Stereoselectivity in the formation of tris-diimine complexes of Fe(II), Ru(II), and Os(II) with a C_2-symmetric chiral derivative of 2,2′-bipyridine†

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A C_2-symmetric enantiopure 4,5-bis(pinene)-2,2′-bipyridine ligand (−)-**L** was used to investigate the diastereoselectivity in the formation of $[ML_3]^{2+}$ coordination species (M = Fe(II), Ru(II), Os(II), Zn(II), Cd(II), Cu(II), Ni(II)), and $[ML_2Cl_2]$ (M = Ru(II), Os(II)). The X-ray structures of the $[ML_3]^{2+}$ complexes were determined for Δ-$[FeL_3](PF_6)_2$, Δ-$[RuL_3](PF_6)_2$, Λ-$[RuL_3](PF_6)_2$, Δ-$[OsL_3](PF_6)_2$, and Λ-$[OsL_3](TfO)_2$. All of these compounds were also characterized by NMR, CD and UV/VIS absorption spectroscopy. The $[FeL_3]^{2+}$ diastereoisomers were studied in equilibrated solutions at various temperatures and in several solvents. The $[RuL_3]^{2+}$ complexes, which are thermally stable up to 200 °C, were photochemically equilibrated.

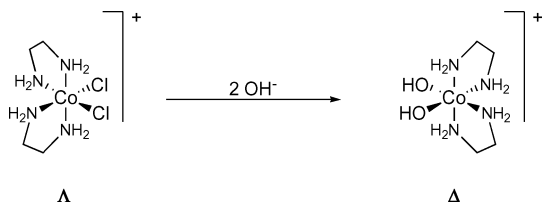
Introduction

In the third edition of his book from 1913,[1] Alfred Werner mentions a series of substitution reactions at metal centres containing the $Co^{III}(en)_2$ moiety. Werner assumes that in all these transformations, *e.g.* in eqn (1), the absolute configuration is retained.

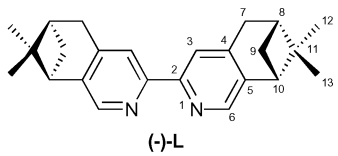
$$(-)\text{-}[CoCl_2(en)_2]^+ + CO_3^{2-} \rightarrow (+)\text{-}[Co(CO_3)(en)_2]^+ \qquad (1)$$

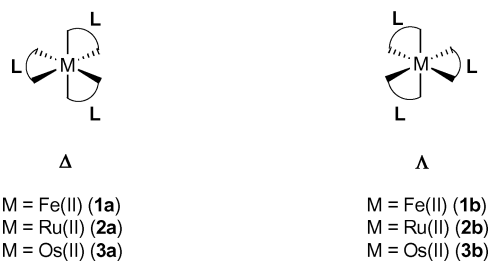
At that time, a definitive proof of the stereochemical course of this type of reaction could not be easily given. It seems that Werner has assumed that chiral octahedral coordination centres undergo substitution reactions in which the configuration is *always* retained (except for cases when racemization occurs). An analogous statement for tetrahedral reaction centres had already been dispelled by Walden in 1896 and 1897.[2] For octahedral centres the first observation of an inversion in a substitution reaction was reported by John C. Bailar Jr in 1934[3] for the reaction of chiral Co^{III} complexes (Scheme 1). This reaction has been studied by W. G. Jackson[4] in detail and it was shown that two Cl^- ligands are simultaneously substituted. But even 70 years after Bailar's report, a general mechanistic explanation of an inversion process at an octahedral centre seems to be missing,[4] whereas inversion at tetrahedral centres is a well understood process.

The observation of opposite configurations at the metal centre in the diastereoselective formation of tris-complexes with an enantiopure derivative of bipyridine (−)-**L** (Scheme 2) prompted us to investigate the stereochemical course of the reactions leading to ML_3 species. Special emphasis was put on the problem of whether inversion could occur upon substitution at octahedral centres under certain conditions with this type of ligand.



Scheme 1 Bailar inversion at an octahedral centre.





Scheme 2

Recently, interesting investigations on the diastereoselectivity of the formation of tris-bpy type complexes have been published.[25] These cases, however, are not directly comparable to our system, since the selective interactions are mainly determined by polar substituents of the bpy core.

Results and discussion

Ligand synthesis

The ligand (−)-**L** 4,5-bis(pinene)-2,2′-bipyridine was prepared according to a previously described strategy[5] using double Kröhnke cyclization[6] of pyridinium salts (Scheme 3).

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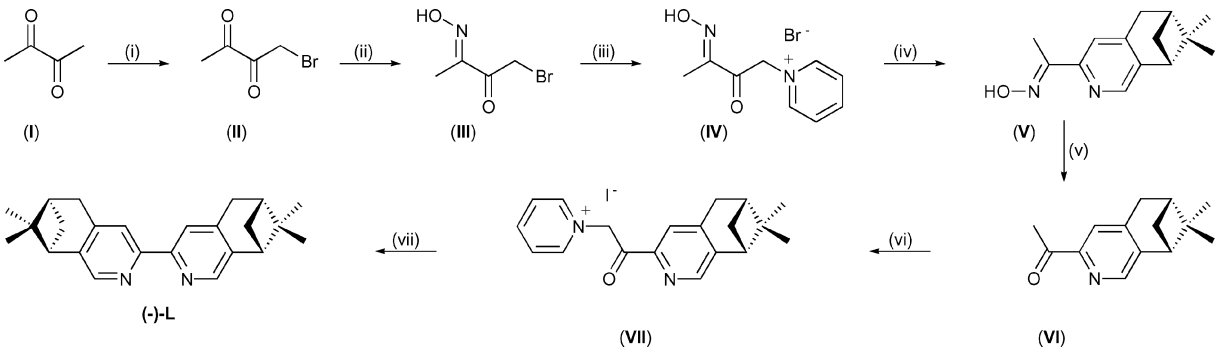


Scheme 3 Synthesis of the ligand (−)-**L**. (i) Br_2, 0 °C; (ii) 50% aq. NH_2OH, 0 °C; (iii) pyridine, Et_2O, rt; (iv) (−)-myrtenal, NH_4OAc, formamide, rt, 5 d; (v) aq. HCl, reflux; (vi) I_2, pyridine; (vii) (−)-myrtenal, NH_4OAc, formamide, rt, 5 d.

The synthesis consists of the monobromination of butane-2,3-dione (**I**),[24] formation of the monooxime (**III**), and alkylation of pyridine giving the first Kröhnke salt (**IV**), which undergoes a condensation reaction with (−)-myrtenal in presence of ammonium acetate to yield the oxime intermediate (**V**). The latter is hydrolyzed to ketone (**VI**), the second Kröhnke salt (**VII**) is formed, and final cyclization with (−)-myrtenal gives the desired ligand (−)-**L**. The protocol presented here (see ESI†) brings some improvement to our formerly published approach,[7] and it also represents an alternative to a synthesis reported by Kočovský.[8]

Formation of the complexes and analysis of their configurations

A distinct difference in the behaviour of tris-diimine complexes of the group 8 metals Fe(II), Ru(II) and Os(II) is the lability with respect to ligand exchange reactions. For example, for all three metals, the $[M(bpy)_3]^{2+}$ complexes formed as racemates, Δ-$[M(bpy)_3]^{2+}$, and Λ-$[M(bpy)_3]^{2+}$ which can be resolved by chiral auxiliaries. However, $[Ru(bpy)_3]^{2+}$ and $[Os(bpy)_3]^{2+}$ are highly stable in their optically active forms, while Δ-$[Fe(bpy)_3]^{2+}$ and Λ-$[Fe(bpy)_3]^{2+}$ racemize within minutes in aqueous solutions at room temperature.[9]

Ligand (−)-**L** forms the complex $[FeL_3]^{2+}$ as a mixture of two diastereoisomers, Δ-$[FeL_3]^{2+}$ (**1a**) and Λ-$[FeL_3]^{2+}$ (**1b**). The Δ-(**1a**) diastereoisomer is the more abundant species in the reaction product, and can be obtained in crystalline form, and its structure was determined by X-ray diffraction. The iron centre is relatively labile, and the isomeric ratio changed quite drastically upon variation of the temperature and solvent. The isomerization of Δ-$[FeL_3]^{2+}$ (**1a**) was observed by CD and NMR spectroscopy after the pure crystalline diastereoisomer had been dissolved at room temperature in various solvents. Fig. 1 shows the ^{1}H

