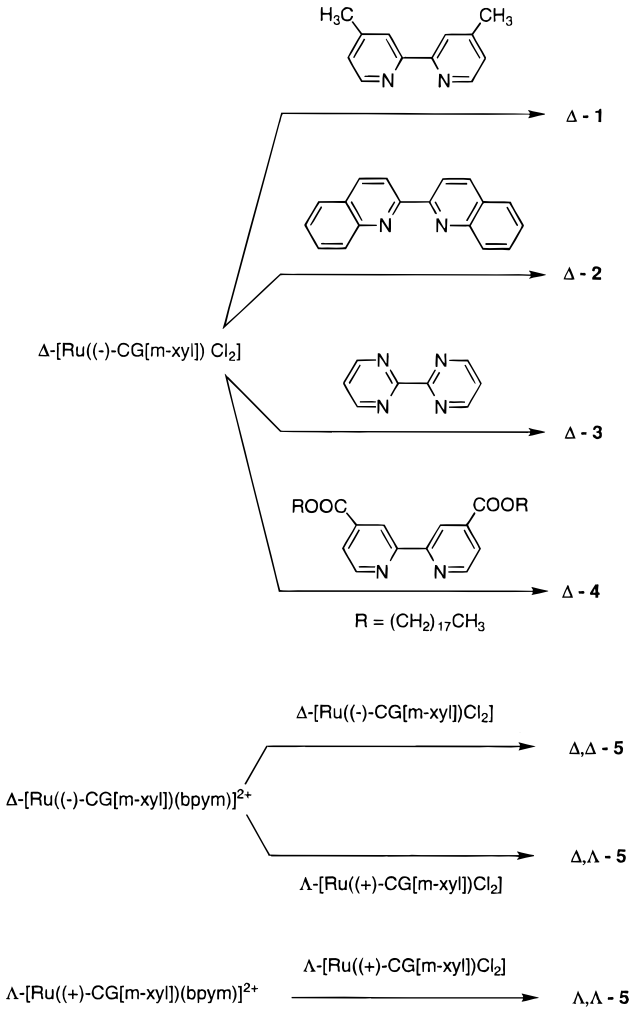


Figure 2. Dangling bpy subunit in the complex Δ-$[Ru(CG[m\text{-xyl}])_2]^{2+}$.

Scheme 2. Mononuclear and Dinuclear Ru(II) Complexes Synthesized Starting from the Chiral Building Blocks Δ- and Λ-$[Ru(CG[m\text{-xyl}])Cl_2]$



The major byproduct of the reaction is the complex Δ- or Λ-$[Ru(CG[m\text{-xyl}])_2]^{2+}$. This compound is interesting because it comprises a dangling bipyridine subunit that can potentially coordinate to another metallic center (Figure 2).

Synthetic Value of Δ- and Λ-$[Ru(CG[m\text{-xyl}])Cl_2]$ as Chiral Building Blocks. To demonstrate the synthetic usefulness of the chiral building blocks Δ- and Λ-[Ru(CG[*m*-xyl])-Cl_2], the mononuclear and dinuclear Ru(II) complexes depicted in Scheme 2 were synthesized and fully characterized. Replacement of the two chloride ligands of the chiral building blocks with the various bidentate ligands always occurs with *retention*

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of the helical chirality at the metal center. This is demonstrated by the CD spectra, which are discussed below. Most compounds were obtained within minutes, refluxing the chiral building blocks and the ligand in a modified microwave oven.[15] The reaction with the sterically nondemanding 4,4′-dimethyl-2,2′-bipyridine (DMbpy) is *quantitative*; however, with the sterically demanding ligand 2,2′-biquinoline (biq), the complex is formed in only 10% yield. The low yield is probably due to strong steric interactions between the pinene moiety and biq. The spectroscopic data of this compound are in agreement with the reported data for *rac*-$[Ru(bpy)_2(biq)](PF_6)_2$.[16] Reaction of the chiral building blocks Δ- and Λ-$[Ru(CG[m\text{-xyl}])Cl_2]$ with the bridging ligand 2,2′-bipyrimidine (bpym) led almost exclusively to the mononuclear complex Δ- or Λ-$([RuCG[m\text{-xyl}])(bpym)]^{2+}$. The homochiral dinuclear complexes Δ,Δ-$[Ru_2((-)\text{-}CG[m\text{-xyl}])_2(bpym)]^{4+}$ and Λ,Λ-$[Ru_2((+)\text{-}CG[m\text{-xyl}])_2(bpym)]^{4+}$ were obtained in a second reaction step by the slow addition of 1 equiv of the appropriate chiral building block to the mononuclear complexes. The *meso* form Δ,Λ-$[Ru_2((-)\text{-}CG[m\text{-xyl}])((+)\text{-}CG[m\text{-xyl}])(bpym)]^{4+}$ was likewise obtained by the addition of Λ-$[Ru((+)\text{-}CG[m\text{-xyl}])Cl_2]$ to a solution of Δ-$[Ru((-)\text{-}CG[m\text{-xyl}])(bpym)]^{2+}$. This reaction had to be carried out in refluxing ethanol, since in refluxing ethylene glycol a statistical distribution of the three stereoisomers Δ,Δ, Λ,Λ, and Δ,Λ was obtained.

