Enantiomeric programming in tripodal transition metal scaffolds

Nicholas C. Fletcher,* Ciarán Martin and Heather J. Abraham

Received (in Durham, UK) 13th March 2007, Accepted 8th May 2007 First published as an Advance Article on the web 25th May 2007 DOI: 10.1039/b703761a

A new route to the isolation of the enantiopure tris-chelate complex (Δ/Λ) -fac- $[Ru(L^1)_3]^{2+}$ (where L^1 is 2,2'-bipyridine-5-carboxylic acid) is demonstrated, where the transition metal centre retains the memory of the chirality present in a simple tripodal tether used to control the metal centred geometry.

The isolation of enantiomerically pure coordination complexes has become increasingly important in recent years arising from their continued use in material science,¹⁻³ asymmetric catalysis⁴ and medicinal chemistry.⁵⁻⁷ In particular, tris-chelate diimine complexes of Ru(II), Os(II), Ir(III) and Rh(III) have proved to be extremely useful in this respect due to their stability to racemization and optical properties, presenting as two enantiomers Δ and Λ .⁸ The isolation of metal complexes as a single asymmetric form has not received the same level of attention as that paid to the tetrahedral carbon atom.⁹ Overwhelmingly, the majority of examples have relied upon diastereotopic crystallization with a chiral counter-ion, a method exploited by Werner in 1911.¹⁰ The parent complex $[Ru(bipy)_3]^{2+}$ (where bipy is 2,2'-bipyridine) was enantiomerically resolved by diastereomeric crystallization with antimonyl tartrate by Dwyer in 1949,¹¹ and subsequently a number of other related species have been isolated by similar methods.^{12–15} Chromatographic techniques, either using a chiral stationary phase,¹⁶ or a chiral anion in the eluent (cationexchange chromatography),^{17,18} have allowed enantiomeric separation to be achieved in a number of cases on a moderate scale and a number of review articles have explored this rapidly expanding topic over recent years.¹⁹⁻²²

In addition to the metal centred stereochemistry, if the bidentate ligand has C_{s} -symmetry, arising from a different substitution pattern of the two halves of the chelate, meridional (mer) and facial (fac) isomerism will be present. In the majority of the diimine ligands investigated, this diastereomeric difference will favour the less sterically hindered mer form and subsequent separation can be problematic.²³ To overcome the difficulty of isolating solely the *fac* isomer, we have reported a tripodal cage-like system to orientate the three functional groups along the C_3 -axis present in the fac-isomer.²⁴ By using mild base hydrolysis, the ester linkages connecting the tris-chelates can then be removed to give the desired geometric isomer. A similar procedure has been employed by Weizman et al. with the additional benefit that with the inclusion of three L-alanine groups in the structure, the chirality at the metal centre can also be directed.²⁵ The use of

School of Chemistry and Chemical Engineering, Queen's University Belfast, Stranmillis Road, Belfast, Northern Ireland, UK BT9 5AG. E-mail: n.fletcher@qub.ac.uk

natural products to direct the metal-centred chirality in caged 2,2'-bipyridine complexes has given rise to excellent control over the metal centred stereochemistry, using either terpenoids^{26–28} or simple amino acids.²⁹ However in all of the previously reported examples, the final product contains the organic fragment used to govern the metal centred chirality, giving considerable steric bulk to the material. In this paper we explore the possible development of a new chiral tether, and its disconnection, leaving an enantiopure complex bearing only the memory of the tether.

In the preceding communication²⁴ we reported the preparation of fac-[Ru(L¹)₃]²⁺ (where L¹ is 2,2'-bipyridine-5carboxylic acid) by tethering the three ligands together with the triethanolamine. To direct the metal centred stereochemistry, the tether itself must contain the chirality, which can then be removed subsequent to the complexation step. Following a literature procedure, two enantiopure trialkanolamines N(CH₂-(*S/R*)-CHROH)₃ (where R = Me or Ph) were prepared by reaction of either *S*- or *R*-propylene oxide or *R*-styrene oxide with ammonia.³⁰ From these, the tripodal ligands *S*- or *R*-L^{Me} and *R*-L^{Ph} were isolated in reasonable yield (72 and 38%, respectively) from L¹ via the acyl chloride (Scheme 1). Both ligands were unstable with respect to saponification and rapidly decomposed on silica, presumably due



Scheme 1 (ia) SOCl₂ reflux, (ib) N(CH₂-(*R*)-CH(Ph)OH)₃, NEt₃-THF reflux, (ii) [Ru(DMSO)₄Cl₂], AgNO₃-ethanol in high dilution, reflux, (iii) KOH-water.