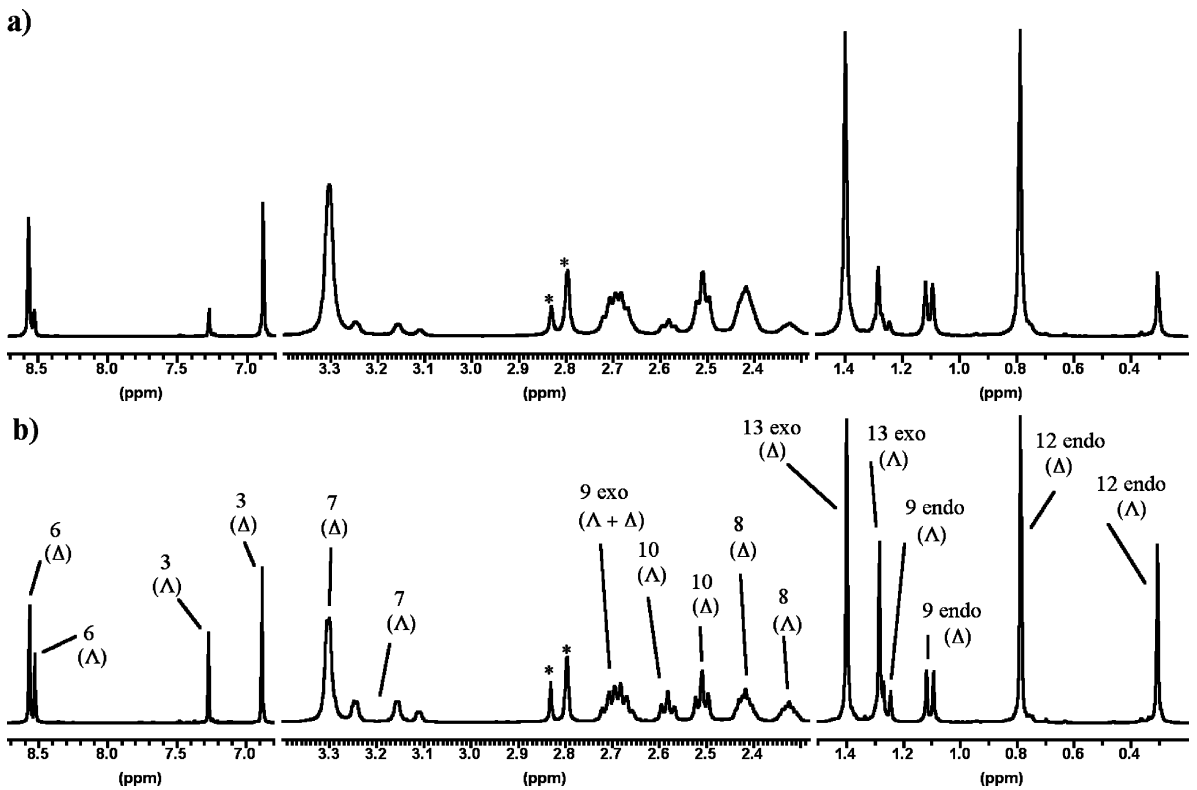


Fig. 1 ^{1}H NMR spectra of Δ/Λ-$[FeL_3]^{2+}$ in acetone-d_6: (a) Δ-$[FeL_3]^{2+}$, 5 min after dissolving; (b) Δ-$[FeL_3]^{2+}$, equilibrated solution after *ca.* 1 h.

NMR spectrum of a solution obtained by dissolving deep red crystals of Δ-$[FeL_3](PF_6)_2$ in acetone-d_6 after *ca.* 5 min, and after equilibration (*ca.* 1 h). The NMR pattern is relatively simple due to the high symmetry (D_3) of the complexes. The two diastereoisomers are clearly discernible, and their assignment to the two species Δ-$[FeL_3]^{2+}$ (**1a**), and Λ-$[FeL_3]^{2+}$ is straightforward. The following diastereomeric ratios were observed in equilibrated solutions (eqn (2)), after *ca.* 3 d at room temperature; $\Delta/\Lambda = 1.7$ (acetone), 2.8 (DMSO), 6.3 (acetonitrile), and 25 (ethylene glycol).

$$\Lambda\text{-}[FeL_3]^{2+} \rightleftharpoons \Delta\text{-}[FeL_3]^{2+} \quad (2)$$

Fig. 2 shows the CD spectrum of an equilibrated solution of Δ/Λ-$[FeL_3]^{2+}$ in acetonitrile at room temperature. The sign of the exciton couplet in the π–π* region (275–320 nm) corresponds to the contribution of the preponderant Δ-configured complex.[10] The CD activity in the MLCT region (430–580 nm) is much smaller, but has the same sign.

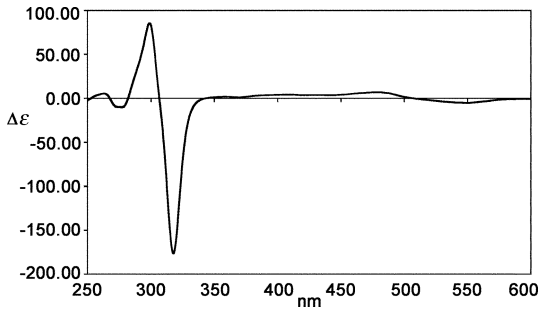
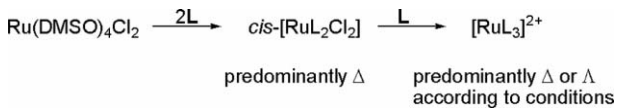


Fig. 2 CD spectra of an equilibrated acetonitrile solution of $[FeL_3]^{2+}$ in favour of Δ-diastereoisomer ($\Delta/\Lambda = 6.3$).

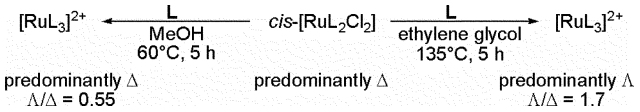
Thus for Fe^{II}, Δ is the more stable diastereoisomer in all solvents examined. The free energy differences vary between 1.32 kJ mol^{-1} for acetone, and 7.98 kJ mol^{-1} for ethylene glycol. The temperature dependence of equilibrium (2) was determined by NMR spectroscopy in acetonitrile-d_3 over the range 0–40 °C. The data fit a van't Hoff plot with the values of $\Delta H° = -8.9$ kJ mol^{-1} and $\Delta S° = -15$ J mol^{-1} K^{-1}. Although we were not able to crystallize the thermodynamically less stable Λ-$[FeL_3]^{2+}$ (**1b**), we can unambiguously assign the Δ-$[FeL_3]^{2+}$ (**1a**) complex as the thermodynamically preferred product.

While the $[FeL_3]^{2+}$ complexes form at room temperature, and equilibrium between diastereoisomers is reached within hours, as reported above, Ru^{II}, and, as will be shown later, Os^{II} complexes can only be synthesized at higher temperatures. Convenient starting materials for the Ru^{II} complexes are $Ru(DMSO)_4Cl_2$ and $Ru(MeCN)_4Cl_2$, respectively. After reaction of these compounds with 2 (−)-**L** in methanol, an intermediate compound *cis*-$[RuL_2Cl_2]$ can be isolated (Scheme 4).



Scheme 4

Its CD spectrum indicates clearly a predominance of the Δ-configured diastereoisomer. Further substitution of the two remaining chloride ligands by (−)-**L** leads to $[RuL_3]^{2+}$, which, surprisingly, shows a preference for either the Δ-, or the Λ-configured species, depending on reaction conditions (Scheme 5).



Scheme 5

If $[RuL_3]^{2+}$ is prepared in a one step reaction starting from $Ru(DMSO)_4Cl_2$ with a small excess of (−)-**L** (Ru : L = 1 : 3.3) in ethylene glycol, the same ratio of $\Lambda/\Delta = 1.7$ is obtained, as shown in Fig. 3, which is the ^1H NMR spectrum of the raw product after precipitation of its PF_6^- salt.

Thus, under these conditions (reaction medium: ethylene glycol), the opposite configuration is preferred, as compared to the $[FeL_3]^{2+}$ complex, whereas the same configuration is preferred when the reaction is carried out starting from the predominantly Δ-configured intermediate *cis*-$[RuL_2Cl_2]$ in methanol.

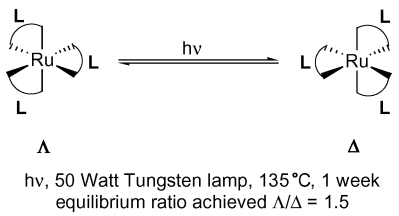
Are these differences due to thermodynamic or kinetic control? Could it be possible that in one of the substitution steps an inversion occurs? In order to answer these two questions, several other experiments were carried out.

Separation of the two diastereoisomers Δ-$[RuL_3]^{2+}$ (**2a**), and Λ-$[RuL_3]^{2+}$ (**2b**) by crystallization led to the pure PF_6^- salts, which could be completely characterised by X-ray structure analysis and NMR, CD, and UV/VIS spectroscopy.

Fig. 4 shows the CD spectra of the two pseudo-enantiomers Δ-$[RuL_3]^{2+}$ and Λ-$[RuL_3]^{2+}$, respectively.

A comparative discussion of the UV/VIS spectra of the Fe^{II}, Ru^{II}, and Os^{II} complexes will be given later in this publication.

Both Δ-, and Λ-$[RuL_3]^{2+}$ were dissolved in ethylene glycol and heated in a pressure tube to 200 °C for one week. After that time no change in the NMR spectra could be observed. Thus, thermal equilibrium could not be established between the two species. However, under the influence of relatively weak irradiation in the visible region by a 50 W tungsten lamp, equilibrium has been established at 135 °C in ethylene glycol after *ca.* 7 d. A ratio of $\Lambda/\Delta = 1.5$ was reached from either side under these conditions (Scheme 6).