Reaction of Δ-$[Ru((-)\text{-}CG[m\text{-xyl}])Cl_2]$ with 4,4′-dicarboxy-2,2′-bipyridine dioctadecyl ester (diobpy) in the microwave oven always caused partial cleavage of the ester groups. The complex was finally obtained *via* a reactive Ru(II) solvent species.[17] Molecules with a chiral Ru(II) complex as a polar head and long aliphatic chains as nonpolar tails are of interest in view of their surfactant chemistry. The behavior of related racemic compounds was widely studied.[18−21] Enantioselective effects in surfactant chemistry, e.g., nonlinear optical properties and liquid crystal phases, could be investigated with well-characterized chiral model complexes of this type.

CD Spectra. As reported previously, the phenomenon of *statistical chiral amplification* upon complexation for ligands of the chiragen type can be observed.[11] Although (+)-CG[*m*-xyl] is of considerably lower optical purity (ee = 76% for the starting (+)-α-pinene) than the (−)-CG[*m*-xyl] ligand (ee = 98% for the starting (1*R*)-(−)-myrtenal), the Λ and Δ chiral building blocks $[Ru(CG[m\text{-xyl}])Cl_2]$ show almost identical, although opposite, values for Δε in the CD spectra (Figure 3). The spectra are in good agreement in the visible region with reported data for photochemically produced Δ-$[Ru(bpy)_2Cl_2]$.[9] The signs for Δε in the UV region are also consistent, although the intensities of the two bands in the couplet are inverted. Whereas Δ-$[Ru(bpy)_2Cl_2]$ shows a larger Cotton effect in the band at longer wavelength (298 and 280 nm, respectively),[9] for Δ- and Λ-$[Ru(CG[m\text{-xyl}])Cl_2]$ the band at shorter wavelength (317 and 303 nm, respectively) is more important. Since this

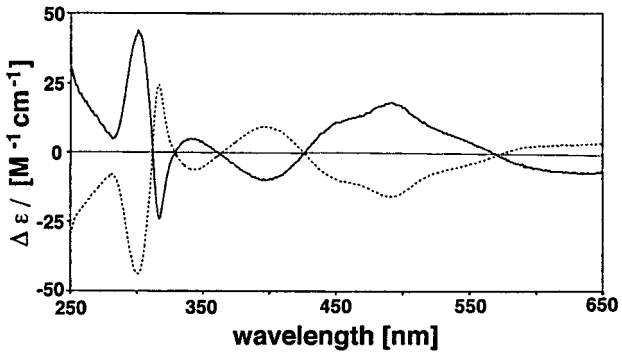

Figure 3. CD spectra of Δ-$[Ru((-)\text{-}CG[m\text{-xyl}])Cl_2]$ (solid line) and Λ-$[Ru((-)\text{-}CG[m\text{-xyl}])Cl_2]$ (dashed line) measured in dichloromethane.

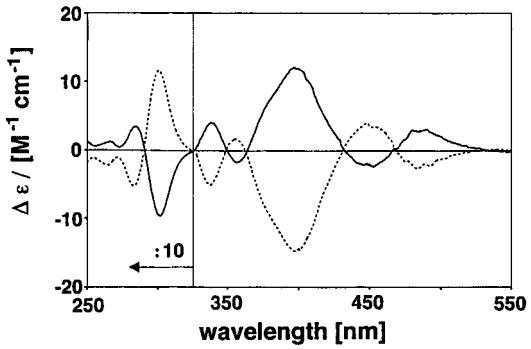

Figure 4. CD spectra of Δ-$[Ru((-)\text{-}CG[m\text{-xyl}])(bpym]^{2+}$ (solid line) and Λ-$[Ru((-)\text{-}CG[m\text{-xyl}])(bpym]^{2+}$ (dashed line) measured in acetonitrile. The values for Δε below 325 nm were divided by a factor of 10.

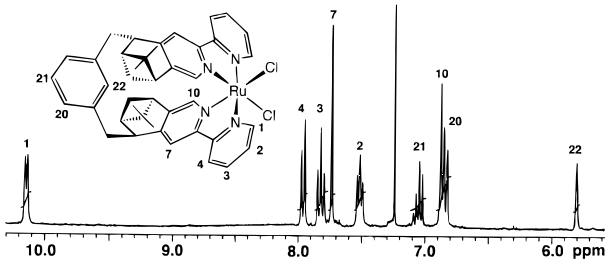

Figure 5. Aromatic region of the ^{1}H-NMR spectrum of Δ-$[Ru((-)\text{-}CG[m\text{-xyl}])Cl_2]$ measured in $CDCl_3$.

is the region of ligand-centered $\pi-\pi^*$ transitions, we believe this to be an effect of the pinene substituents at the bipyridine backbone.

The helical chirality at the metal center is conserved in all the substitution reactions reported. This is demonstrated by the conservation of the couplet signs in the region of 300 nm. As an example, the CD spectra of Δ- and Λ-**3** are shown in Figure 4. The spectrum of Δ-**3** is in agreement with the one reported for Δ-$[Ru((+)\text{-}CG[5])(bpym)]^{2+}$.[22] As expected, the nature of the bridge in the chiragen ligand seems to have only minor influence on the spectroscopic properties.

