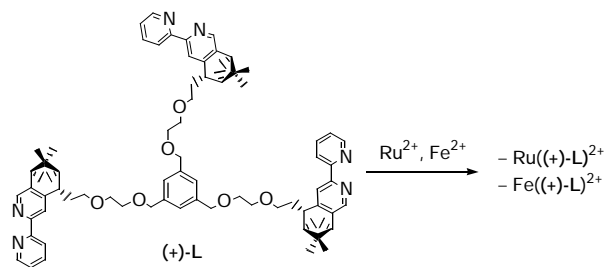Diastereoselective Synthesis of Coordination Compounds: A Chiral Tripodal Ligand Based on Bipyridine Units and its Ruthenium (II) and Iron (II) complexes

Christine Hamann, Alexander von Zelewsky[*], Antonia Neels, Helen Stoeckli-Evans

A chiral, enantiomerically pure, tripod ligand containing three bipyridine moieties coordinates with Fe(II) and Ru(II) in a completely stereoselective manner.

Diastereoselective Synthesis of Coordination Compounds: A Chiral Tripodal Ligand Based on Bipyridine Units and its Ruthenium (II) and Iron (II) complexes

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The enantiomerically pure chiral tris-chelating ligand **(+)-(7S, 10R)-L** (**L**) comprising three 4,5-pineno-bipyridine subunits connected through a mesityl spacer has been synthesized. Complexes of **L** with Ru[II] and Fe[II] have been prepared and characterised. NMR spectroscopy indicates that only one diastereoisomer is formed, and the CD spectra show that the complexes have the   configuration on the metal centre. X-ray crystal structure of the iron complex shows that in the octahedral complex, the ligand **L** coils around the metal and confirm the absolute configuration. The Ru[II] and Fe[II] compounds were also characterised by mass spectroscopy, electronic absorption, and, in the case of Ru(II) , fluorescence spectroscopy. The photostability of the ruthenium compound was checked by photochemical experiments.

Introduction

Diastereoselective synthesis, formerly called asymmetric synthesis, is a well established method in organic chemistry since it's introduction 110 years ago by E. Fischer.[1] A.P. Smirnoff introduced in a little known publication of 1920 an analogous procedure for coordination compounds.[2] However, even today, stereoselective synthesis of coordination compounds is not as widely practiced as it is in organic chemistry.[3]

C_3 symmetric ligands have been used before for stereoselective syntheses of octahedral metal complexes.[4-8] Since the introduction of "chiralized" pyridine ligands[9] a large

number of stereoselective syntheses with various members of this class of chelates has been carried out.[10]Most of these ligands comprise bipyridine moieties. Recently a C_3 symmetrical pinene pyridine ligand (scheme 1 **L₁**) was described where three pinene pyridine groups are connected through a tris(pyrazolyl)borate core.[11] The chiral centres of this hexa-dentate ligand are located in a peripheral situation with respect to the central metal that can coordinate to all six donor groups of the chelate. The tight binding of the three didentate coordination units through the borate centre favours a trigonal prismatic coordination, which was observed for the Tl(I) and the Tb(III) metal centres. Trigonal prismatic coordination geometry provides no bases for chirality at the metal centre.

We therefore designed new hexadentate ligands that will predetermine the configuration at octahedral metal centres. First attempts to form complexes with CHIRAGEN type ligands[12] where three pinene-bipyridine groups are linked through a simple mesityl group **L₂** (scheme 1)[13] failed to give well defined octahedral mononuclear complexes, presumably because of steric crowding. The introduction of spacer groups as in **L** (scheme 1) finally yielded the target complexes in good yields. Fe(II) and Ru(II) afford complexes in highly stereoselective reactions. That means that one and only one of the two possible helical configurations   or   at the metal centre are formed. The absolute configuration depends on the choice of the enantiomer of the 4,5-pinene-bipyridine. Both enantiomers of this key ligand are easily accessible, which means that also the metal complexes can be synthesized in either of the two absolute configurations.
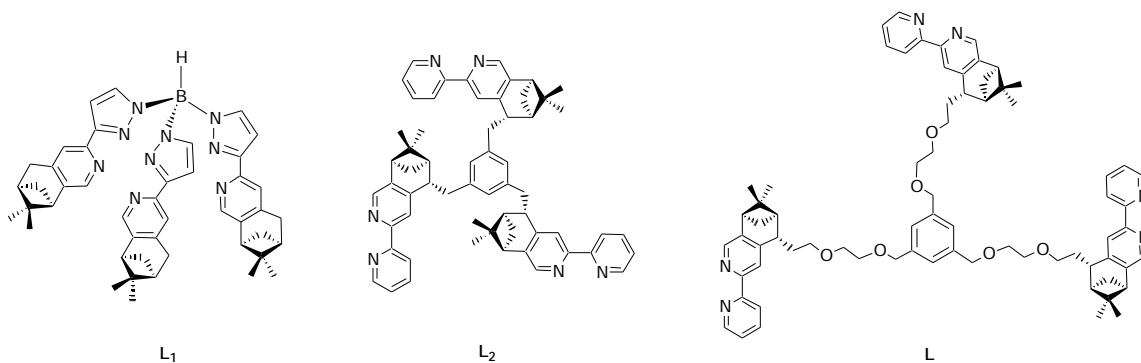
Scheme 1

Experimental

General.