Scheme 6

This photodiastereoisomerization is analogous to the well known photoracemization of $[Ru(bpy)_3]^{2+}$.[11] The activation of this process is believed to proceed through a thermal population of a ^3MC (metal-centred) state from the lowest excited ^3MLCT state of the complexes.[11] The photon in Scheme 6 can be considered to catalyse the reaction, leading to thermodynamic equilibrium.

Accordingly for $[RuL_3]^{2+}$, the Λ-configured species seems to be 1.38 kJ mol^{-1} more stable, which corresponds to a $K_{equilib.} = 1.5$. Photocatalytic diastereoisomerization was repeated for Δ,Λ-

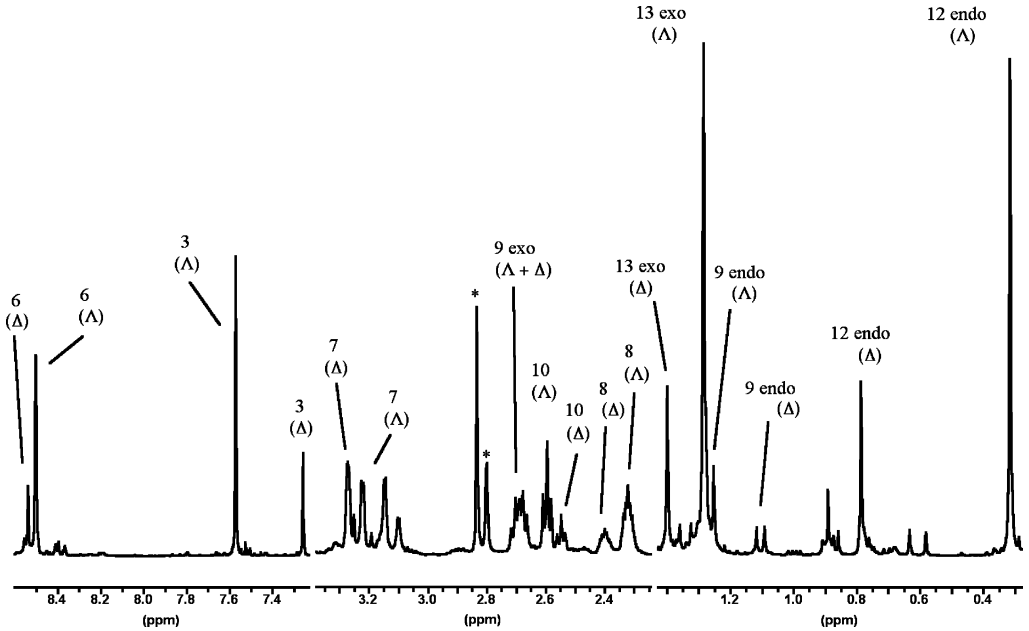


Fig. 3 ^{1}H-NMR spectra of $[RuL_3]^{2+}$ in acetone-d_6 (raw product after precipitation of its PF_6^- salt, $\Lambda/\Delta = 1.7$).

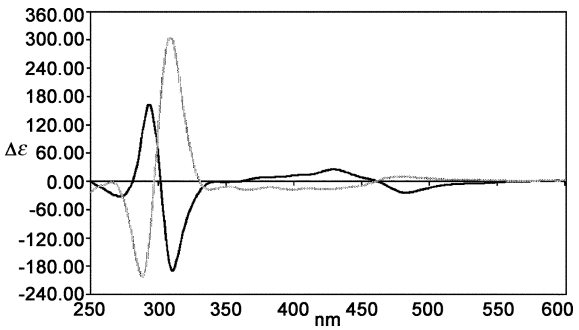
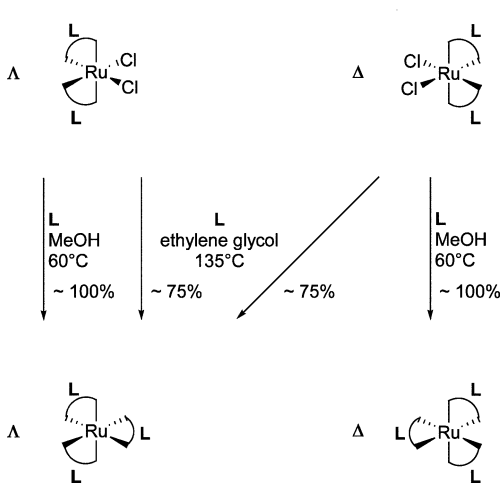


Fig. 4 CD spectra of the two diastereomeric complexes Δ-$[RuL_3]^{2+}$ (black line) and Λ-$[RuL_3]^{2+}$ (grey line).

$[Ru(bpy)_2(L\text{-trp})]^+$ (where L-trp is the L-tryptophane anion) by Williams *et al.*[12] The process was called "photochemical inversion". In our opinion this rearrangement does *not* represent a true inversion, as *e.g.* that observed by Bailar,[3] but rather an *equilibration* between two diastereoisomers.

The occurrence of the intermediate complex *cis*-$[RuL_2Cl_2]$ mentioned above offers the possibility to probe deeper into the stereoselectivity of the substitution reaction. The complex *cis*-$[RuL_2Cl_2]$ can be separated into its two diastereoisomers Δ-, and Λ-$[RuL_2Cl_2]$, respectively, by chromatographic methods (see Experimental). Their substitution reactions under various conditions are given in Scheme 7. All reactions proceed with the indicated stereoselectivities of at least 75%, approaching 100% in several cases. It clearly emerges that the substitution of two chloride ligands by (−)-**L** in methanol at 60 °C proceeds in a kinetically controlled reaction with complete *retention* of configuration. In ethylene glycol no reactivity is observed below 100 °C. Above this temperature both diastereoisomers, Λ- and Δ-$[RuL_2Cl_2]$, yield preferentially the Λ-configured $[RuL_3]^{2+}$ complex. The most probable explanation of this outcome is the assumption of a thermodynamically controlled process. Thus, no real inversion



Scheme 7

occurs, although, starting from Δ-$[RuL_2Cl_2]$, an excess of Λ-$[RuL_3]^{2+}$ is formed. This, however, is due to thermodynamic equilibration between diastereoisomeric species and not to a genuine inversion process. The same can be stated for the photocatalysis (Scheme 6), mentioned above, where the pure Δ form transforms into an equilibrium mixture, which contains an excess of the Λ-isomer. The difference in reactivity in the two solvents (methanol and ethylene glycol) is due to the substitution of a chloride ligand by MeOH, clearly indicated by a colour change from violet to red when $[RuL_2Cl_2]$ is dissolved in methanol. This can be also shown by MS measurements (see Experimental). Thus, methanol facilitates the leaving of the chloride ligand. Recently, the influence of the solvent in isomerization reactions of Ru^{II} complexes has been studied in several cases.[26] A detailed non-speculative mechanistic explanation in our system is not possible, however.

The corresponding Os^{II} complexes with (−)-**L** were prepared according to Scheme 8. As expected, the reactions require

a)

$(NH_4)_2OsCl_6$ —(1. 2 L; 2. $Na_2S_2O_4$; 180°C; ethylene glycol)→ *cis*-$[OsL_2Cl_2]$ predominatly Δ

b)

cis-$[OsL_2Cl_2]$ predominatly Δ —(L; 180°C; ethylene glycol)→ $[OsL_3]^{2+}$ predominatly Λ, Λ/Δ = 2.1

Scheme 8

a higher temperature than in the case of Ru^{II}. Reactions in solvents with lower boiling points than ethylene glycol such as methanol or ethanol did not yield the corresponding products. The stereochemical outcome is very similar for Os^{II} and Ru^{II}. Again, both diastereoisomers give similar CD spectra (Fig. 5) and the complexes appear to be thermally stable at 200 °C. In contrast to the Ru^{II} complexes, the Os^{II} compounds are even stable at 200 °C and under irradiation from a 1000 W lamp (the Ru^{II} complexes photoisomerize under irradiation from a 50 W lamp).

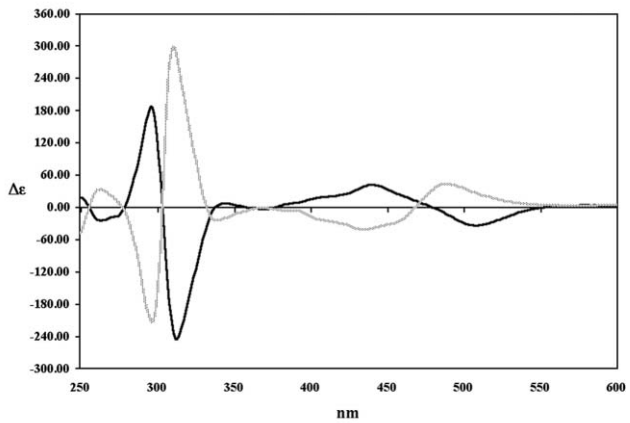


Fig. 5 CD spectra of the two diastereomeric complexes Δ-$[OsL_3]^{2+}$ (black line) and Λ-$[OsL_3]^{2+}$ (grey line).

We concluded that the Os^{II} and Ru^{II} complexes behave very similarly, albeit the activation energies are significantly higher for Os^{II}.