NMR Spectra. The ^{1}H NMR spectra for all mononuclear complexes are relatively simple, owing to the C_2 symmetry of the species. The dinuclear homochiral complexes Δ,Δ-**5** and Λ,Λ-**5** and the heterochiral *meso* form Δ,Λ-**5** are of even higher symmetry, namely, D_2 and C_{2v}. As an example, the aromatic part of the spectrum of Δ-$[Ru((-)\text{-}CG[m\text{-xyl}])Cl_2]$ is given in Figure 5. In Δ- and Λ-$[Ru(CG[m\text{-xyl}])_2]^{2+}$ (see Figure 2), the symmetry is broken by the second unilaterally coordinated ligand. Thus, the symmetry of the complexes is C_1, resulting in a complicated spectral pattern (Figure 6). The ligand

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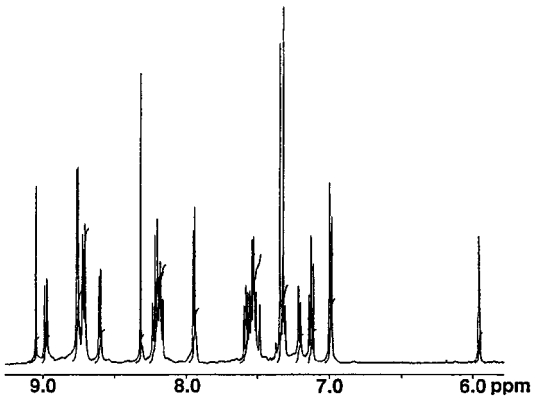

Figure 6. Aromatic region of the ^{1}H-NMR spectrum of Δ-[Ru((−)-CG[*m*-xyl])$_2$]$^{2+}$ measured in acetone-d_6.

coordinated to Ru(II) in a tetradentate manner still effectively shows C_2 symmetry, whereas the ligand with the dangling bipyridine moiety appears in the spectrum with significant differences between the two halves of the molecule. All lines can be assigned unambiguously in a 500 MHz ^{1}H-NMR spectrum (see the Experimental Section). A noteworthy feature in all spectra is the singlet signal for the proton between the two substituents of the *m*-xylene bridge. It appears at a relatively high field (approximately 5.9 ppm) in all compounds due to its position in the complexes between two pyridine rings.

Experimental Section

General Data. The NMR studies (^{1}H and ^{13}C NMR, 2D-COSY, ^{1}H^{13}C-HETCOR, and decoupling experiments) were performed on a Varian Gemini 300 and a Bruker Avance DRX500 instrument, respectively, using solvent as the internal standard. Chemical shifts are reported in ppm on the δ scale. Mass spectral data were collected with a VG Instruments 7070E mass spectrometer with a FAB inlet system. Electronic spectra were measured using a Perkin-Elmer Lambda 5 UV/vis spectrophotometer. CD spectra were measured on a Jobin-Yvon autodichrograph Mark V. Rotation angles have been obtained with a Perkin-Elmer MC 241 polarimeter. A kd scientific 200 syringe pump was used.

Unless otherwise specified, commercial chemicals were used as supplied. 4,4′-Dimethyl-2,2′-bipyridine and 2,2′-biquinoline were obtained from Aldrich; 2,2′-bipyrimidine was obtained from Johnson Matthey. 4,4′-Dicarboxy-2,2′-bipyridine dioctadecyl ester was kindly donated by Dr. E. Steiner, Ciba AG Basel, Switzerland. All other materials were purchased from Fluka. Vacuum liquid chromatography was conducted on silica gel H (Fluka No. 60770).

Δ-[Ru((−)-CG[*m*-xyl])Cl$_2$]. (−)-CG[*m*-xyl][11] (150 mg, 0.25 mmol) and freshly prepared [Ru(CH$_3$CN)$_4$Cl$_2$][8] from [Ru(dmso)$_4$Cl$_2$][23] (121 mg, 0.25 mmol) were dissolved in two portions of methanol (50 mL). The two solutions were added simultanously with the aid of a syringe pump (rate 4 mL h^{-1}) in special high-dilution glassware.[12] After further dilution the two components were added to refluxing methanol (500 mL) containing LiCl (100 g). Once the addition was finished, the reaction mixture was refluxed for an additional 2 h and then reduced to a volume of 400 mL. The deep violet solution was extracted with 1,2-dichloroethane (3 × 200 mL). The combined 1,2-dichloroethane fractions were evaporated to dryness under reduced pressure at 40 °C. Residual free ligand was extracted with hexane (3 × 10 mL). The complex was dissolved in a minimum of dichloromethane and transferred to the top of a packed silica gel column and eluted with absolute ethanol using vacuum liquid chromatography (VLC).[24,25] The violet fractions collected were combined, evaporated to dryness at 40 °C and recrystallized from chloroform/pentane, yielding 174 mg (90%).

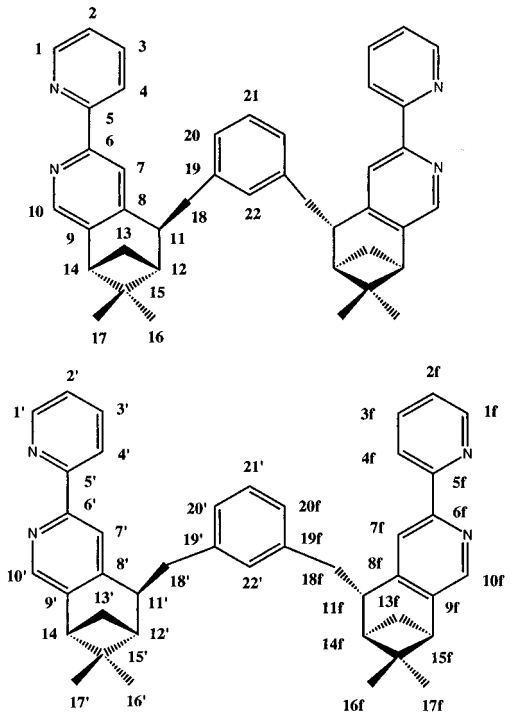

Figure 7. Numbering scheme for the two nonequivalent (−)-CG[*m*-xyl] ligands in the complex Δ-[Ru((−)-CG[*m*-xyl])$_2$](PF$_6$)$_2$.