NMR spectra were recorded on a Varian Gemini-300 (for 300 MHz NMR) or on a Bruker Advance DRX400 (for 400 MHz NMR) spectrometers. Chemical shifts are given in ppm using the solvent as internal standard. Mass spectral data were acquired on a Bruker FTMS 4.7 T BioApex II using a standard electrospray ion source (ESI). UV/Visible spectra were measured on a Perkin Elmer Lambda 40 spectrometer. Emission spectra were recorded on a Perkin Elmer LS 50B spectrometer. Circular dichroism (CD) spectra were recorded on a Jasco J-715 spectropolarimeter. The photochemical experiments were carried out on PF_6^- salts at room temperature in CH_2Cl_2 solutions. Irradiation was performed with a 500W Hg lamp (Thermo Oriel Universal Arc Lamp, model 66902) using a filter to isolate a band centred at 450 nm. The irradiated solutions were contained in a 1 cm spectrometer cell. Successive values of the CD absorption were taken after irradiation to follow the occurence of the photoreaction.

Materials.

Oxygen or water-sensitive reactions were conducted under a positive pressure of argon in oven-dried glassware, using Schlenk techniques. Unless otherwise stated, commercial grade reagents were used without further purification. The following materials were prepared according to literature procedures: 4,5-pineno-2,2'-bipyridine (**1**)[9], 2-(2'-iodoethoxy)ethyl-2''-tetrahydro-2H-pyran ether[14], 1,3,5-tris-bromomethyl-benzene (**2**)[15] and Ru(DMSO)$_4$Cl$_2$[16].

Precursor 3. To a freshly prepared solution of LDA (12 mmol in THF) cooled to –40°C, was added a degassed solution of **1** (1.51 g, 6.03 mmol in anhydrous THF) over 40 min. The solution turned dark blue and was stirred below –40°C for 2 h ; then 2-(2'-iodoethoxy)ethyl-2''-tetrahydro-2H-pyran ether (3.64 g, 12.1 mmol) dissolved in dry THF (30 ml) was added. The mixture was stirred overnight, and the reaction was quenched with water (2 ml). After evaporation of the THF *in vacuum*, the residue was taken up in a CH_2Cl_2/H$_2$O mixture and the organic layer was dried over MgSO$_4$ and filtered. Following removal of the solvent, the residue was purified by column

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chromatography on silica gel with hexane/ether/triethylamine (5 :1 :0.1 to 5 :3 :0.1) to yield the pure products as a colourless oil (2.01 g , 81%).

$_H$ (CDCl$_3$, 300 MHz): 8.64 (d, 1H, H$_{6'}$) ; 8.33 (d, 1H, H$_{3'}$) ; 8.32 (s, 1H, H$_3$) ; 8.18 (s, 1H, H$_6$) ; 7.76 (dd, 1H, H$_{4'}$) ; 7.25 (dd, 1H, H$_{5'}$) ; 4.65 (m, 1H, H$_{a'}$) ; 3.87 (m, 1H, H$_{e'}$) ; 3.67-3.60 (m, 6H, H$_{b,c,d}$) ; 3.14 (ddd, 1H, H$_7$) ; 2.84 (dd, 1H, H$_{10}$) ; 2.52 (ddd, 1H, H$_{9exo}$) ; 2.29-2.19 (m, 2H, H$_{8,aendo}$) ; 1.91-1.38 (m, 7H, H$_{b',c',d',aexo}$) ; 1.48 (s, 3H, H$_{13}$) ; 1.25 (d, 1H, H$_{9endo}$) ; 0.57 (s, 3H, H$_{12}$). $_C$ (CDCl$_3$, 100 MHz) : 157.1 ; 155.2 ; 150.0 ; 149.4 ; 145.8 ; 143.1 ; 137.2 ; 123.6 ; 121.2 ; 120.2 ; 99.4 ; 70.6 ; 70.5 ; 69.6 ; 67.1 ; 62.6 ; 45.5 ; 43.9 ; 41.4 ; 33.9 ; 31.0 ; 28.8 ; 26.7 ; 25.8 ; 21.4 ; 19.8. ESI-MS : m/z 423.26 ([M+H]$^+$)

Precursor 4. 3 (2.05 g, 4.85 mmol) dissolved in 100 ml of ethanol, was brought to reflux under argon before 2 drops HCl 37% were added. The solution was refluxed for 5h and ethanol was then removed. The residue was taken up in CH$_2$Cl$_2$/H$_2$O mixture. The aqueous layer was washed with 20 ml of a saturated solution of NaHCO$_3$ and extracted with CH$_2$Cl$_2$ (2x50 ml). The organic layers were combined, dried over MgSO$_4$ and the solvent was removed to leave an oil whose purity was good enough (>95 % by NMR) to be used without purification.