X-Ray structures

The data for the five complexes examined, Δ-$[FeL_3]^{2+}$, Δ-, and Λ-$[RuL_3]^{2+}$, Δ-, and Λ-$[OsL_3]^{2+}$ are given in Tables 1 and 2 together with data from literature for the corresponding tris-bpy species $[M(bpy)_3]^{2+}$ (see also the ESI†). Table 2 (see Experimental) gives the general results for the structure measurement, whereas Table 1 compares same specific measures within the coordination species. As an example, an ORTEP[28] presentation of Δ-$[OsL_3]^{2+}$ is given in Fig. 6.

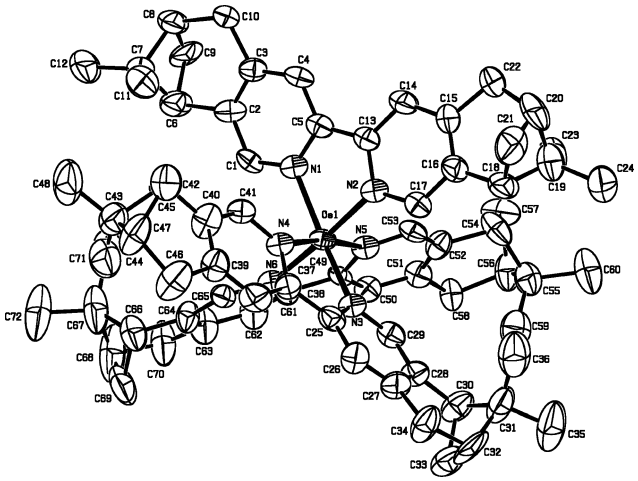


Fig. 6 ORTEP presentation of Δ-$[OsL_3]^{2+}$.

The values given in Table 1 indicate slight distortions in the $[ML_3]^{2+}$ complexes, as compared to their $[M(bpy)_3]^{2+}$ analogues. For all of the four parameters given (*trans*, chelate, prismatic and antiprismatic), the distortions in the cases of Δ/Λ diastereoisomers of $[RuL_3]^{2+}$ and $[OsL_3]^{2+}$ are in opposite directions from the respective values for the $[M(bpy)_3]^{2+}$ complexes. For example, the *trans* angles are Δ-$[RuL_3]^{2+}$ 174.9°; Λ-$[RuL_3]^{2+}$ 171.7°; $[Ru(bpy)_3]^{2+}$ 172.6°; *etc*. Also, the distortions in the Δ-$[FeL_3]^{2+}$ have the same signs as in Δ-$[RuL_3]^{2+}$ and Δ-$[OsL_3]^{2+}$. Thus, the "distortions" due to the chiral pinene groups, albeit small, are highly systematic.

UV/VIS absorption spectra

These spectra are surprisingly variable, especially in the visible region. The π–π* absorptions in the UV around 300 nm are given in Fig. 7. They are almost identical for the Δ and Λ pairs of $[OsL_3]^{2+}$ and $[RuL_3]^{2+}$(data are given in the Experimental). Fig. 8 gives the MLCT bands, including the relatively strong spin forbidden triplet absorption at long wavelength (Os^{II}). While the characteristic ^{1}MLCT transitions for Δ-$[FeL_3]^{2+}$, and Δ-$[RuL_3]^{2+}$ show the typical shoulder, which is also observed in $[Fe(bpy)_3]^{2+}$ and $[Ru(bpy)_3]^{2+}$, Δ-$[OsL_3]^{2+}$ exhibits a prominent splitting of this band, which is

Table 1 Average structural data (3 × *trans*, 3 × chelate, 3 × prismatic, 6 × antiprismatic angles; 6 × M–N bond lengths) indicating the distortion of diastereomeric species with respect to the parent $[M(bpy)_3]^{2+}$ complexes

Angle[a]	Δ-$[FeL_3]^{2+}$	$[Fe(bpy)_3]^{2+}$ [b]	Λ-$[RuL_3]^{2+}$	Δ-$[RuL_3]^{2+}$	$[Ru(bpy)_3]^{2+}$ [c]	Λ-$[OsL_3]^{2+}$	Δ-$[OsL_3]^{2+}$	$[Os(bpy)_3]^{2+}$ [d]
trans/°	173.4(10)	175.2(2)	174.9(1)	171.7(2)	172.6(2)	175.0(3)	170.7(3)	172.4
chelate/°	81.8(9)	81.6(1)	78.6(1)	79.0(1)	78.6(2)	77.8(3)	78.2(3)	77.8(4)
prismatic/°	93.5(7)	95.0(1)	97.8(1)	95.1(1)	95.7(12)	98.6(2)	95.3(2)	96.3(3)
antiprismatic/°	91.5(9)	88.7(1)	86.0(1)	91.3(1)	89.4(2)	85.2(3)	91.9(3)	90.1(4)
M–N/Å	1.966(2)	1.956(2)	2.055(2)	2.051(2)	2.053(2)	2.057(5)	2.064(5)	2.056(8)

[a] Defined as in ref. 21. [b] Ref. 22. [c] Ref. 21. [d] Ref. 23.

Table 2 General crystallographic data for the complexes

	Δ-[FeL_3]$(PF_6)_2$ (**1a**)	Δ-[RuL_3]$(PF_6)_2$ (**2a**)	Λ-[RuL_3]$(PF_6)_2$ (**2b**)	Δ-[OsL_3]$(PF_6)_2$ (**3a**)	Λ-[OsL_3]$(TfO)_2$ (**3b**)
Formula	$C_{72}H_{78}FeN_6P_2F_{12}\cdot 4.75CHCl_3$	$C_{72}H_{78}RuN_6P_2F_{12}\cdot 5CHCl_3$	$C_{72}H_{78}RuN_6P_2F_{12}\cdot 6CHCl_3$	$C_{72}H_{78}OsN_6P_2F_{12}$	$C_{72}H_{78}RuN_6C_2F_6S_2O_6\cdot 4(C_3H_6O)$
M_r	1940.19	2015.25	2134.62	1513.59	1719.83
Crystal shape	Block	Block	Block	Block	Tube
Crystal colour	Dark red	Orange	Orange	Black	Blue
Crystal size/mm	0.55 × 0.55 × 0.40	0.50 × 0.45 × 0.40	0.35 × 0.30 × 0.25	0.50 × 0.30 × 0.30	0.50 × 0.10 × 0.10
Temp./K	223(2)	223(2)	223(2)	153(2)	173(2)
Crystal system	Triclinic	Triclinic	Monoclinic	Triclinic	Monoclinic
Space group	*P*1	*P*1	$P2_1$	*P*1	$P2_1$
a/Å	11.6777(10)	11.8288(11)	14.9231(10)	11.5876(7)	14.8936(13)
b/Å	15.3081(14)	15.4650(14)	23.3654(14)	15.6490(11)	21.6543(12)
c/Å	15.8171(14)	15.8323(14)	15.2120(9)	15.6557(12)	15.3712(12)
α/°	103.645(10)	117.650(9)	90.00	119.681(8)	90.00
β/°	109.925(10)	93.330(11)	118.930(7)	90.714(8)	118.321(6)
γ/°	110.641(10)	110.796(10)	90.00	111.307(8)	90.00
V/Å^3	2274.8(3)	2309.9(4)	4642.3(5)	2232.0(3)	4364.0(6)
Z	1	1	2	1	2
F (000)	992	1024	2164	772	1748
ρ_{calcd}/g cm^{-3}	1.416	1.449	1.527	1.126	1.309
μ/mm^{-1}	0.688	0.706	0.791	1.525	1.579
Number of refl.	17894	17663	34933	17893	32416
Indep. refl.	14809	14765	17860	14785	14480
R_{int}	0.0460	0.0324	0.0650	0.0865	0.1179
Observed refl.	11284	14101	10004	12830	8432
Criterion	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
Parameters	1069	1016	1057	750	292
R_1(obs./all)[a]	0.0606/0.0792	0.0612/0.0634	0.0562/0.1137	0.0724/0.0811	0.0824/0.1130
wR_2(obs./all)[b]	0.1474/0.1569	0.1650/0.1670	0.1164/0.1316	0.1798/0.1862	0.2013/0.2173
g_{el}/e Å^{-3}	−0.538/ + 0.748	−0.857/ + 1.177	−0.821/ + 0.761	−1.639/ + 1.603	−1.274/ + 2.016
Flack parameter[c] *x*	−0.004(17)	−0.01(3)	−0.02(3)	−0.013(12)	0.040(16)

[a] $R_1 = \sum(||F_o| - |F_c||)/\sum|F_o|$. [b] $wR_2 = [\sum(w(F_o^2 - F_c^2)^2)/\sum(wF_o^4)]^{1/2}$. [c] Ref. 27.

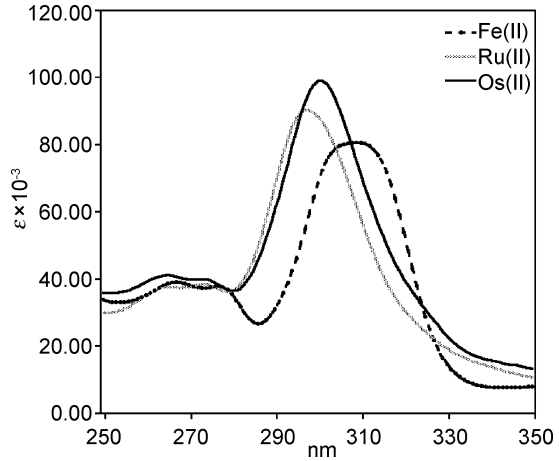


Fig. 7 UV absorption spectra of Δ-$[FeL_3]^{2+}$, Δ-$[RuL_3]^{2+}$, and Δ-$[OsL_3]^{2+}$ in acetonitrile.