^{1}H NMR (CDCl$_3$, 300 MHz): δ 10.14 (d, 2H, ^3J = 5.5 Hz), 7.96 (d, 2H, ^3J = 7.6 Hz), 7.82 (t, 2H, ^3J = 7.4 Hz), 7.74 (s, 2H), 7.52 (t, 2H, ^3J = 5.8 Hz), 7.05 (t, 1H, ^3J = 7.6 Hz), 6.88 (s, 2H), 6.84 (d, 2H, ^3J = 7.7 Hz), 5.84 (s, 1H), 3.50 (dm, 2H, ^2J = 15.6 Hz), 3.33 (br s, 2H), 2.93 (dd, 2H, ^2J = 15.8 Hz, ^3J = 6.6 Hz), 2.25 (dd, 2H, ^3J = 5.4 Hz, ^4J = 5.4 Hz), 2.08 (td, 2H, ^3J = 5.9 Hz, ^2J = 10.1 Hz), 2.02 (td, 2H, ^3J = 5.9 Hz, ^3J = 1.8 Hz), 1.17 (s, 3H), 0.87 (d, 2H, ^2J = 9.8 Hz), 0.42 (s, 3H). ^{13}C NMR (CDCl$_3$, 75.44 MHz): δ 159.15 (q), 158.71 (q), 155.19, 148.11, 145.57 (q), 144.49 (q), 136.83 (q), 134.32, 129.40, 129.22, 128.52, 124.93, 120.63, 117.90, 44.56, 44.44, 42.69 (q), 39.70, 38.98, 28.06, 25.58, 20.72. MS (FAB): *m*/*z* 774 (48, M$^+$), 739 (85, M$^+$ − Cl$^-$), 603 (30, C$_{42}$H$_{42}$N$_4^+$). UV−vis (dichloromethane, 1.098E−5 M): 580 (6000), 486 (3600), 385 (7800), 307 (35 000), 235 (30 500). CD (dichloromethane, 1.098E−5 M): 491 (19), 397 (−10), 343 (7.0), 317 (−24), 302 (44).

Λ-[Ru((+)-CG[*m*-xyl])Cl$_2$]. This product was synthesized starting from (+)-CG[*m*-xyl][11] following the same procedure as given above, yielding 139 mg (72%). UV−vis (dichloromethane, 4.066E−5 M): 579 (6200), 483 (4100), 385 (8800), 307 (39 700), 236 (32 300). CD (dichloromethane, 4.066E−5 M): 492 (−16), 395 (10), 343 (−6.8), 317 (24), 302 (−44).

Δ-[Ru((−)-CG[*m*-xyl])$_2$](PF$_6$)$_2$. This orange side product of the preparation of Δ-[Ru((−)-CG[*m*-xyl])Cl$_2$] was eluted from the VLC column described above with methanol, precipitated with NH$_4$PF$_6$, and then further purified by preparative thick layer chromatography eluting with ethanol/water/NH$_4$OOCCH$_3$ (1:1:0.3). Yield: 32 mg (8%). The numeration scheme of the ligands used for the assignement of the ^{1}H- and ^{13}C-NMR resonances is presented in Figure 7. ^{1}H NMR (acetone-d_6, 500.13 MHz): δ 9.05 (s, 1H, H(7f)), 8.98 (d, 1H, H(4f), ^3J = 8.2 Hz), 8.75 (s, 3H, H(7), H(7′)), 8.72 (dm, 3H, H(4), H(4′), ^3J = 8.3 Hz), 8.60 (dm, 1H, H(1f), ^3J = 5.6 Hz), 8.32 (s, 1H, H(10f)), 8.24−8.16 (m, 4H, H(3), H(3′), H(3f)), 7.94 (dm, 3H, H(1), H(1′), ^3J = 5.6 Hz), 7.59−7.50 (m, 4H, H(2), H(2′), H(2f)), 7.48 (s, 1H, H(22′)), 7.34 and 7.32 (s, 3H, H(10), H(10′)), 7.32 (t, 1H, H(21′), ^3J = 7.6), 7.22 (dd, 2H, H(20′), H(20f), ^3J = 7.6, ^4J = 1.6 Hz), 7.13 (t, 1H, H(21), ^3J = 7.6 Hz), 6.99 (d, 2H, H(20), ^3J = 7.6 Hz), 5.96 (s, 1H, H(22)), 3.88 (d, 3H, H(18b), H(18b′), ^2J = 15.4 Hz), 3.70−3.60 (m, 5H, H(11), H(11′), H(11f), H(18bf)), 3.15−3.10 (m, 3H, H(18a), H(18a′)), 2.81 (dd, 1H, H(18af), ^2J = 12.3, ^3J = 11.4 Hz), 2.73 (dd, 1H, H(14f), ^3J = 5.4, ^4J = 5.4 Hz), 2.58−2.50 (m, 4H, H(14), H(14′), H(13bf)), 2.20−2.14 (m, 6H, H(12), H(12′), H(13b), H(13b′)), 2.06−2.02 (m, 1H, H(12f)), 1.33 (d, 1H, H(13af), ^2J = 10.0 Hz), 1.28 (s, 3H, H(17f)),