$_H$ (CDCl$_3$, 300 MHz) : 8.63 (d, 1H, H$_{6'}$) ; 8.46 (s, 1H, H$_3$) ; 8.36 (d, 1H, H$_{3'}$) ; 8.18 (s, 1H, H$_6$) ; 7.77 (dd, 1H, H$_{4'}$) ; 7.27 (dd, 1H, H$_{5'}$) ; 3.81 (m, 1H, H$_d$) ; 3.67-3.60 (m, 6H, H$_{b,c}$) ; 3.16 (ddd, 1H, H$_7$) ; 2.85 (dd, 1H, H$_{10}$) ; 2.49 (ddd, 1H, H$_{9exo}$) ; 2.27-2.19 (m, 2H, H$_{8,aendo}$) ; 1.88 (m, 1H, H$_{a\ exo}$) ; 1.41 (s, 3H, H$_{13}$) ; 1.25 (d, 1H, H$_{9endo}$) ; 0.61 (s, 3H, H$_{12}$). $_C$ (CDCl$_3$, 100 MHz) : 157.0 ; 154.9 ; 149.8 ; 149.3 ; 145.8 ; 143.1 ; 137.4 ; 123.7 ; 121.3 ; 120.6 ; 72.8 ; 70.0 ; 62.2 ; 45.4 ; 45.2 ; 41.6 ; 38.9 ; 34.6 ; 29.0 ; 26.7 ; 21.4. ESI-MS : m/z 339.20 ([M+H]$^+$).

(+)-(7S,10R)-L. To a suspension of NaH (0.41 g, 50% in mineral oil) in dry THF (30 ml) was added **4** (1.4 g, 3.9 mmol) at room temperature. The mixture was stirred at room temperature during 1h before 1,3,5-tris-bromomethyl-benzene (0.33 g, 0.97 mmol) in dry THF (5 ml) was added. The solution, which turned homogeneous was stirred 2 days and the reaction was quenched with ethanol (2 ml). The solvent was then removed *in vacuum* and the residue was extracted with CH$_2$Cl$_2$. The organic layer was washed with H$_2$O (3x20 ml) and dried over MgSO$_4$. After removing the solvent, the residue was first purified by column chromatography (Al$_2$O$_3$, eluent : hexane/EtOAc 4 :1 to 1 :1) and then

by preparative thin-layer chromatography (SiO$_2$, eluent : hexane/EtOAc/NEt$_3$ 1 :1 :0.1) to yield a white powder (0.42 g, 42%).

$_H$ (CDCl$_3$, 300 MHz) : 8.65 (d, 3H, H$_{6'}$) ; 8.35 (d, 3H, H$_{3'}$) ; 8.32 (s, 3H, H$_3$) ; 8.20 (s, 3H, H$_6$) ; 7.79 (dd, 3H, H$_{4'}$) ; 7.28-7.24 (m, 6H, H$_{5',a}$) ; 4.54 (s, 6H, H$_{e1,e2}$) ; 3.71-3.57 (m, 18H, H$_{b,c,d}$) ; 3.17 (m, 3H, H$_7$); 2.86 (dd, 3H, H$_{10}$) ; 2.56 (ddd, 3H, H$_{9exo}$) ; 2.35 (m, 3H, H$_{a\ endo}$) ; 2.26 (m, 3H, H$_8$) ; 1.81 (m, 3H, H$_{a\ exo}$) ; 1.42 (s, 9H, H$_{13}$) ; 1.26 (d, 3H, H$_{9endo}$) ; 0.62 (s, 9H, H$_{12}$). $_C$ (CDCl$_3$, 100 MHz) : 156.9 ; 155.0 ; 149.8 ; 149.3 ; 145.7 ; 143.0 ; 138.9 ; 137.1 ; 126.6 ; 123.5 ; 121.0 ; 120.1 ; 73.5 ; 70.5 ; 69.9 ; 69.6 ; 45.3 ; 43.8 ; 41.2 ; 38.4 ; 33.7 ; 28.7 ; 26.6 ; 21.3. ESI-MS : m/z 1129.67 ([M+H]$^+$). [ ]$_D$ = + 570°, 25°C, 0.044 g.L^{-1}.

- **[Ru.L](PF$_6$)$_2$.** **L** (46.6 mg, 0.041 mmol) and Ru(DMSO)$_4$Cl$_2$ (20.02 mg, 0.041 mmol) were dissolved in two portions of a mixture of EtOH and CHCl$_3$ (1 :1 ; 20 ml). The two solutions were simultaneously added dropwise to refluxing EtOH (400 ml) with the aid of a syringe pump (rate 1ml.h^{-1}) and under vigorous stirring. After the addition, the orange mixture was refluxed for 3 additional hours, evaporated and purified by preparative thin layer chromatography (SiO$_2$) eluting with acetonitrile/ethanol/water/sat.aq. KNO$_3$ (8 :1 :1 :0.1). The product was extracted from silica with acetone containing 10% ammonium hexafluorophosphate to yield an orange powder (37 mg, 58%).