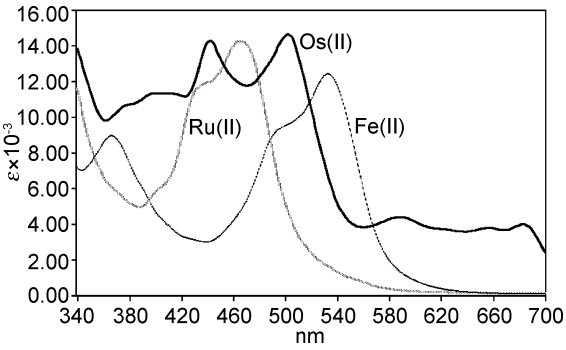


Fig. 8 VIS absorption spectra of Δ-$[FeL_3]^{2+}$, Δ-$[RuL_3]^{2+}$, and Δ-$[OsL_3]^{2+}$ in acetonitrile.

also present in $[Os(bpy)_3]^{2+}$, but in a much less pronounced manner (Fig. 9).

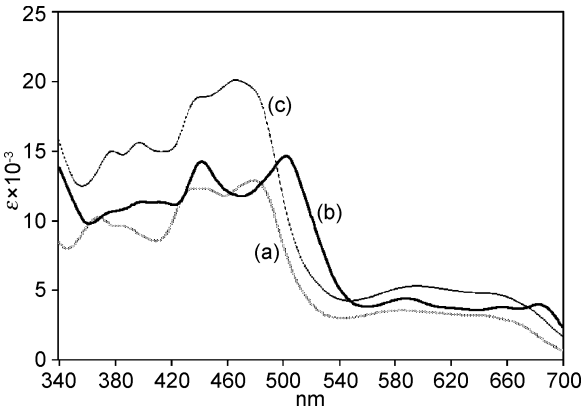


Fig. 9 VIS absorption spectra of (a) $[Os(bpy)_3]^{2+}$, (b) Δ-$[OsL_3]^{2+}$, and (c) Λ-$[OsL_3]^{2+}$ in acetonitrile.

Apparently, this must be due to the distortions observed in the structures, since the diastereomeric Λ-$[OsL_3]^{2+}$ does not show this splitting to the same extent. For the latter a distinct solvatochromism is observed (Fig. 10), which is also present in the Λ-$[RuL_3]^{2+}$ case (Fig. 11). On the contrary, the Δ complexes

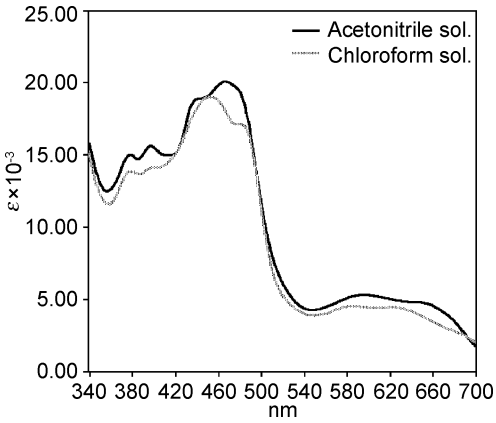


Fig. 10 VIS absorption spectra of Λ-$[OsL_3]^{2+}$ in acetonitrile and chloroform, respectively.

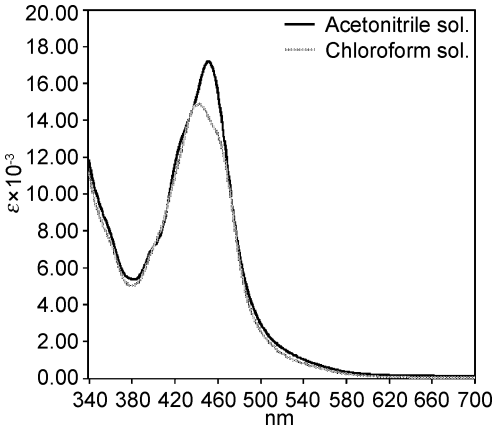


Fig. 11 VIS absorption spectra of Λ-$[RuL_3]^{2+}$ in acetonitrile and chloroform, respectively.

do not show this solvatochromic effect. Most of these phenomena can be observed by the eye. While a Δ-$[OsL_3]^{2+}$ solution is brown, Λ-$[OsL_3]^{2+}$ in acetonitrile and other polar solvents, is deep green.

In order to extend these investigations to other coordination centres, preliminary measurements (CD and ^{1}H NMR) were carried out with the series of labile metal ions Zn(II), Cd(II), Cu(II), and Ni(II). For all of these metals, CD spectra (see Experimental) clearly indicate a diastereoselectivity in favour of the Δ isomer. At room temperature, the diamagnetic ions Zn(II) and Cd(II) yield observable ^{1}H NMR spectra of the complexes $[ML_3]^{2+}$. In the case of Zn(II), the two diastereoisomers show resolved splittings indicating a value $\Delta/\Lambda = 1.5$, whereas in the case of Cd(II), ligand exchange obviously averages the signals of the two diastereoisomers.

Conclusions

The C_2-symmetric ligand (−)-**L** used in the present investigation induces stereoselectivity in the formation of the chiral metal complexes $[ML_3]^{2+}$ (M = Fe(II), Ru(II), Os(II), Zn(II), Cd(II), Cu(II), Ni(II)). The diastereoselectivity is, however, quite weak, representing energy differences between the Δ and Λ isomers of few kJ mol^{-1}. In all cases except Ru(II) and Os(II), the Δ isomer is the thermodynamically preferred configuration, using the (−)-**L** ligand. The detailed investigations of the reaction course,

especially in the case of Ru(II) and Os(II) gave no evidence for true inversion processes, although coordination species with opposite configurations have been observed for intermediate species.

Experimental

General

Unless otherwise specified, materials were purchased from commercial suppliers and used without further purification. Ruthenium trichloride and ammonium hexachloroosmate were purchased from Johnson Matthey and Branderberger AG. NMR spectra were measured on a Varian Gemini 300, Bruker DRX 500 or Bruker Avance 400 in acetonitrile-d_3 (*d*, 99.8%), dichloromethane-d_2 (*d*, 99.9%), chloroform-*d* (*d*, 99.8%), acetone-d_6 (*d*, 99.9%), ethylene glycol-d_6 (*d*, 99%), or dimethylsulfoxide-d_6 (*d*, 99.8%) (deuterated solvents were purchased from Cambridge Isotope Laboratories and Armar Chemicals (glycol)). Varian Gemini 300 (^{1}H: 300.075 MHz), Bruker Avance 400 (^{1}H: 400.13 MHz, ^{13}C: 100.62 MHz), Bruker DRX 500 (^{1}H: 500.13 MHz, ^{13}C: 125.76 MHz). Chemical shifts (δ scale, ppm) are given relative to the internal Me_4Si (^{1}H, ^{13}C) standard or the solvent itself was used as internal standard. Assignment of the NMR signals is based on ^{1}H, ^{13}C{^{1}H}, ^{13}C APT, COSY, ^{13}C HMQC. UV/VIS spectra were recorded on a Perkin–Elmer Lambda 25 spectrometer. CD spectra were recorded on a Jasco J-715 spectropolarimeter. Mass spectra were recorded on a Bruker Bio APEX II (ESI) and on a VG-Instruments 7070E (FAB). A diffractometer STOE IPDS-2 was used to record X-ray diffractions. The Ecole d'ingénieurs et d'architectes de Fribourg performed the elemental analysis. $[Ru(DMSO)_4Cl_2]$,[13] $[Ru(MeCN)_4Cl_2]$,[14] and *rac*-$[Os(bpy)_3](PF_6)_2$ [15] were synthesized using literature procedures.