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1.26 (s, 9H, H(17), H(17′)), 1.08 (dm, 3H, H(13a), H(13a′), ^2J = 9.1 Hz), 0.73 (s, 3H, H(16f)), 0.62 (s, 9H, H(16), H(16′)). ^{13}C NMR (acetone-d_6, 125.76 MHz): δ 159.31 (q), 158.62 (q), 157.27, (q), 157.22 (q), 156.38 (q), 154.07 C(1f), 152.58 and 152.43 (C(1), C(1′)), 152.22 (q), 152.17 (q), 151.37 (q), 149.55 C(10f), 147.84 (q), 147.80 (q), 147.60 (q), 147.25 (C(10), C(10′)), 140.80 (q), 138.66 (C(3), C(3′)), 138.36 C(3f), 138.07 (q), 131.09 C(22′), 130.38 and 130.33 (C(20), C(22)), 129.56 C(21), 129.36 C(21′), 128.35 (C(20′), C(20f)), 127.82 (C(2), C(2′)), 127.42 C(2f), 125.10 C(4f), 124.84 and 124.76 (C(4), C(4′)), 124.44 C(7f), 122.05 (C(7), C(7′)), 45.76 C(14f), 45.46 and 45.37 (C(14), C(14′)), 45.29 (C(12), C(12′)), 44.23 C(11f), 43.30 (q), 43.27 (q), 43.14 C(12f), 41.52 (q), 40.49 (C(11), C(11′)), 39.96 (C(18), C(18′)), 39.70 C(18f), 28.30 (C(13), C(13′)), 27.81 C(13f), 26.30 C(17f), 25.79 (C(17), C(17′)), 21.16 C(16f), 20.89 and 20.85 (C(16), C(16′)). MS (FAB): *m*/*z* 1451 (100, $M^+ - PF_6^-$), 1307 (80, $M^+ - 2PF_6^-$). UV−vis (acetonitrile, 1.443E−5 M): 448 (17 900), 296 (97 000). CD (acetonitrile, 1.443E−5 M): 478 (−7.0), 305 (−193), 287 (134). $[\alpha]_{365}$ = −3275°, 26 °C, 0.318 mg in 20 mL of acetonitrile.

Λ-[Ru((+)-CG[*m*-xyl])$_2$](PF$_6$)$_2$. The orange product was obtained as described for Δ-[Ru((−)-CG[*m*-xyl])$_2$](PF$_6$)$_2$, yielding 26 mg (7%). UV−vis (acetonitrile, 1.144E−5 M): 449 (20 000), 296 (110 000). CD (acetonitrile, 1.144E−5 M): 480 (8.5), 305 (206), 287 (−129). $[\alpha]_{365}$ = 2270°, 26 °C, 0.141 mg in 20 mL of acetonitrile.

Δ-[Ru((−)-CG[*m*-xyl])(DMbpy)](PF$_6$)$_2$ (Δ-1). Δ-[Ru((−)-CG[*m*-xyl])Cl$_2$] (50 mg, 64.5 μmol) and 4,4′-dimethyl-2,2′-bipyridine (11.9 mg, 64.5 μmol) were mixed in 2-methoxyethanol (5 mL) and then refluxed for 5 min in a modified microwave oven.[15] The solution was diluted with water (80 mL) and heated to 60 °C and the complex precipitated with NH_4PF_6 (1 g). The product was collected on Celite, washed with several portions of water and diethyl ether, and then extracted with acetone. The compound was recrystallized in acetone/diethyl ether, yielding 75 mg (quantitative) of orange product. For analytical data of this compound see ref 11.