$_H$ (acetone-d^6, 400 MHz) : 8.69 (d, 3H, H$_{3'}$) ; 8.63 (s, 3H, H$_3$) ; 8.04 (dd, 3H, H$_{4'}$) ; 7.69 (d, 3H, H$_{6'}$) ; 7.30 (dd, 3H, H$_{5'}$) ; 7.25 (s, 3H, H$_6$) ; 7.02 (s, 3H, H$_a$) ; 4.34 (d, 3H, H$_{e1}$) ; 4.03 (d, 3H, H$_{e2}$) ; 3.72-3.27 (m, 21H, H$_{b,c,d,7}$) ; 3.03 (m, 3H, H$_{aendo}$) ; 2.98 (m, 6H, H$_{9exo,10}$) ; 2.27 (m, 3H, H$_8$) ; 1.99 (m, 3H, H$_{aexo}$) ; 1.84 (d, 3H, H$_{9exo}$) ; 1.41 (s, 9H, H$_{13}$) ; 0.19 (s, 9H, H$_{12}$). $_C$ (acetone-d^6, 100 MHz) : 158.8 ; 154.3 ; 151.9 ; 151.3 ; 147.7 ; 146.4 ; 137.9 ; 137.5 ; 130.7 ; 126.5 ; 123.6 ; 123.4 ; 72.3 ; 70.5 ; 68.0 ; 67.2 ; 44.7 ; 44.2 ; 41.3 ; 39.1 ; 32.7 ; 27.9 ; 25.8 ; 20.1. ESI-MS : m/z 1375.50 ([M-PF$_6^-$]$^+$) ; 615.28 ([M-2PF$_6^-$]$^{2+}$). UV-Vis (CH$_2$Cl$_2$) : 449 (= 18400 dm^3 mol^{-1} cm^{-1}), 424 (sh, 15200), 301 (80700). Emission (CH$_2$Cl$_2$) : excitation 454 nm, emission 612 nm. CD (CH$_2$Cl$_2$ in nm (in mol CD)) : 300 (214) ; 282 (-110).

- **[Fe.L](PF$_6$)$_2$.** To a solution of **L** (17 mg, 0.015 mmol) in ethanol/CHCl$_3$ (1 :1, 10 ml) was added Fe(SO$_4$)$_2$(NH$_4$)$_2$. 6H$_2$O (5.9 mg, 0.015 mmol) dissolved in water. The mixture was heated at reflux for 24h under argon after which the volume was reduced to 1 mL,

and the product was precipitated with the addition 10% aqueous ammonium hexafluorophosphate solution. The fuchsia solid was filtered off and purified by column chromatography (SiO$_2$, eluent : acetonitrile/ethanol/water/sat.aq. KNO$_3$ (10 :1 :1 :0.1) (8 mg, 32%).

$_H$ (acetone-d^6, 400 MHz) : 8.68 (d, 3H, H$_{3'}$) ; 8.64 (s, 3H, H$_3$) ; 8.08 (dd, 3H, H$_{4'}$) ; 7.36 (d, 3H, H$_{6'}$) ; 7.30 (dd, 3H, H$_{5'}$) ; 7.02 (s, 3H, H$_6$) ; 6.97 (s, 3H, H$_a$) ; 4.35 (d, 3H, H$_{e1}$) ; 4.05 (d, 3H, H$_{e2}$) ; 3.74-3.25 (m, 21H, H$_{b,c,d,7}$) ; 3.05 (m, 3H, H$_{aendo}$) ; 2.90 (m, 6H, H$_{9exo,10}$) ; 2.25 (m, 3H, H$_8$) ; 1.99 (m, 3H, H$_{aexo}$) ; 1.86 (d, 3H, H$_{9exo}$) ; 1.41 (s, 9H, H$_{13}$) ; 0.15 (s, 9H, H$_{12}$); $_C$ (acetone-d^6, 100 MHz) :161.5 ; 157.1 ; 154.1 ; 153.0 ; 150.3 ; 146.8 ; 138.7 ; 138.1 ; 130.9 ; 126.7 ; 123.7 ; 123.2 ; 72.7 ; 70.6 ; 68.4 ; 67.3 ; 44.9 ; 44.5 ; 41.5 ; 39.3 ; 32.9 ; 28.1 ; 26.0 ; 20.3. ESI-MS : m/z 1329.56 ([M-PF$_6$$^-$]$^+$), 592.29 ([M-2PF$_6$$^-$]$^{2+}$); UV-vis (CH$_2Cl_2$) : 523 (= 11500 dm^3 mol^{-1} cm^{-1}), 472 (sh, 9300) , 354 (12000) , 308 (57000); CD (CH$_2$Cl$_2$ in nm (in mol CD)) : 313 (179) , 296 (-89).

X-ray Crystallography.

Suitable single crystals of -[Fe.**L**](PF$_6$)$_2$ were obtained by slow diffusion of diisopropylether into CH$_2$Cl$_2$ solution of the complex at room temperature.

Crystallographic data for -[Fe.**L**](PF$_6$)$_2$ are collected in Table 1. Data were measured at –120°C using Mo-Ka radiation (= 0.71073 Å) with a Stoe Mark II-Imaging Plate Diffractometer System (Stoe & Cie, 2002) equipped with a graphite-monochromator. The structure was solved by direct methods using the program SHELXS-97[17] and refined by full matrix least squares on F^2 with SHELXL-97[18]. The absolute structure was determined based on the presence of heavy atoms (iron) in the structure. All hydrogen atoms were included in calculated positions and treated as riding atoms using SHELXL-97 default parameters.