View Article Online

to the considerable steric strain put on the system. Consequently, purification was achieved by the use of a large excess of the bipyridine precursor, and recrystallization from acetone (the inorganic salts and starting acid/acyl chloride being sparingly soluble).

The complexation of the ligand to Ru(II) was achieved by the slow addition of the precursors to a large volume of refluxing ethanol, containing an excess of silver nitrate giving an almost immediate colour change to the characteristic red of the complex. The product was purified on a short cationexchange column to give the mononuclear product, and the two complexes $[Ru(R-L^{Ph})]^{2+}$ and $[Ru(S-L^{Me})]^{2+}$ isolated as the hexafluorophosphate salts. The ¹H NMR spectra of both complexes (Fig. 1) indicated the C_3 -symmetry of the fac isomer. Only one set of signals was observed for the bipyridine peaks. For both of the complexes, the CH protons adjacent to the carboxylate group presented as a multiplet since the CH₂ is inequivalent due to the restricted configuration. However, these CH₂ signals indicate the presence of one dominant diastereomer (de in excess of 90%), in both complexes presenting as two doublets of doublets at 2.80 and 2.26 ppm for $[Ru(R-L^{Ph})]^{2+}$ and at 2.78 and 2.33 ppm for $[Ru(R-L^{Me})]^{2+}$ (12.0 Hz J^1 coupling). Compared to the 85% yield of the racemic mixture obtained using the achiral triethanolamine tether,²⁴ the unoptimized yield of up to 22% was disappointing although anticipated given the ligand's stability. Significantly, a large quantity of red material could not be precipitated or extracted following the purification, which is typical of the presence of free carboxylate groups as a result of deesterification.

Both complexes $[Ru(R-L^{Ph})](PF_6)_2$ and $[Ru(R-L^{Me})](PF_6)_2$ were dissolved in acetonitrile, and stirred with an excess of an aqueous solution of KOH. The resulting solution was observed to darken significantly in colour, as the complexes hydrolysed. Following acidification, and the addition of NH_4PF_6 , the complex (Δ or Λ)-[Ru(L¹)₃](PF₆)₂ could be isolated with difficulty. The extraction procedure proved problematic, given the hydrophilicity of the carboxylic acid groups. Drying the extraction with anhydrous magnesium sulfate and recrystallization from dichloromethane and hexane gave sufficient product for ¹H NMR characterization (despite

9.00 8.50 8.00 7.50 7.00 6.50 5.50 5.00 6.00 4.50 9.50 Fig. 1 ¹H NMR spectra of (a) $R-L^{Me}$ (300 MHz, CDCl₃, 25 °C), (b) [Ru(R-L^{Me})](PF₆)₂ (500 MHz, acetone-d₆, 25 °C).



Scheme 2 Conversion of fac-[Ru(L¹)₃](PF₆)₂ to fac-[Ru(L²)₃](PF₆)₂ to (ia) SOCl₂-CH₃CN reflux, (ib) 3,4-dimethoxyanaline, NEt₃-THF reflux, (ic) KPF₆(aq).

retaining an excess of ammonium salts), indicating the absence of the characteristic aliphatic signals. Due to the problems in isolating (Δ or Λ)-[Ru(L¹)₃](PF₆)₂, and its propensity to ester formation, it was reacted without isolation to form the tri-amide complex ($\Delta \text{or }\Lambda$)-[Ru(L²)₃](PF₆)₂ (Scheme 2). The formation of the tri-acyl chloride proved problematic, and the direct use of thionyl chloride gave only intractable oils. However, the use of a 10% mixture of thionyl chloride in acetonitrile proved successful, followed by the addition of the aromatic amine 3, 4-dimethoxyaniline (4-aminoveratrole), and the product could be achieved in a reasonable yield of 67% from [Ru- $(R-L^{Me})$](PF₆)₂ as the fac isomer, as demonstrated by ¹H NMR spectroscopy and mass spectrometry.