Δ-[Ru((−)-CG[*m*-xyl])(biq)](PF$_6$)$_2$ (Δ-2). Δ-[Ru((−)-CG[*m*-xyl])-Cl$_2$] (50 mg, 64.5 μmol) and 2,2′-biquinoline (16.5 mg, 64.5 μmol) were reacted as described for **Δ-1**. The residue of the filtration trough Celite was further purified by consecutive preparative thick layer chromatography eluting with ethanol/water/NH_4OOCCH_3 (1:1:0.3) and acetonitrile/water/KNO_3 (0.3:0.6:0.1), respectively, yielding 8 mg (10%) of the bright red product. ^{1}H NMR (acetone-d_6, 300 MHz): δ 9.20 (d, 2H, ^3J = 8.9 Hz), 9.89 (d, 2H, ^3J = 8.5 Hz), 8.87 (s, 2H), 8.76 (dt, 2H, ^3J = 8.2 Hz, ^4J = 1.0 Hz), 8.26 (ddd, 2H, ^3J = 5.7 Hz, ^4J = 1.5 Hz, ^5J = 0.8 Hz), 8.19 (dt, 2H, ^3J = 5.7 Hz, ^4J = 1.6 Hz), 8.18 (d, 2H, ^3J = 8.2 Hz), 7.76 (dd, 2H, ^3J = 8.2 Hz, ^4J = 0.8 Hz), 7.67 (dt, 2H, ^3J = 7.0 Hz, ^4J = 1.1 Hz), 7.54 (s, 2H), 7.52 (ddd, 2H, ^3J = 7.0 Hz, ^3J = 5.7 Hz, ^4J = 1.3 Hz), 7.37 (ddd, 2H, ^3J = 7.0 Hz, ^3J = 6.9 Hz, ^4J = 1.6 Hz), 7.15−7.00 (m, 3H), 6.02 (s, 1H), 3.92 (dm, 2H, ^2J = 15.6 Hz), 3.67 (dm, 2H, ^3J = 6.7 Hz), 3.15 (dd, 2H, ^2J = 15.7 Hz, ^3J = 6.5 Hz), 2.63 (dd, 2H, ^3J = 5.5 Hz, ^4J = 5.5 Hz), 2.23−2.14 (m, 4H), 1.27 (s, 6H), 1.18 (d, 2H, ^2J = 10.0 Hz), 0.63 (s, 6H). ^{13}C NMR (acetone-d_6, 75.44 MHz): δ 161.65 (q), 159.29 (q), 157.11 (q), 153.82, 153.82 (q), 152.39 (q), 148.08 (q), 147.73, 140.06, 139.11, 137.99 (q), 132.10, 130.51, 130.42, 130.34, 130.07, 129.64 (q), 128.00, 127.08, 125.35, 123.27, 122.54, 45.46, 45.40, 43.63 (q), 40.64, 39.97, 27.63, 25.64, 20.84. MS (FAB): *m*/*z* 1106 (14, $M^+ - PF_6^-$), 960 (14, $M^+ - 2PF_6^-$); UV−vis (acetonitrile, 1.952E−5 M): 527 (7700), 452 (5400), 375 (12 100), 297 (41 100), 266 (40 500). CD (acetonitrile, 1.952E−5 M): 634 (−2.7), 558 (−2.7), 460 (−4.1), 402 (4.8), 380 (−13), 338 (−30), 307 (−66), 289 (47). $[\alpha]_{365}$ = −3360°, 24 °C, 0.610 mg in 25 mL of acetonitrile.

Δ-[Ru((−)-CG[*m*-xyl])(bpym)](PF$_6$)$_2$ (Δ-3). Δ-[Ru((−)-CG[*m*-xyl])Cl$_2$] (50 mg, 64.5 μmol) and 2,2′-bipyrimidine (10.2 mg, 64.5 μmol) were reacted as described for **Δ-1**. The residue of the filtration through Celite was further purified by preparative thick layer chromatography eluting with acetonitrile/water/1-butanol/KNO_3 (4:1:1:0.1), yielding 41 mg (55%) of the orange product. ^{1}H NMR (acetone-d_6, 300 MHz): δ 9.29 (dd, 2H, ^3J = 4.7 Hz, ^4J = 2.0 Hz), 9.05 (dd, 2H, ^3J = 5.7 Hz, ^4J = 2.0 Hz), 8.80 (s, 2H), 8.74 (d, 2H, ^3J = 7.9 Hz), 8.23 (dt, 2H, ^3J = 7.8 Hz, ^4J = 1.5 Hz), 8.19 (dm, 2H, ^3J = 5.1 Hz), 7.75 (dd, 2H, ^3J = 4.7 Hz, ^3J = 5.7 Hz), 7.54 (ddd, 2H, ^3J = 7.6 Hz, ^3J = 5.6 Hz, ^4J = 1.3 Hz), 7.36 (s, 2H), 7.1−7.0 (m, 3H), 5.94 (s, 1H), 3.89 (dm, 2H, ^2J = 15.4 Hz), 3.63 (dm, 2H, ^3J = 6.8 Hz), 3.12 (dd 2H, ^2J = 16.0 Hz, ^3J = 6.5 Hz), 2.55 (dd, 2H, ^3J = 5.5 Hz, ^4J = 5.5 Hz), 2.20−2.15 (m, 4H), 1.26 (s, 6H), 1.07 (dm, 2H, ^2J = 9.7 Hz), 0.61 (s, 6H). ^{13}C NMR (acetone-d_6, 75.44 MHz): δ 164.17 (q), 162.06, 158.84 (q), 158.64, 157.01 (q), 153.01, 152.59 (q), 147.73 (q), 147.35, 139.08, 137.88 (q), 130.21, 129.96, 129.39, 127.69, 124.70, 124.58, 122.19, 45.33, 45.04, 43.26 (q), 40.35, 39.73, 28.15, 25.59, 20.74. MS (FAB): *m*/*z* 1008 (79, $M^+ - PF_6^-$), 862 (100, $M^+ - 2PF_6^-$). UV−vis (acetonitrile, 4.300E−5 M): 450 (7200), 401 (6500), 295 (34 800), 234 (30 600). CD (acetonitrile, 4.300E−5 M): 486 (3.7), 451 (−3.1), 399 (11), 358 (−3.7), 336 (5.8), 301 (−97), 284 (35). $[\alpha]_{365}$ = −2910°, 27 °C, 1.486 mg in 30 mL of acetonitrile.