Preparations

4,5-Bis(pinene)-2,2′-bipyridine-ligand (−)-L. was synthesized according to improved procedure (see ESI†), and analytical data agree with those previously described in literature.[7,8]

$[FeL_3](PF_6)_2$. A mixture of the ligand (−)-**L** (50 mg, 0.15 mmol) and $(NH_4)_2Fe(SO_4)_2{\cdot}6H_2O$ (20 mg, 0.051 mmol) was heated in 5 mL of a 9 : 1 mixture of ethylene glycol : water containing one drop of 1 M HCl at 150 °C for 4 h. The resulting mixture was cooled to 100 °C, and NH_4PF_6 (250 mg, 1.5 mmol) in 3 mL of water was added. The solution was kept at 100 °C for 1 h, and allowed to cool to room temperature. Deep red crystals of Δ-$[FeL_3](PF_6)_2$ were filtered off in quantitative yield. ^{1}H NMR (500.13 MHz, acetone-d_6); Δ diastereoisomer: δ 0.76 (s, 3H-12, *endo* CH_3), 1.08 (d, 1H-9, *endo* CH_2, $J = 10.0$ Hz), 1.37 (s, 3H-13, *exo* CH_3), 2.39 (m, 1H-8, CH), 2.48 (dd, 1H-10, CH, $J = 5.5$ Hz, $J = 5.5$ Hz), 2.66 (m, 1H-9, *exo* CH_2), 3.27 (d, 2H-7, CH_2, $J = 2.4$ Hz), 6.85 (s, 3H-3, aromatic CH), 8.53 (s, 3H-6, aromatic CH); Λ diastereoisomer: δ 0.28 (s, 3H-12, *endo* CH_3), 1.23 (d, 1H-9, *endo* CH_2, $J = 9.9$ Hz), 1.26 (s, 3H-13, *exo* CH_3), 2.30 (m, 1H-8, CH), 2.56 (dd, 1H-10, CH, $J = 5.4$ Hz, $J = 5.4$ Hz), 2.66 (m, 1H-9, *exo* CH_2), 3.17 (ddd, 2H-7, CH_2, $J = 66.9$ Hz, $J = 18.8$ Hz, $J = 2.6$ Hz), 7.24 (s, 3H-3, aromatic CH), 8.49 (s, 3H-6, aromatic CH). ^{13}C{^{1}H}NMR (125.76 MHz, acetone-d_6); Δ diastereoisomer: δ 21.96 (C-12, *endo* CH_3), 25.86 (C-13, *exo* CH_3), 31.49 (C-9, CH_2), 33.55 (C-7, CH_2), 39.65 (C-11), 40.36 (C-8, CH), 45.90 (C-10, CH), 124.28 (C-6, aromatic CH), 148.84 (C-3, aromatic CH), 147.49, 149.24, 159.32 (C-5, C-4, C-2); Λ diastereoisomer: δ 20.93 (C-12, *endo* CH_3), 25.71 (C-13, *exo* CH_3), 31.44 (C-9, CH_2), 33.48 (C-7, CH_2), 39.39 (C-11), 40.40 (C-8, CH), 45.26 (C-10, CH), 123.37 (C-6, aromatic CH), 150.02 (C-3, aromatic CH), 147.28, 148.72, 158.87 (C-5, C-4, C-2). UV-VIS ($c = 2 \times 10^{-5}$ mol dm^{-3}, acetonitrile equlibrated solution): 267 (39 100), 277 (37 830), 309 (80 600), 366 (8960), 533 nm (12 420); CD ($c = 2 \times 10^{-5}$ M, ethylene glycol): 319 (−296), 299 nm (150). MS (ESI): *m*/*z* 1233.61 (62%, M^+–PF_6^-), 544.32 (100%, M^+–2 × PF_6^-). Anal.: Calcd for $C_{72}H_{84}N_6FeP_2F_{12}$: C, 62.70; H, 6.14; N, 6.09; Found: C, 62.51; H, 5.83; N, 6.33.

***cis*-$[RuL_2Cl_2]$.** The freshly prepared $[Ru(MeCN)_4Cl_2]$ (18.4 mg, 0.055 mmol), ligand (−)-**L** (37.8 mg, 0.11 mmol), and anhydrous lithium chloride were dissolved in dry methanol (80 mL), and the mixture was refluxed for 40 h under argon. The volume of the violet solution was reduced to 40 mL, a portion of water was added (20 mL), and the polar phase was extracted with toluene until the latter was nearly colourless. The organic phase was dried over sodium sulfate, the solvent was evaporated, and the remaining black powder was washed with hexane to remove traces of non-coordinated ligand (−)-**L** giving the product $[RuL_2Cl_2]$ predominantly with Δ configuration at the ruthenium centre (yield: 30 mg, 0.0035 mmol). This labile species has been characterized unambiguously by its ^{1}H NMR, and MS spectra. Elemental analysis yielded in most cases unsatisfactory results. ^{1}H NMR (300.075 MHz, $CDCl_3$): δ 0.18, 0.58, 0.71, 0.75, 0.90, 1.12, 1.20, 1.23, 1.30, 1.38, 1.40, 1.42, 2.30, 2.35, 2.50, 2.60, 2.78, 2.90, 2.93, 3.08, 3.20, 3.78, 6.80, 6.83, 7.69, 7.70, 7.85, 7.90, 9.03, 9.08. MS (FAB): *m*/*z* 861.29 (100%, $M^+ + H$). MS (ESI) (in MeOH): *m*/*z* 825.35 (100%, $[RuL_2Cl]^+$), 857.38 (90%, $[RuL_2Cl(MeOH)]^+$), 860.38 (80%, M^+); (in THF): *m*/*z* 860.38 (100%, M^+).

Separation of the diastereoisomers by column chromatography (neutral aluminium oxide, isopropyl alcohol : hexane mixture of 1 : 20) gave highly enriched complexes Δ-$[RuL_2Cl_2]$ and Λ-$[RuL_2Cl_2]$ in a poor preparative yield of 18% ($[RuL_2Cl_2]$ partially reacted with Al_2O_3). UV-VIS: Δ diastereoisomer ($c = 1.4 \times 10^{-6}$ mol dm^{-3}, dichloromethane): 268 (25 800), 279 (23 600), 311 (48 000), 382 (8700), 550 nm (8000); Λ diastereoisomer ($c = 1.9 \times 10^{-6}$ mol dm^{-3}, dichloromethane): 267 (22 900), 278 (21 800), 312 (45 800), 380 (7700), 548 nm (6700). CD: Δ diastereoisomer ($c = 1.4 \times 10^{-6}$ mol dm^{-3}, dichloromethane): 485 (9), 405 (−9.8), 319 (−105), 301 nm (49); Λ diastereoisomer ($c = 1.9 \times 10^{-6}$ mol dm^{-3}, dichloromethane): 480 (−6.5), 408 (6.8), 318 (59), 299 nm (−28).

$[RuL_3](PF_6)_2$. A mixture of the ligand (−)-**L** (50 mg, 0.15 mmol) and $[Ru(DMSO)_4Cl_2]$ (24 mg, 0.050 mmol) was heated in 5 mL of a 9 : 1 mixture of ethylene glycol : water containing one drop of 1 M HCl at 135 °C for 5 h. After cooling the solution to 100 °C, a solution of NH_4PF_6 (250 mg, 1.5 mmol) in water (3 mL) was added. Precipitated orange red complex $[RuL_3](PF_6)_2$ was collected on a filter (yield: 65 mg, 91%). The raw product was recrystallized from chloroform. The Λ diastereoisomer crystallized first. After repeated crystallization Δ-$[RuL_3](PF_6)_2$ was enriched in the mother liquor. ^{1}H NMR (500.13 MHz, acetone-d_6); Δ-diastereoisomer: δ 0.76 (s, 3H-12, *endo* CH_3), 1.08 (d, 1H-9, *endo* CH_2, $J = 10.0$ Hz), 1.38 (s, 3H-13, *exo* CH_3), 2.38 (m, 1H-8, CH), 2.52 (dd, 1H-10, CH, $J = 5.5$ Hz, $J = 5.5$ Hz), 2.67 (m, 1H-9, *exo* CH_2), 3.25 (br s, 2H-7, CH_2), 7.24 (s, 3H-3, aromatic CH), 8.52 (s, 3H-6, aromatic CH); Λ diastereoisomer: δ 0.29 (s, 3H-12,

endo CH_3), 1.24 (d, 1H-9, *endo* CH_2, $J = 9.9$ Hz), 1.26 (s, 3H-13, *exo* CH_3), 2.31 (m, 1H-8, CH), 2.57 (dd, 1H-10, CH, $J = 5.5$ Hz, $J = 5.5$ Hz), 2.66 (m, 1H-9, *exo* CH_2), 3.16 (ddd, 2H-7, CH_2, $J = 59.2$ Hz, $J = 18.8$ Hz, $J = 2.9$ Hz), 7.54 (s, 3H-3, aromatic CH), 8.47 (s, 3H-6, aromatic CH). $^{13}C\{^1H\}$NMR (125.76 MHz, acetone-d_6); Δ diastereoisomer: δ 21.82 (C-12, *endo* CH_3), 25.87 (C-13, *exo* CH_3), 31.56 (C-9, CH_2), 33.60 (C-7, CH_2), 39.68 (C-11), 40.38 (C-8, CH), 45.65 (C-10, CH), 124.52 (C-6, aromatic CH), 146.27 (C-3, aromatic CH), 147.63, 148.10, 155.39 (C-5, C-4, C-2); Λ diastereoisomer: δ 20.97 (C-12, *endo* CH_3), 25.72 (C-13, *exo* CH_3), 31.46 (C-9, CH_2), 33.51 (C-7, CH_2), 39.67 (C-11), 40.41 (C-8, CH), 45.04 (C-10, CH), 123.65 (C-6, aromatic CH), 147.59 (C-3, aromatic CH), 147.30, 147.65, 156.50 (C-5, C-4, C-2). UV-VIS: Δ diastereoisomer ($c = 8.4 \times 10^{-6}$ mol dm^{-3}, acetonitrile): 265 (37 500), 273 (38 400), 297 (90 200), 465 nm (14300); Λ diastereoisomer ($c = 1.2 \times 10^{-5}$ mol dm^{-3}, acetonitrile): 265 (38 400), 275 (40 800), 301 (100 000), 452 nm (17 100); ($c = 1.2 \times 10^{-5}$ mol dm^{-3}, chloroform): 443 nm (15 000). CD: Δ diastereoisomer ($c = 8.4 \times 10^{-6}$ mol dm^{-3}, acetonitrile): 482 (−24), 429 (26), 310 (−190), 293 (162), 271 nm (−32); Λ diastereoisomer ($c = 1.2 \times 10^{-5}$ mol dm^{-3}, acetonitrile): 479 (10), 422 (−17), 309 (304), 288 nm (−202). MS (ESI): *m*/*z* 1279.56 (88%, M^+–PF_6^-), 567.31 (100%, M^+–2 × PF_6^-). Anal.: Calcd for $C_{72}H_{84}N_6RuP_2F_{12}\cdot 2H_2O$: C, 59.21; H, 6.07; N, 5.75; Found: C, 58.86; H, 6.15; N, 5.74.