The UV/Vis spectra of all of the complexes show the characteristic $\pi - \pi^*$ transitions at approximately 290 nm. and the strong metal to ligand charge transfer (MLCT) absorption at 484 nm for $[Ru(R-L^{Me})](PF_6)_2$ and 486 nm for [Ru- $(R-L^{Ph})](PF_6)_2$. The MLCT absorption is red shifted for both complexes relative to [Ru(bipy)₃)](PF₆)₂ (445 nm) presumably due to the electron withdrawing nature of the ligand, and a steric strain causing deviation from the ideal coordination geometry. On conversion to fac-[Ru(L²)₃](PF₆)₂ the MLCT moves back to 460 nm, in keeping with the removal of the constraints. A contribution from aromatic transitions, attributed to the 3,4-dimethoxyaniline group, is apparent at 460 nm. The fluorescence observed for complex $[Ru(R-L^{Me})](PF_6)_2$ and fac-[Ru(L²)₃](PF₆)₂ were similarly red shifted when compared to $[Ru(bipy)_3)](PF_6)_2$, with significantly lower quantum yields, as would be expected from the electron withdrawing carbonyl group (Table 1).

An investigation of the circular dichroism (CD) spectra of all of the complexes indicates that a strong Cotton effect is observed, typical of a dominant single enantiomer. In keeping with the NMR data, the size of the Cotton effect would indicate that a single diastereomer is present for both of the tripodal ligand systems with [Ru(S-L^{Me})](PF₆)₂ and [Ru- $(R-L^{Ph})](PF_6)_2$ adopting a Δ -configuration, and [Ru- $(R-L^{Me})](PF_6)_2$ the opposite Λ form (by comparison of the sign of the Cotton effect in the π - π * ligand transitions).³² The addition of sodium hydroxide to the CD sample (in an aqueous-acetonitrile mixture) resulted in conversion to fac- $[Ru(L^{1})_{3}](PF_{6})_{2}$ with complete retention of the metal centred stereochemistry (Fig. 2). The disconnection of the tether is accompanied by a blue shift in the MLCT Cotton effect, consistent with the visible absorption spectrum. Disappointingly, the conversion of complex $[Ru(R-L^{Me})](PF_6)_2$ to



Table 1 UV/Vis abs	sorption and emi	ission spectral data r	ecorded in aceto	nitrile at room temp	erature (concent	ration typically 1–2	$\times 10^{-6}$ mol dm ⁻	-3)		
	Absorption								Emission ^a	
Complex	$\lambda_{ m max} \pm 1/$ nm	$\epsilon imes 10^3/{ m dm}^{-3}$ mol $^{-1}$ cm $^{-1}$	$\lambda_{ m max}\pm 1/$ nm	$arepsilon imes rac{10^3}{\mathrm{mol}^{-1}}\mathrm{cm}^{-3}$	$\lambda_{ m max}\pm 1/$ nm	$arepsilon imes 10^3/{ m dm}^{-3}$ mol $^{-1}$ cm $^{-1}$	$\lambda_{ m max}\pm 2/$ nm	$arepsilon imes 10^3/{ m dm}^{-3} { m mol}^{-1} { m cm}^{-1}$	$\lambda_{\max^a}\pm 2/$ nm ^a	$\Phi_{ m em} \; \lambda_{ m max} \pm 5\%$
$[Ru(R-L^{Me})](PF_6)_2$	246	34.0	287	89.6	365	sh	484	9.56	637	0.049
$[Ru(R-L^{Ph})](PF_6)_2$	251	39.5	291	103.2			486	11.4	n/a	n/a
Δ -[Ru(L ²) ₃](PF ₆) ₂	245	41.3	288	83.5	351	sh	460	9.71	634	0.020
$[Ru(bpy)_3](PF_6)_2$	245	25.4	287	82.4			450	13.9	614	0.062
^a Excited at 450 nm i	n a solution nor	malised to an absorp	otion of 0.1 in a	1 cm cell. ^b By integ	gration and comp	parison to published	value of [Ru(bp	$y_{3}](PF_{6})_{2}$. ³¹		