Formula	$C_{77 \cdot 50}H_{96}Cl_{15}F_{12}FeN_6O_{6 \cdot 50}P_2$
Molecular weight	1738.64
Crystal system	Monoclinic
Space group	P21
a(Å)	11.2488(4)
b(Å)	26.3679(7)
c(Å)	27.9714(1)
(deg)	90.00
(deg)	94.361(3)
(deg)	90.00
V(Å^3)	8272.5(5)
Z	4
Dcalc(g.cm^{-3})	1.396
μ(mm-1)	0.464
Temperature(K)	153(2)
Wavelength(Å)	0.71073
Reflections measured	45053
Independent reflections	26453
Observed reflections	23388
Goodness-of-fit on F^2	1.022
Rint	0.0486
R indices (I>2SI) R1[a]	0.0611
wR2[b]	0.1613

[a] R1 = F0 - Fc / F0 . [b]wR2 = [w(F0 - Fc)^2/ w(F0 ^{2})]$^{1/2}$.

**Table 1**. Crystal data and structure refinement details for -[Fe.L](PF$_6$)$_2$ complex.

Results and discussion

Design and Synthesis.

The chelating sidearms were attached to the mesityl tripode **2** *via* an alkoxy chain derivative to allow sufficient flexibility to organise them around six-coordinate metal ions, preventing unwanted complex formation such as polynuclear compounds :

The preparation of intermediates **3** and **4** from the precursor **1** and the synthesis of the ligand **L** are represented in scheme 2.
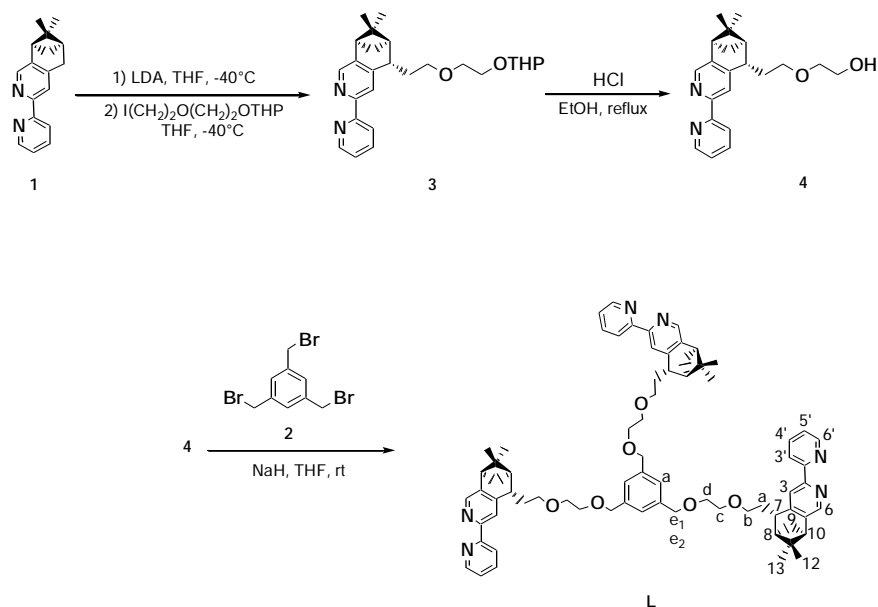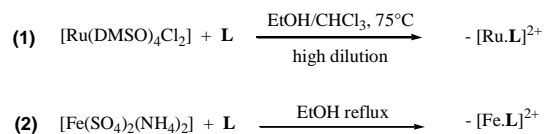
Scheme 2

The preparation of **1** was previously described[9, 19] where the key step is a Kröhnke-type reaction.[20-22] The chiral pinene-type framework of **1** is deprotonated regioselectively by LDA. The anion formed is then alkylated 100% stereoselectively at the less hindered side with 2-(2'-iodoethoxy)ethyl-2''-tetrahydro-*2H*-pyran ether to give **3**. The THP protective group is then cleaved by an acidic treatment to yield **4**. The ligand **L** is finally obtained according to a convergent strategy in which three molecules **4** are connected to the tripode **2** as shown in scheme 2.

The chelating properties of ligand **L** were tested on Ru(II) and Fe(II) (Scheme 3). Ru(DMSO)$_4$Cl$_2$ reacts with stoechiometric amounts of **L** in refluxing ethanol and in high dilution conditions in order to avoid the formation of polynuclear complexes.[23, 24] The crude product can be purified by preparative plate silica chromatography. The complex was isolated as its hexafluorophosphate salt.

The iron complex is prepared by mixing stoichiometric amounts of Fe(SO$_4$)$_2$(NH$_4$)$_2$ and ligand **L** in a 1 :1 mixture of EtOH/H$_2$O and then heated at reflux temperature for 24 h.

$$\textbf{(1)} \quad [\text{Ru(DMSO)}_4\text{Cl}_2] \; + \; \textbf{L} \xrightarrow[\text{high dilution}]{\text{EtOH/CHCl}_3, \, 75°\text{C}} \; \text{-} \, [\text{Ru.L}]^{2+}$$

$$\textbf{(2)} \quad [\text{Fe(SO}_4)_2(\text{NH}_4)_2] \; + \; \textbf{L} \xrightarrow{\text{EtOH reflux}} \; \text{-} \, [\text{Fe.L}]^{2+}$$

Scheme 3

^{1}H-NMR Spectra

The complexation of **L** is completely diastereoselective as shown by the ^{1}H-NMR spectra (the pineno methyl peaks give a good indication of the number of isomers present). A comparison of the spectra of the free ligand **L**, [Ru.**L**](PF$_6$)$_2$, and [Fe.**L**](PF$_6$)$_2$ is shown in Figure 1. **L** (C$_3$ symmetry) displays the characteristic low field signals for the protons 6 and 6' at, respectively, $= 8.20$ and $= 8.65$ ppm. Homotopic protons e$_1$ and e$_2$ of the mesityl bridge (Scheme 1) appear as a singlet at 4.54 ppm. Coordination of **L** to either of the two metal centres Fe^{2+} or Ru^{2+} produces chiral complexes : as a consequence, protons e$_1$ and e$_2$ become diastereotopic and appear as a pair of doublets.