***cis*-[OsL_2Cl_2].** A mixture of the ligand (−)-**L** (157 mg, 0.576 mmol) and $(NH_4)_2OsCl_6$ (100 mg, 0.228 mmol) was heated in 10 mL of a 9 : 1 mixture of ethylene glycol : water containing one drop of 1 M HCl at 180 °C for 3 h. After cooling the solution to 100 °C, a saturated water solution of sodium dithionite (10 mL) was added. The purple-black precipitate that had formed was isolated by filtration, washed with water to remove $[OsL_3]^{2+}$ and other ionic byproducts, and washed with large volumes of hexane to give the product in 88% yield in favour of the Δ-configured diastereoisomer. This species has been characterized unambiguously by its ^{1}H NMR, and MS spectra. Elemental analysis yielded in most cases unsatisfactory results. ^{1}H NMR (300.075 MHz, $CDCl_3$): δ 0.20, 0.55, 0.75, 0.78, 0.88, 1.11, 1.22, 1.24, 1.30, 1.37, 1.40, 1.42, 2.32, 2.37, 2.51, 2.62, 2.79, 2.92, 2.90, 3.10, 3.24, 3.77, 6.81, 6.83, 7.70, 7.72, 7.85, 7.90, 9.04, 9.09. UV-VIS ($c = 2.5 \times 10^{-5}$ moldm^{-3}, dichloromethane): 275 (32 800), 312 (29 700), 455 (8100), 577 nm (10 000). CD ($c = 2.5 \times 10^{-5}$ mol dm^{-3}, dichloromethane): 363 (−15), 320 nm (17), MS (ESI): *m*/*z* 950.33 (100%, M^+).

[OsL_3](PF_6)$_2$. A mixture of the ligand (−)-**L** (36 mg, 0.105 mmol) and *cis*-[OsL_2Cl_2] (100 mg, 0.105 mmol) was heated in 5 mL of a 9 : 1 mixture of ethylene glycol : water containing one drop of 1 M HCl at 180 °C for 5 h under argon. After cooling the solution to 100 °C, a solution of NH_4PF_6 (250 mg) in water (3 mL) was added. The precipitate was collected on a filter (yield: 142 mg, 90%). The diastereoisomers were separated by column chromatography (neutral aluminium oxide, acetonitrile : toluene, 1 : 3) to yield pure Λ-[OsL_3](PF_6)$_2$ and Δ-[OsL_3](PF_6)$_2$ as deep green, and dark brown crystalline solids, respectively. ^{1}H NMR (500.13 MHz, acetone-d_6); Δ diastereoisomer: δ 0.77 (s, 3H-12, *endo* CH_3), 1.07 (d, 1H-9, *endo* CH_2, $J = 9.9$ Hz), 1.37 (s, 3H-13, *exo* CH_3), 2.37 (m, 1H-8, CH), 2.49 (dd, 1H-10, CH, $J = 5.4$ Hz, $J = 5.4$ Hz), 2.66 (m, 1H-9, *exo* CH_2), 3.25 (dd, 2H-7, CH_2, $J = 5.0$ Hz, $J = 2.7$ Hz), 7.20 (s, 3H-3, aromatic CH), 8.48 (s, 3H-6, aromatic CH); Λ diastereoisomer: δ 0.29 (s, 3H-12, *endo* CH_3), 1.24 (d, 1H-9, *endo* CH_2, $J = 10.0$ Hz), 1.25 (s, 3H-13, *exo* CH_3), 2.29 (m, 1H-8, CH), 2.54 (dd, 1H-10, CH, $J = 5.4$ Hz, $J = 5.4$ Hz), 2.66 (m, 1H-9, *exo* CH_2), 3.26 (ddd, 2H-7, CH_2, $J = 64.1$ Hz, $J = 18.7$ Hz, $J = 2.9$ Hz), 7.42 (s, 3H-3, aromatic CH), 8.46 (s, 3H-6, aromatic CH). $^{13}C\{^1H\}$NMR (125.76 MHz, acetone-d_6); Δ diastereoisomer: δ 21.76 (C-12, *endo* CH_3), 25.88 (C-13, *exo* CH_3), 31.64 (C-9, CH_2), 33.40 (C-7, CH_2), 39.80 (C-11), 40.40 (C-8, CH), 45.58 (C-10, CH), 124.69 (C-6, aromatic CH), 145.08 (C-3, aromatic CH), 147.17, 148.11, 158.98 (C-5, C-4, C-2); Λ diastereoisomer: δ 20.97 (C-12, *endo* CH_3), 25.73 (C-13, *exo* CH_3), 31.55 (C-9, CH_2), 33.35 (C-7, CH_2), 39.50 (C-11), 40.41 (C-8, CH), 44.96 (C-10, CH), 123.81 (C-6, aromatic CH), 146.72 (C-3, aromatic CH), 146.89, 147.79, 158.41 (C-5, C-4, C-2). UV-VIS: Δ diastereoisomer ($c = 8.1 \times 10^{-6}$ mol dm^{-3}, acetonitrile): 265 (41 100), 273 (39 800), 300 (99 000), 399 (11 400), 411 (11 300), 442 (14 300), 502 (14 600), 588 (4400), 657 (3800), 683 nm (4000); Λ diastereoisomer ($c = 5.3 \times 10^{-6}$ mol dm^{-3}, acetonitrile): 265 (51 000), 275 (49 200), 303 (136 200), 378 (15 000), 397 (15 600), 467 (20 000), 596 nm (5300); ($c = 5.9 \times 10^{-6}$ mol dm^{-3}, chloroform): 378 (13 900), 397 (14 100), 452 (19 000), 587 (4500), 622 nm (4400). CD: Δ diastereoisomer ($c = 8.1 \times 10^{-6}$ mol dm^{-3}, acetonitrile): 508 (−34), 440 (42), 313 (−245), 296 (187), 263 nm (−24); Λ diastereoisomer ($c = 5.3 \times 10^{-6}$ mol dm^{-3}, acetonitrile): 489 (44), 435 (−41), 311 (299), 297 (−213), 263 nm (34). MS (ESI): *m*/*z* 1370.74 (50%, M^+–PF_6^-), 612.36 (100%, M^+ − 2 × PF_6^-). Anal.: Calcd for $C_{72}H_{84}N_6OsP_2F_{12}$: C, 56.47; H, 5.59; N, 5.55; Found: C, 56.09; H, 5.67; N, 5.43.

[ZnL_3](PF_6)$_2$. A mixture of the ligand (−)-**L** (31 mg, 0.09 mmol) and $ZnCl_2$ (4 mg, 0.03 mmol) in ethanol (7 mL) was heated under reflux for 2 h. A solution of NH_4PF_6 (250 mg) in water (3 mL) was added, and the precipitate was collected on a filter to yield the product (41 mg) in 98% preparative yield. ^{1}H NMR (400.13 MHz, acetone-d_6); Δ diastereoisomer: δ 0.71 (s, 3H-12, *endo* CH_3), 1.09 (d, 1H-9, *endo* CH_2, $J = 12.0$ Hz), 1.40 (s, 3H-13, *exo* CH_3), 2.38 (m, 1H-8, CH), 2.53 (dd, 1H-10, CH, $J = 5.5$ Hz, $J = 5.5$ Hz), 2.68 (m, 1H-9, *exo* CH_2), 3.20 (br s, 2H-7, CH_2), 7.09 (s, 3H-3, aromatic CH), 8.24 (s, 3H-6, aromatic CH); Λ diastereoisomer: δ 0.29 (s, 3H-12, *endo* CH_3), 1.25 (d, 1H-9, *endo* CH_2, $J = 12.0$ Hz), 1.33 (s, 3H-13, *exo* CH_3), 2.34 (m, 1H-8, CH), 2.65 (dd, 1H-10, CH, $J = 5.5$ Hz, $J = 5.5$ Hz), 2.68 (m, 1H-9, *exo* CH_2), 3.14 (m, 2H-7, CH_2), 7.41 (s, 3H-3, aromatic CH), 8.12 (s, 3H-6, aromatic CH). UV-VIS: predominantly Δ diastereoisomer ($c = 5.4 \times 10^{-5}$ mol dm^{-3}, acetonitrile): 215 (72 800), 270 (35 300), 311 (53 900), 324 nm (46 500). CD: predominantly Δ diastereoisomer ($c = 5.4 \times 10^{-5}$ mol dm^{-3}, acetonitrile): 325 (−148), 301 nm (41). MS (ESI): *m*/*z* 1241.57 (90%, M^+–PF_6^-), 548.30 (100%, M^+ − 2 × PF_6^-). Anal.: Calcd for $C_{72}H_{84}N_6ZnP_2F_{12}$: C, 61.50; H, 6.09; N, 6.05; Found: C, 61.09; H, 6.20; N, 5.93.