Fig. 2 Circular dichroism spectrum of (a) Λ -[Ru(R-L^{Me})](PF₆)₂ (black) and Λ -[Ru(L^1)](PF₆)₂ (grey), (b) Δ -[Ru(R-L^{Ph})](PF₆)₂ (black) and Δ -[Ru(L^1)](PF₆)₂ (grey); (5 × 10⁻⁵ mol dm⁻³, 50% aqueous CH₃CN at 25 °C).

fac-[Ru(L²)₃](PF₆)₂ resulted in a significant drop in the Cotton effect, despite retaining the *fac* geometry, indicating that in the process of the amidification a degree of racemization can occur. It is assumed that this occurs *via* a ligand dissociation of the complex following amidification, due to the increased steric bulk of the ligand in keeping with observations made with similar complexes.³³

In summary we have managed to demonstrate for the first time, an elegant synthetic route to the isolation of a single enantiomeric form of fac-[Ru(L¹)₃]²⁺, with the complex retaining the memory of a chiral auxiliary used to control the geometry. While the yields are currently a little disappointing, we are in the process of optimising the synthetic procedures and extending the methodology to other metal centres. This may permit the isolation of enantiopure materials that are not readily accessible by traditional techniques.

Experimental

(+)-(2S,2'S,2''S) and (-)-(2R,2'R,2''R)-triisopropanolamine and (+)-(2R,2'R,2''R)-triphenylethan-2-olamine were prepared according to a literature procedure from the appropriate epoxide.³⁰ 2,2'-Bipyridine-5-carboxylic acid was isolated by oxidation of 5-methyl-2,2'-bipyridine.²³

Ligand *R*-L^{Me} (S-L^{Me} prepared similarly)

2,2'-Bipyridine-5-carboxylic acid (1.003 g, 5.0 mmol) was refluxed in thionyl chloride (40 ml) for 3 h. The thionyl

chloride was removed by distillation and the acyl chloride dried in vacuo. The residue was dissolved in dry THF (60 ml) and brought to reflux under nitrogen. To this a mixture of (2R,2'R,2"R)-triisopropanolamine (0.275 g, 1.44 mmol), THF (10 ml) and triethylamine (2 ml) were added dropwise over 1 h and then refluxed for a further 16 h. The solvent was removed and the solid dissolved in DCM (100 ml). The solution was washed with water (5 \times 50 ml) and the organic layer collected and dried over magnesium sulfate, filtered and evaporated to dryness. The solid was dissolved in acetone, and an insoluble white material was removed by filtration. The solvent was removed giving the product as a syrupy brown oil. Yield: 0.764 g (72%), ¹H NMR (500 Hz, CDCl₃) $\delta_{\rm H}$ 9.28 (1H, s, BpyH⁶), 8.71 (1H, d, J = 4.7 Hz, BpyH⁶) 8.51 (1H, d, J =8.2 Hz, BpyH³), 8.48 (1H, d, J = 8.2 Hz, BpyH^{3'}), 8.42 (1H, d, J = 8.2 Hz, BpyH⁴), 7.85 (1H, dd, J = 8.2, 7.6 Hz, BpyH⁴), 7.36 (1H, dd, J = 4.6, 7.6 Hz, BpyH^{5'}), 5.46 (1H, m, OCH, 2.56–2.39 (2H, m, NCH₂), 1.37 (3H, d, J = 6.4 Hz, CH₃); ESMS: [M]⁺ 738.4.

Ligand R-L^{Ph}

The ligand was prepared following a similar procedure to that used for *R*-L^{Me} using (2R,2'R,2''R)-triphenylethan-2-olamine and purified by column chromatography eluted with DCM containing 2% methanol, collecting the second major fraction (unoptimized yield 38%). ¹H NMR (500 Hz, CDCl₃) $\delta_{\rm H}$ 9.20 (1H, s, BpyH⁶), 8.68 (1H, d, J = 5.0 Hz, BpyH^{6'}) 8.43 (1H, d, J = 8.2 Hz, BpyH³), 8.34 (1H, d, J = 8.2 Hz, BpyH⁴), 8.28 (1H, d, J = 8.2 Hz, BpyH^{3'}), 7.78 (1H, dd, J = 8.2, 7.6 Hz, BpyH^{4'}), 7.42–7.20 (6H, m, Ph + BpyH^{5'}), 6.28 (1H, d, J = 9.1 Hz, OCH), 3.40 (1H, m, NCH₂), 1.93 (1H, m, NCH₂); ESMS: [M]⁺ 924.5.