Λ-[Ru((+)-CG[*m*-xyl])(bpym)](PF$_6$)$_2$ (Λ-3). The product was obtained starting from Λ-[Ru((+)-CG[*m*-xyl])Cl$_2$] as described for **Δ-1**, yielding 37 mg (50%) of orange complex. UV−vis (acetonitrile, 3.872E−5 M): 450 (9500), 402 (8750), 295 (44 500), 235 (38 100). CD (acetonitrile, 3.872E−5 M): 483 (−4.4), 449 (2.4), 397 (−16), 358 (4.1), 337 (−6.1), 301 (116), 283 (−53). $[\alpha]_{365}$ = 3540°, 20 °C, 1.115 mg in 25 mL of acetonitrile.

Δ-[Ru((−)-CG[*m*-xyl])(diobpy)](CF$_3$SO$_3$)$_2$ (Δ-4). 4,4′-Dicarboxy-2,2′-bipyridine dioctadecyl ester (21.1 mg, 28.3 μmol) was dissolved under N_2 in refluxing chloroform (5 mL). To this solution was slowly added (2 h) the reactive solvent complex prepared from Δ-[Ru((−)-CG[*m*-xyl])Cl$_2$] (20 mg, 25.8 μmol) according to the procedure described by Sullivan *et al*.[17] After an additional 1 h under reflux conditions, the solvents were evaporated and the residue was dissolved in acetone. The undissolved excess of Diobpy was filtered off and the complex dried under vacuum, yielding 31 mg (70%) of the orange product. ^{1}H NMR (acetone-d_6, 300 MHz): δ 9.38 (d, 2H, ^4J = 1.1 Hz), 8.94 (d, 2H, ^3J = 5.8 Hz), 8.83 (s, 2H), 8.77 (d, 2H, ^3J = 8.0 Hz), 8.20 (dt, 2H, ^3J = 7.9 Hz, ^4J = 1.4 Hz), 7.98 (dd, 2H, ^3J = 5.9 Hz, ^4J = 1.7 Hz), 7.52 (ddd, 2H, ^3J = 7.6 Hz, ^3J = 5.6 Hz, ^4J = 1.3 Hz), 7.37 (s, 2H), 7.33 (dm, 2H, ^3J = 5.8 Hz), 7.1−7.0 (m, 3H), 5.94 (s, 1H), 4.45 (t, 4H, ^3J = 6.6 Hz), 3.90 (dm, 2H, ^2J = 16.2 Hz), 3.55 (dm, 2H, ^3J = 6.9 Hz), 3.12 (dd, 2H, ^2J = 16.2 Hz, ^3J = 6.8 Hz), 2.56 (dd, 2H, ^3J = 5.3 Hz, ^4J = 5.3 Hz), 2.20−2.13 (m, 4H), 1.83 (qui, 4H, ^3J = 6.7 Hz), 1.27 (m, 30H), 1.19 (s, 6H), 1.07 (dm, 2H, ^2J = 9.6 Hz), 0.86 (s, 6H), 0.63 (s, 6H). ^{13}C NMR (acetone-d_6, 75.44 MHz): δ 164.33 (q), 158.88 (q), 156.85 (q), 155.44 (q), 153.07 (q), 152.91, 148.05, 147.21, 139.32, 139.16 (q), 138.07 (q), 130.36, 130.22, 129.53, 127.96, 126.85, 125.10, 124.80, 122.36, 67.18, 45.48, 45.22, 43.27 (q), 40.53, 39.98, 32.58, 30.34, 28.30, 26.61, 25.77, 23.28, 20.97. MS (FAB): *m*/*z* 1602 (10, $M^+ - CF_3SO_3^-$), 1452 (12, $M^+ - 2CF_3SO_3^-$), 855 (100, $M^+ - C_{38}H_{74}O_4$). UV−vis (acetonitrile, 5.007E−5 M): 476 (7200), 360 (4700), 298 (29 300). CD (acetonitrile, 5.007E−5 M): 489 (2.4), 400 (3.5), 304 (−70), 284 (34). $[\alpha]_{365}$ = −740°, 27 °C, 1.754 mg in 20 mL of acetonitrile.

Δ,Δ-[Ru$_2$((−)-CG[*m*-xyl])$_2$(bpym)](PF$_6$)$_4$ (Δ,Δ-5). Δ-[Ru((−)-CG[*m*-xyl])Cl$_2$] (9.3 mg, 12.1 μmol) were dissolved in ethanol (5 mL) and then added over a period of 6 h to the refluxing ethanolic solution (10 mL) of Δ-[Ru((−)-CG[*m*-xyl])(bpym)](PF$_6$)$_2$ (13.9 mg, 12.1 μmol). After an additional 1 h under reflux, the reaction mixture was cooled to room temperature and diluted with water (100 mL). The complex was precipitated after heating to 60 °C by the addition of NH_4PF_6 (1 g). The product was collected on Celite, washed with several portions of water and diethyl ether, and then extracted with acetone. The pure target compound was obtained after preparative thick layer chromatography eluting with acetonitrile/water/1-butanol/KNO_3 (4:1:1:0.1), yielding 18 mg (70%) of the green product. ^{1}H NMR (acetone-d_6, 300 MHz): δ 9.25 (d, 4H, ^3J = 5.7 Hz), 8.86 (s, 4H), 8.82 (d, 4H, ^3J = 8.0 Hz), 8.35 (d, 4H, ^3J = 5.6 Hz), 8.33 (dt, 4H, ^3J = 7.9 Hz, ^4J = 1.4 Hz), 7.80 (t, 2H, ^3J = 5.7 Hz), 7.67 (ddd, 4H, ^3J = 7.0 Hz, ^3J = 5.7 Hz, ^4J = 1.3 Hz), 7.29 (s, 4H), 7.14−6.99 (m, 6H), 5.91 (s, 2H), 3.90 (dm, 4H, ^2J = 15.6 Hz), 3.59 (dm, 4H, ^3J = 6.3 Hz), 3.14 (dd, 4H, ^2J = 15.5 Hz, ^3J = 6.2 Hz), 2.51 (dd, 4H, ^3J = 5.5 Hz, ^4J = 5.5