Upon Ru(II) coordination, the protons 6 and 6' are shifted upfield ($= - 0.94$ ppm for 6 and $= - 0.96$ ppm for 6') because the deshielding effect of the metal centre on the protons a to the nitrogen atoms is counterbalanced by the shielding field of the other bipyridines units. The protons e$_1$ and e$_2$ also move upfield ($= - 0.20$ ppm and $= - 0.51$ ppm, respectively) because the twist of the ligand places them in the shielding cone of the bipyridine moieties.

The spectrum of [Fe.**L**](PF$_6$)$_2$ is very similar to that of [Ru.**L**](PF$_6$)$_2$ except for the protons closest to the metal centre (i.e. 6 and 6'), which are shifted more upfield. This could be in relation to the smaller size of the Fe^{2+} cation by comparison with Ru^{2+}, which places these protons closer to the shielding cone of the bipyridines units.
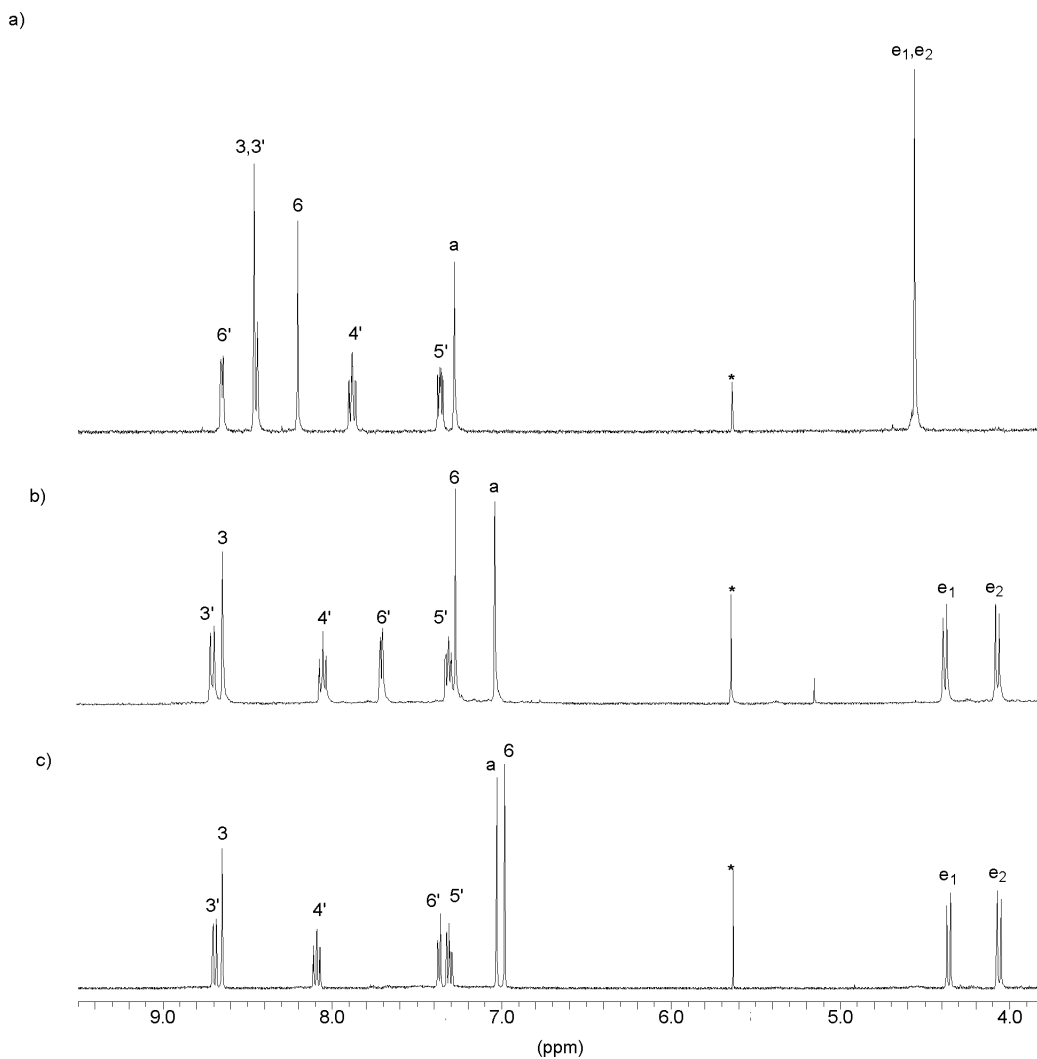
Figure 1. 400 MHz ^{1}H spectra in acetone d^6 of a) ligand **L**, b) complex ∆-[Ru.**L**]$^{2+}$ and c) complex ∆-[Fe.**L**]$^{2+}$ (298 K) ; * corresponds to small traces of CH$_2$Cl$_2$.