$[Ru(R-L^{Me})](PF_6)_2$

Silver nitrate (1.01 g, 60 mmol) was dissolved in refluxing ethanol (500 ml) under nitrogen. To this, a mixture of $R-L^{Me}$ (0.570 g, 0.773 mmol) and [Ru(DMSO)₄Cl₂] (0.36 g, 0.744 mmol) dissolved in ethanol (30 ml) and DMSO (20 ml) was slowly added by mechanical pumping over 4 h and refluxed for an additional 2 h. The mixture was cooled and sodium chloride (~ 1 g) was added. The brown solution was filtered under gravity and the ethanol removed at reduced pressure. The residues were suspended in water (150 ml), filtered onto a SP Sephadex[®] C-25 cation exchange column, and the divalent product eluted with aqueous toluenesulfonic acid sodium salt (0.15 M, 10% acetone) solution. The product was isolated by the addition of ammonium hexafluorophosphate (0.30 g) to the major fraction and recrystallized from acetone-water. Yield: 0.190 g (22%). Analysis Found: C 45.31; H 4.11; N 7.56%, C42H39N7O6RuP2F12 · 2(CH3)2CO · 2H2O requires C 45.01; H 4.33; N 7.65%, ¹H NMR (500 MHZ, d₆ acetone) $\delta_{\rm H}$ 8.95 (3H, m, bipyH^{3,3',6}), 8.70 (1H, d, J = 8.6 Hz, BpyH⁴), 8.30 (1H, dd, J = 8.2, 7.7 Hz, BpyH^{4'}), 7.86 (1H, d, J = 5.7 Hz, BpyH⁶), 7.73 (1H, dd, J = 5.7, 7.7 Hz, BpyH^{5'}), 5.39 (1H, m, OCH), 2.78 (1H, dd, $J = 12.0, 12.0, \text{NCH}_a$), 2.33 (1H, dd, J =3.3, 12.0, NCH_b), 1.24 (3H, d, J = 6.0 Hz, CH₃), ESMS. m/z 984.2 $[M - PF_6]^+$, 838.2 $[MH - 2PF_6]^+$, 419.5 $[M - 2PF_6]^{2+}$.

$[Ru(R-L^{Ph})](PF_6)_2$

The complex was prepared following a similar procedure to $[Ru(R-L^{Me})](PF_6)_2$ and purified using SP Sephadex[®] C-25 cation exchange column with the divalent product obtained when eluted with aqueous toluenesulfonic acid sodium salt (0.20 M, 10% acetone) solution. The product was isolated by the addition of ammonium hexafluorophosphate (0.30 g) to the major fraction and recrystallized from acetone water. Yield 10%. Analysis Found: C 47.32; H 4.35; N 5.88%, $C_{57}H_{45}N_7O_6RuP_2F_{12} \cdot 7H_2O$ requires C 47.51; H 4.13; N 6.80%, ¹H NMR (500 MHZ, d₆ acetone) $\delta_{\rm H}$ 9.11 (1H, s, bipyH⁶), 8.92 (1H, d, J = 8.6 Hz, BpyH³), 8.88 (1H, d, J = 8.2 Hz, BpyH^{3'}), 8.70 (1H, d, J = 8.6 Hz, BpyH⁴), 8.21 (1H, dd, J = 8.2, 7.7 Hz, BpyH^{4'}), 7.87 (1H, d, J = 5.7 Hz, BpyH⁶), 7.65 (1H, m, BpyH^{5'}), 7.42–7.20 (5H, m, Ph), 6.22 (1H, m, OCH), 2.80 (1H, m, $J = 12.0, 12.0, NCH_a$), 2.26 (1H, m, J = 3.3, 12.0,NCH_b), ESMS. m/z 1170.3 $[M - PF_6]^+$, 512.7 $[M - 2PF_6]^{2+}$.