Hz), 2.20−2.13 (m, 8H), 1.25 (s, 12H), 1.04 (d, 4H, ^2J = 9.7 Hz), 0.58 (s, 12H). ^{13}C NMR (acetone-d_6, 75.44 MHz): δ 161.85, 158.89 (q), 157.21 (q), 153.72, 153.56 (q), 148.33 (q), 147.65, 140.01, 138.02 (q), 130.43, 130.01, 129.60, 128.51, 126.79, 125.23, 122.53, 45.54, 45.16, 43.23 (q), 40.61, 39.90, 28.35, 25.68, 20.85. MS (FAB): *m*/*z* 2003 (18, $M^+ - PF_6^-$), 1855 (28, $M^+ - 2PF_6^-$), 1713 (15, $M^+ - 3PF_6^-$). UV−vis (acetonitrile, 2.340E−5 M): 595 (7000), 407 (18 800), 294 (66 200), 236 (47 900). CD (acetonitrile, 2.340E−5 M): 400 (8.0), 359 (−8.5), 328 (−17), 299 (−112), 280 (29). $[\alpha]_{365}$ = −1450°, 26 °C, 0.502 mg in 10 mL of acetonitrile.

Λ,Λ-[Ru$_2$((+)-CG[*m*-xyl])$_2$(bpym)](PF$_6$)$_4$ (Λ,Λ-5). This compound was prepared as above starting from Λ-**3** and Λ-[Ru((+)-CG[*m*-xyl])-Cl_2], yielding 19 mg (75%) of the green product. UV−vis (acetonitrile, 9.992E−6 M): 594 (6900), 405 (18 300), 293 (56 200), 237 (43 800). CD (acetonitrile, 9.992E−6 M): 400 (−12), 359 (2.7), 328 (11), 298 (77), 279 (−33). $[\alpha]_{365}$ = 1215°, 26 °C, 0.536 mg in 25 mL of acetonitrile.

Λ,Δ-[Ru$_2$((+)-CG[*m*-xyl])(bpym)((−)-CG[*m*-xyl])(PF$_6$)$_4$ (Λ,Δ-5). This compound was prepared as above starting from Δ-**3** and Λ-[Ru-((+)-CG[*m*-xyl])Cl_2], yielding 15 mg (58%) of the green product. ^{1}H NMR (acetone-d_6, 300 MHz): δ 9.24 (d, 4H, ^3J = 5.7 Hz), 8.85 (s, 4H), 8.79 (d, 4H, ^3J = 7.9 Hz), 8.47 (dm, 4H, ^3J = 5.6 Hz), 8.32 (dt, 4H, ^3J = 7.9 Hz, ^4J = 1.4 Hz), 7.83 (ddd, 4H, ^3J = 7.6 Hz, ^3J = 5.7 Hz, ^4J = 1.3 Hz), 7.77 (t, 2H, ^3J = 5.7 Hz), 7.31 (s, 4H), 7.15−7.00 (m, 6H), 5.92 (s, 2H), 3.90 (dm, 4H, ^2J = 15.4 Hz), 3.65 (dm, 4H, ^3J = 6.3 Hz), 3.14 (dd, 4H, ^2J = 15.5 Hz, ^3J = 6.2 Hz), 2.54 (dd, 4H, ^3J = 5.2 Hz, ^4J = 5.2 Hz), 2.20−2.13 (m, 8H), 1.27 (s, 12H), 1.04 (d, 4H, ^2J = 9.7 Hz), 0.59 (s, 12H). ^{13}C NMR (acetone-d_6, 75.44 MHz): δ 167.55 (q), 161.78, 158.83 (q), 157.23 (q), 153.86, 153.45 (q), 148.30 (q), 147.63, 140.01, 138.04 (q), 130.42, 130.04, 129.58, 128.45, 126.78, 125.09, 122.51, 45.59, 45.18, 43.23 (q), 40.60, 39.93, 28.37, 25.70, 20.89. UV−vis (acetonitrile, 1.165E−5 M): 592 (9600), 405 (25 300), 292 (78 000), 237 (61 800).

Conclusions

Through the high-yield synthesis of enantiomerically pure building blocks of the type Δ- or Λ-[Ru(CG[*m*-xyl])Cl_2], numerous coordination species with well-defined stereochemistry can be obtained. For the first time, a chiral building block that cannot racemize, even under harsh reaction conditions, is now available. The lability of the two chloride ligands and the nonionic character of the complexes, resulting in high solubility in most organic solvents, render these new building blocks extremely useful.

Applications can be envisaged in the design of extended structures for photochemical molecular devices,[26] and chiral complexes in surfactant chemistry[18−21] and in the stereospecific interaction of coordination species with biomolecules.[27−29] The availability of corresponding Os(II) complexes would be important for electron- and energy-transfer studies in mixed Ru(II)/Os(II) compounds. Studies to apply the synthetic principles reported to Os(II) analogues are underway.

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