[CdL_3](PF_6)$_2$. The same procedure used to prepare [ZnL_3](PF_6)$_2$ complex was applied, and $CdCl_2\cdot 2H_2O$ (6 mg, 0.03 mmol) was used for this complex. The product was filtered off (yield: 38 mg, 88%). ^{1}H NMR (400.13 MHz, acetone-d_6): δ 0.59 (br s, 3H-12, *endo* CH_3), 1.14 (d, 1H-9, *endo* CH_2, $J = 12.0$ Hz), 1.39 (br s, 3H-13, *exo* CH_3), 1.58 (m, 1H-8, CH), 2.37 (m, 1H-10, CH), 2.69 (m, 1H-9, *exo* CH_2), 3.16 (br s, 2H-7, CH_2), 7.56 (s, 3H-3, aromatic CH), 8.14 (s, 3H-6, aromatic CH). UV-VIS: predominantly Δ diastereoisomer ($c = 3.5 \times 10^{-5}$ mol dm^{-3},

acetonitrile): 213 (87 900), 264 (32 600), 308 (53 900), 322 nm (42 500). CD: predominantly Δ diastereoisomer ($c = 3.5 \times 10^{-5}$ mol dm^{-3}, acetonitrile): 324 (−71), 298 nm (18). MS (ESI): m/z 1289.52 (33%, M^+–PF_6^-), 573.29 (100%, $M^+ - 2 \times PF_6^-$). Anal.: Calcd for $C_{72}H_{84}N_6CdP_2F_{12}$: C, 60.23; H, 5.90; N, 5.85; Found: C, 59.98; H, 5.95; N, 5.47.

[NiL$_3$](PF$_6$)$_2$. The same procedure used to prepare [ZnL$_3$](PF$_6$)$_2$ complex was applied, and $NiCl_2 \cdot 6H_2O$ (7 mg, 0.03 mmol) was used for this preparation. The light pink product was filtered off (yield: 35 mg, 84%). UV-VIS: predominantly Δ diastereoisomer ($c = 3.4 \times 10^{-5}$ mol dm^{-3}, acetonitrile): 220 (80 200), 265 (46 900), 311 (52 200), 324 nm (45 200). CD: predominantly Δ diastereoisomer ($c = 4.4 \times 10^{-5}$ mol dm^{-3}, acetonitrile): 326 (−165), 298 nm (34). MS (ESI): m/z 1235.57 (41%, M^+–PF_6^-), 545.31 (100%, $M^+ - 2 \times PF_6^-$). Anal.: Calcd for $C_{72}H_{84}N_6NiP_2F_{12}$: C, 61.85; H, 6.13; N, 6.08; Found: C, 61.19; H, 6.18; N, 5.99.

[CuL$_3$](PF$_6$)$_2$. The same procedure used to prepare [ZnL$_3$](PF$_6$)$_2$ complex was applied, and $CuCl_2 \cdot 2H_2O$ (5 mg, 0.03 mmol) was used for this preparation. The green product was filtered off (yield: 37 mg, 90%). UV-VIS: predominantly Δ diastereoisomer ($c = 4.4 \times 10^{-5}$ mol dm^{-3}, acetonitrile): 215 (76 700), 264 (46 900), 312 (40 400), 324 nm (44 700). CD: predominantly Δ diastereoisomer ($c = 4.4 \times 10^{-5}$ mol dm^{-3}, acetonitrile): 327 (−37), 305 nm (12). MS (ESI): m/z 1240.61 (70%, M^+–PF_6^-), 547.80 (100%, M^+–2xPF_6^-). Anal.: Calcd for $C_{72}H_{84}N_6CuP_2F_{12}$: C, 61.67; H, 6.10; N, 6.06; Found: C, 61.24; H, 6.22; N, 5.90.

Crystal structure determinations

Intensity data were colleted using a Stoe Imaging Plate Diffractometer System (Stoe & Cie, 1995) equipped with a one-circle φ goniometer and a graphite monochromator. Data collection was performed at −50 °C (−100 °C for **3b**), using Mo Kα radiation ($\lambda = 0.71073$ Å). 190 or 200 exposures (3 min per exposure) were obtained at an image plate distance of 70 mm with $0 < \varphi <$ 190 or 200° and with the crystal oscillating through 1° in φ. The resolution was D_{min}–D_{max} 12.45–0.81 Å. The structures were solved by direct methods using the program SHELXS-97[16] and refined by full matrix least squares on F^2 with SHELXL-97.[17] The non-hydrogen atoms were refined anisotropically, unless stated below. The hydrogen atoms were included in calculated positions and treated as riding atoms using SHELXL-97 default parameters. The atomic coordinates of the various structures correspond to the absolute structures of the molecules in the crystals. This is indicated by the refined Flack[27] x parameters and also corresponds to the absolute structure of the ligand used. Structures **1a** and **2a** have the same space group and similar cell parameters and appear to be isostructural. More crystallographic details are given in Table 2 and significant bond lengths and angles are listed in Table 1. The figures were drawn with the program PLATON.[18]

Δ-[FeL$_3$](PF$_6$)$_2$ (1a). This compound crystallized with one independent complex cation, two hexafluorophosphate anions and 5 chloroform molecules per asymmetric unit. One PF_6^- anion and one of the co-crystallised solvent molecules are strongly disordered. One $CHCl_3$ molecule has an occupancy of 0.75.

Δ-[RuL$_3$](PF$_6$)$_2$ (2a). The compound crystallized with two PF_6^- anions, one being strongly disordered with occupancies of 0.5 for all fluorine atomic positions (F7 to F12, and F7A to F12A), and five chloroform molecules. Two of these solvent molecules are disordered, having occupancies of 0.5 for Cl1, Cl1A, Cl2, Cl2A, Cl4, Cl4A, Cl5, Cl5A, Cl6, Cl6A, Cl7, Cl7A, Cl8, Cl8A, C56 and C56A. P–F distances for the disordered PF_6^- anion and C–Cl distances for the disordered chloroform molecules were constrained to their theoretical values[20] with estimated standard deviations of 0.05. No absorption correction was applied.

Λ-[RuL$_3$](PF$_6$)$_2$ (2b). This compound crystallized with two PF_6^- anions, one being strongly disordered with occupancies of 0.5 for all of the fluorine atomic positions (F1 to F6, and F1A to F6A), and six chloroform molecules, one of them being disordered (occupancy 0.75 for C56, Cl8, Cl9 and 0.25 for C56A, Cl8A and Cl9A). All atoms having partial occupancies were refined isotropically. P–F distances in the disordered PF_6^- anion and C–Cl distances in the disordered chloroform molecule are constrained to their theoretical values[20] with estimated standard deviations of 0.05. No absorption correction was applied.

Δ-[OsL$_3$](PF$_6$)$_2$ (3a). For this compound the atoms of the counterions PF_6^- were refined isotropically. A semiempirical absorption correction was applied using MULABS (PLATON99,[18] $T_{min} = 0.632$, $T_{max} = 0.830$).

Λ-[OsL$_3$](TfO)$_2$ (3b). For X-ray structural analysis Λ-[OsL$_3$](PF$_6$)$_2$ was converted to the triflate Λ-[OsL$_3$](TfO)$_2$ *via* water soluble chloride salt (*via* Dowex 1 × 2–100 ion exchange resin), and precipitation with lithium triflate. The molecular formula of this compound is $[Os(C_{24}H_{28}N_2)_3](CF_3SO_3)_2\,(C_3H_6O)_4$. As a result of the high disorder found in the anions and the solvent molecules, the SQUEEZE instruction in PLATON03[3] was used to calculate the potential accessible area for anions and solvent molecules in the unit cell; 2095.0 Å^3 were calculated containing *ca.* 560 electrons. Therefore, two molecules of trifluoromethanesulfonate (2 × 73 electrons), and four acetone molecules (4 × 32 electrons) per asymmetric unit were included in all further calculations. The highest residual peak of 2.02 e Å^{-3} was located near to the osmium atom. The thermal parameters of the non-hydrogen atoms in the ligands were constrained to be equal. A semiempirical absorption correction was applied using MULABS (PLATON03,[19] $T_{min} = 0.576$, $T_{max} = 0.781$).

CCDC reference numbers: 281496 (Δ-[FeL$_3$](PF$_6$)$_2$), 281497 (Δ-[RuL$_3$](PF$_6$)$_2$), 281498 (Λ-[RuL$_3$](PF$_6$)$_2$), 281499 (Δ-[OsL$_3$](PF$_6$)$_2$), and 281500 (Λ-[OsL$_3$](TfO)$_2$).

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b512116g

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