Λ -[Ru(L¹)₃](PF₆)₂²⁴

[Ru(*R*-L^{Me})](PF₆)₂ (103 mg, 91.2 µmol) was dissolved in acetonitrile (30 ml) and mixed with an aqueous solution (30 ml) containing potassium hydroxide (0.20 g, 3.6 mmol) for 72 h. The volume of solvent was reduced to 25 ml, acidified with 2 M aqueous HCl to pH 3 and 0.2 g of ammonium hexafluorophosphate added. The product was extracted with DCM (3 × 30 ml), dried over anhydrous sodium sulfate, and dried *in vacuo*. The product retained a high degree of water and salt preventing detailed analysis. The product was used without further characterisation (impure: ¹H NMR (500 MHZ, d₆ acetone) $\delta_{\rm H}$ 8.98 (1H, d, J = 8.4 Hz, BpyH³), 8.93 (1H, d, J = 8.2 Hz, BpyH³), 8.66 (1H, d, J = 8.2, 7.7 Hz, BpyH⁴), 8.13 (1H, d, J = 5.7 Hz, BpyH⁶), 7.66 (1H, m, BpyH⁵).

Λ -[Ru(L²)₃](PF₆)₂²⁴

The crude product $[Ru(L^1)_3](PF_6)_2$ was dissolved in dry acetonitrile (20 ml) and thionyl chloride (5 ml) was added over 5 minutes. The mixture was refluxed for 6 h, and the solvent removed in vacuo. The residues were dissolved in CH₃CN (30 ml) and added over 1 h to a mixture of 3,4dimethoxyaniline (4-aminoveratrole) (0.15 g 9.8 mmol) and triethylamine (1 ml) in acetonitrile (30 ml). The resulting red solution was heated at reflux for 2 h and stirred for 14 h at room temperature. The solvent was removed and the crude product dissolved in water (50 ml), neutralised with a saturated aqueous Na₂CO₃ solution, and purified using a SP Sephadex[®] C-25 cation exchange column. The divalent product was collected having been eluted with aqueous toluenesulfonic acid sodium salt (0.25 M, 20% acetone) solution. The product was isolated by the addition of NH_4PF_6 (0.30 g) and recrystallized from acetone-water and further purified by passage down Sephadex LH20 eluted with methanol-acetonitrile. (Yield from 103 mg of [Ru(S-L^{Me})](PF₆)₂ 85 mg, 67%). Analysis Found: C 47.58; H 4.17; N 7.19%, C₅₇H₅₁N₉O₉RuP₂F₁₂ · 3H₂O requires C 47.18; H 3.96; N 8.69%, ¹H NMR (500 MHZ, d₃ acetonitrile) $\delta_{\rm H}$ 11.09 (1H, s, NH), 8.72 (1H, s, bipyH⁶), 8.53 (1H, d, J = 8.6 Hz, BpyH³), 8.52 (1H, d, J = 8.0 Hz, BpyH³), 8.35 Published on 25 May 2007. Downloaded by Northeastern University on 22/10/2014 17:51:47.

Acknowledgements

This research was supported by the EPSRC, and we thank the EPSRC Mass Spectrometry Service, Swansea for the MS.