CD Spectra

The ligand **L** shows no activity in its CD spectrum between 600 and 250 nm in dichloromethane.

[Fe.**L**](PF$_6$)$_2$ and [Ru.**L**](PF$_6$)$_2$ show a Cotton effect[25] at 282 nm and 300 nm for the ruthenium (II) compound and at 296 nm and 313 nm for the iron (II) complex (Figure 2). The sign of ∆ in the UV region indicates clearly that the ∆ isomers are obtained in both cases.
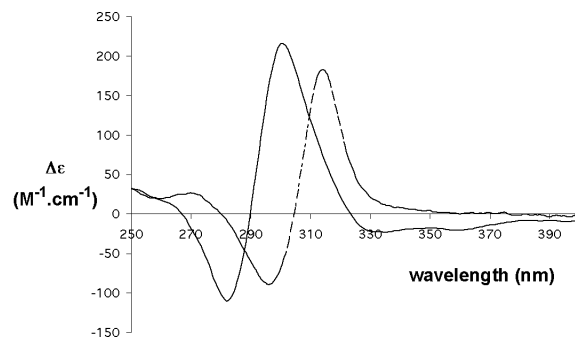
Figure 2. CD spectra of Δ-[Ru.**L**]$^{2+}$ (solid line) and Δ-[Fe.**L**]$^{2+}$ (dashed line) measured in dichloromethane.

UV-Vis Absorption and Emission spectra

The electronic spectroscopy data (absorption and emission) are collected in Table 1, together with those of reference compounds.

Complex	$\lambda_{max} \pm 2$, nm ($10^{-3} \varepsilon$)	$\lambda_{em} \pm 2$, nm
[Ru(bpy)$_3$]$^{2+}$	288 (76.6); 452 (13.6)[26-29]	610[30]
[Fe(bpy)$_3$]$^{2+}$	297 (60.0); 349 (6.3) 523 (8.7)[31]	
Δ-[Ru.L]$^{2+}$	301 (80.7); 449 (18.4)	612
Δ-[Fe.L]$^{2+}$	308 (57.0); 354 (12.0) 523 (11.5)	

**Table 2.** UV-visible Absorption and luminescence data in CH$_2$Cl$_2$ at 298K.

The absorption spectra of the complexes are basically similar to those for other M(tris-diimine) (M = Ru(II), Fe(II)) complexes.

Δ-[Ru.**L**]$^{2+}$ has a spectrum almost identical with that for Ru(bipy)$_3$$^{2+}$[26-29], with a maximum at 449 nm (MLCT transition) and a shoulder at 424 nm. In addition, it exhibits a strong luminescence at approximately the same wavelengths (610 nm) as Ru(bipy)$_3$$^{2+}$.[30]

Also Δ-[Fe.**L**](PF$_6$)$_2$ shows a spectrum very similar to that of Fe(bipy)$_3^{2+}$[31] with a maximum at 523 nm, which is assigned to the MLCT transition.

Photostability

To check the photostability of the complex Δ-[Ru.**L**]$^{2+}$, a solution containing the compound (1.3 x 10^{-5} M in CH$_2$Cl$_2$) was irradiated with 450 nm light (*see experimental section*). No change in the CD spectrum, as well as in the absorption spectrum, is observed, even after 4 hours of irradiation (Figure 3(a)). Under the same experimental conditions, the irradiation of the complex Δ-[Ru(bpy)$_3$]$^{2+}$ (2.3 x 10^{-5} M in CH$_2$Cl$_2$) resulted in a regular decrease in the intensity of the CD spectrum (Figure 3(b)) with no change in the absorption spectrum, indicating that photoracemisation occurs[32, 33] without photodecomposition.
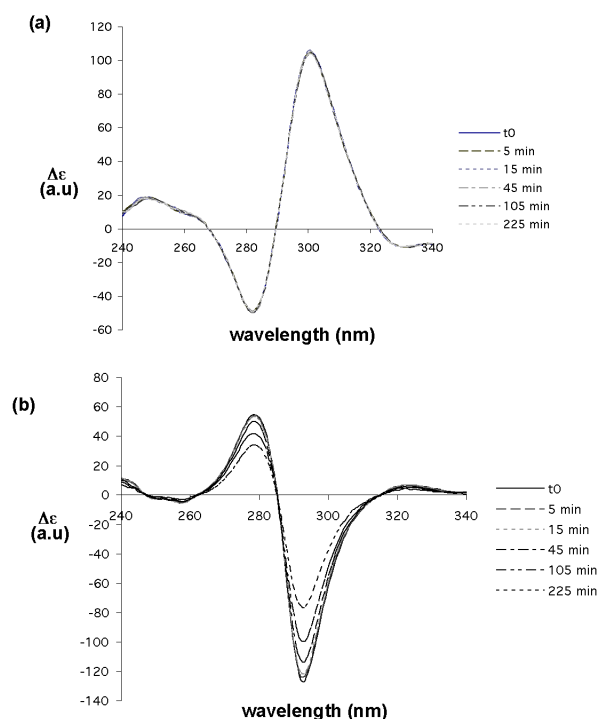

Figure 3. CD spectra obtained after irradiation of Δ-[Ru.L]$^{2+}$ (a), Δ-[Ru(bpy)$_3$]$^{2+}$ (b)

X-Ray structure analysis.