References

- 1 B. Kesanli and W. B. Lin, Coord. Chem. Rev., 2003, 246, 305–326.
- 2 L. Han and M. Hong, Inorg. Chem. Commun., 2005, 8, 406–419.
- 3 M. Heitbaum, F. Glorius and I. Escher, *Angew. Chem., Int. Ed.*, 2006, **45**, 4732–4762.
- 4 I. Ojima, *Catalytic asymmetric synthesis*, Wiley-VCH, New York, 2000.
- 5 N. Farrell, Coord. Chem. Rev., 2002, 232, 1-4.
- 6 I. Kostova, Curr. Med. Chem., 2006, 13, 1085-1107.
- 7 A. S. Abu-Surrah and M. Kettunen, Curr. Med. Chem., 2006, 13, 1337–1357.
- 8 A. Juris, S. Barigelletti, S. Campagna, V. Balzani, P. Belser and A. von Zelewsky, *Coord. Chem. Rev.*, 1988, **84**, 85–277.
- 9 A. von Zelewsky, *Stereochemistry of Coordination Compounds*, Wiley, Chichester, UK, 1996.
- 10 A. Werner, Ber. Dtsch. Chem. Ges., 1911, 44, 1887-1890.
- 11 F. P. Dwyer and E. C. Gyarfas, J. Proc. R. Soc. N.S.W., 1949, 83, 174–176.
- 12 A. E. Aarfa, K. I. Kinnear and J. C. Lockhart, J. Chem. Soc., Chem. Commun., 1992, 61–63.
- 13 X. Hua and A. von Zelewsky, Inorg. Chem., 1995, 34, 5791-5797.
- 14 S. Bodige, A. S. Torres, D. J. Maloney, D. Tate, G. R. Kinsel, A. K. Walker and F. M. MacDonnell, *J. Am. Chem. Soc.*, 1997, **119**, 10364–10369.

- 15 R. Caspar, H. Amouri, M. Gruselle, C. Cordier, B. Malezieux, R. Duval and H. Leveque, *Eur. J. Inorg. Chem.*, 2003, 499–505.
- 16 W. R. Browne, D. Hesek, J. F. Gallagher, C. M. O'Connor, J. S. Killeen, F. Aoki, H. Ishida, Y. Inoue, C. Villani and J. G. Vos, *Dalton Trans.*, 2003, 2597–2602.
- 17 N. C. Fletcher, P. C. Junk, D. A. Reitsma and F. R. Keene, J. Chem. Soc., Dalton Trans., 1998, 133–138.
- 18 E. Holder, G. Trapp, J. C. Grimm, V. Schurig and E. Lindner, *Tetrahedron: Asymmetry*, 2002, 13, 2673–2678.
- 19 J. Jacques, A. Collet and S. H. Wilen, *Enantiomers Racemates and Resolutions*, Krieger, Melbourne, FL, 2nd edn, 1994.
- 20 F. R. Keene, Chem. Soc. Rev., 1998, 27, 185-193.
- 21 F. M. MacDonnell, M. J. Kim and S. Bodige, *Coord. Chem. Rev.*, 1999, **186**, 535–549.
- 22 J. Lacour and V. Hebbe-Viton, *Chem. Soc. Rev.*, 2003, **32**, 373–382.
- 23 N. C. Fletcher, M. Nieuwenhuyzen and S. Rainey, J. Chem. Soc., Dalton Trans., 2001, 2641–2648.
- 24 N. C. Fletcher, R. Prabaharan, M. Nieuwenhuyzen and A. Wilson, *Chem. Commun.*, 2002, 1188–1189.
- 25 H. Weizman, J. Libman and A. Shanzer, J. Am. Chem. Soc., 1998, 120, 2188–2189.
- 26 G. Nuding, F. Vögtle, K. Danielmeier and E. Steckhan, Synthesis, 1996, 71–73.
- 27 C. Hamann, A. von Zelewsky, A. Neels and H. Stoeckli-Evans, *Dalton Trans.*, 2004, 402–406.
- 28 K. D. Oyler, F. J. Coughlin and S. Bernhard, J. Am. Chem. Soc., 2007, 129, 210–217.
- 29 G. Haberhauer, T. Oeser and F. Rominger, *Chem. Commun.*, 2005, 2799–2801.
- 30 W. A. Nugent and R. L. Harlow, J. Am. Chem. Soc., 1994, 116, 6142–6148.
- 31 N. C. Fletcher, F. R. Keene, H. Viebrock and A. von Zelewsky, *Inorg. Chem.*, 1997, 36, 1113–1121.
- 32 T. J. Rutherford, P. A. Pellegrini, J. Aldrich-Wright, P. C. Junk and F. R. Keene, *Eur. J. Inorg. Chem.*, 1998, 1677–1688.
- 33 E. A. P. Armstrong, R. T. Brown, M. S. Sekwale, N. C. Fletcher, X.-Q. Gong and P. Hu, *Inorg. Chem.*, 2004, 43, 1714–1722.