The crystal structure of the iron complex confirms the formation of the cationic 1 :1 complex Δ-[Fe.**L**]$^{2+}$. The Fe(II) compound crystallises with two complex molecules per

asymmetric unit in the non-centrosymmetric space group $P2_1$. A view of the complex is shown in Figure 4 and Table 2 contains selected bond lengths and bond angles. The second complex in the unit cell shows very similar values for these parameters. The structure shows nicely the coiling of the tris-chelate ligand **L** around the Fe(II) centre. The helical threads in the complex adopt a single screw direction, leading to an overall regular triple helical arrangement of the tripode : the isomer is obtained. The metal adopts a pseudo-octahedral geometry with Fe⋯N distances in the range 1.959-1.976 Å and bite angles within each chelate around 82°. Relatively small deformations of the bipyridine subunits are observed : the torsional angles N-C-C-N ranging between 12.0° and 12.9°, but the overall structure shows an almost strain-free coordination of the ligand to the metal centre.
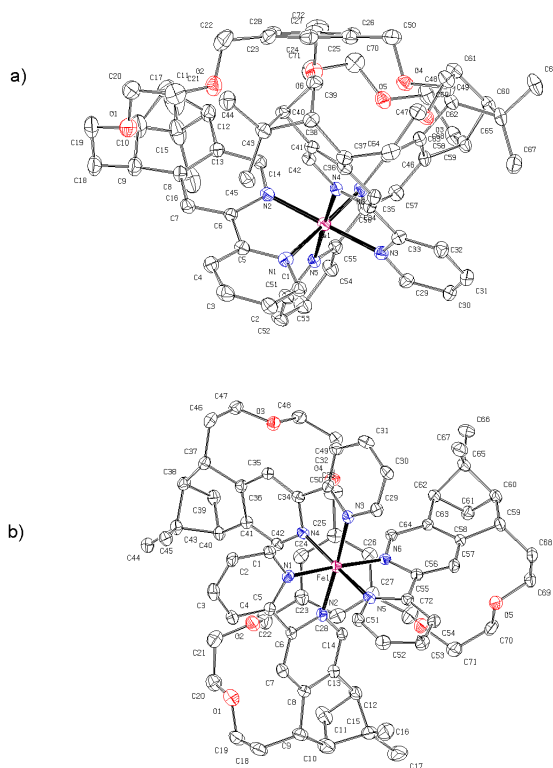
Figure 4. X-ray crystal structure of the cation -[Fe.**L**]$^{2+}$ a) perpendicular to the C_3 axis, b) along the C_3 axis. Thermal ellipsoids are given with 30% probability. Hydrogen atoms are omitted for clarity.

Fe-N1	1.969(4)
Fe-N2	1.959(4)
Fe-N3	1.973(4)
Fe-N4	1.976(4)
Fe-N5	1.961(4)
Fe-N6	1.951(4)
N1-Fe-N4	83.6(6)
N2-Fe-N5	87.0(1)
N6-Fe-N3	85.9(2)
N2-Fe-N1	82.2(6)
N3-Fe-N4	81.9(2)
N6-Fe-N5	81.7(7)
N5-Fe-N4	177.5(0)
N2-Fe-N3	176.8(5)
N6-Fe-N1	177.0(4)

Table 3. Selected bond lengths (Å) and bond angles (deg) in -[Fe.**L**](PF$_6$)$_2$.

Metal d^6 tris-complexes with asymetric chelate ligands can have either a facial (*fac*) or a meridional (*mer*) configuration. In our case, only the facial configuration is obtained, due to the rigidity of the ligand.

Some crystals of the ruthenium complex -[Ru.**L**](PF$_6$)$_2$ were obtained but their quality was not good enough (low resolution). It can be mentioned that its structure is isomorphous with -[Fe.**L**](PF$_6$)$_2$.

Conclusion

The judicious design of a chiral tripod ligand that can be synthesised in an enantiomerically pure form from a chiral pool precursor enables the formation of octahedral metal complexes with predetermined configuration at the metal centre.

The crystal structure of [Fe.**L**]$^{2+}$ reveals that the ligand coils around the metal yielding a helix with   configuration. This absolute configuration is confirmed by the circular dichroïsm (CD) spectra. NMR studies show that Fe.**L** exists in solution as a pure diastereomer. Although we were not able to obtain a crystal structure for [Ru.**L**]$^{2+}$, NMR and CD analyses indicate that this complex displays a structure similar to that found for -[Fe.**L**]$^{2+}$, i.e. only the   isomer is obtained.

The rigid connection of the three bipyridine units renders   -[Ru.**L**]$^{2+}$ much more stable as compared to its extremely well studied parent complex Ru(bpy)$_3{}^{2+}$. This stability manifests itself e.g. in the strongly enhanced photostability of this Ru-complex, which is comparable to that of a cage complex of Ru^{2+}.[34]

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