A highly rigid ditopic conjugate with orthogonal coordination axes and its zinc(II) and copper(II) complexes†

Benoît Champin, Valérie Sartor and Jean-Pierre Sauvage*

Received (in Montpellier, France) 31st August 2007, Accepted 15th January 2008
First published as an Advance Article on the web 5th February 2008
DOI: 10.1039/b713367g

A highly rigid ditopic ligand has been prepared which consists of a terpy fragment connected in the back to a phen nucleus *via* a 1,4-phenylene linker. The chemical structure of the presently reported ligand is such that the coordination axes of the two chelates are orthogonal to one another. The reaction of this phen–terpy conjugate with zinc(II) surprisingly affords in good yield a dinuclear complex in spite of the tension of the generated structure, whereas coordination of copper(II) centres to the two-chelate ligand enables the formation of the trinuclear complex also.

Introduction

The coordination properties of multi-chelate ligands, and in particular the nature of the multi-metallic assemblies obtained after complexation to various metal centres, are strongly dependent on the mutual arrangement of the coordinating subunits within the multifunctional ligand. As far as we know, two-chelate ligands in which the coordination axes of the constitutive chelates are orthogonal to one another are far from being common in the literature. Generally speaking, multi-chelate ligands containing two or several aromatic polyimines have been extensively used, in conjunction with ruthenium(II) and related second and third row d^6 transition metals (Os(II), Re(I), Rh(III) and Ir(III)), especially in relation to electron and energy transfer processes.[1–8] They have also been frequently utilised to construct elegant multinuclear architectures such as grids,[9] helical complexes,[10,11] racks,[12,13] *etc.*, or new topologies such as knots[14,15] or rotaxane oligomers.[16–18] In most cases, the axes of the individual chelates belonging to the multisite ligand are antiparallel or parallel to one another, although different situations can also be found.

By contrast, two-chelate ligands with orthogonal coordination axes for the chelates (Fig. 1) should favour the formation of novel multinuclear complexes and lead to well-defined transition metal-incorporating assemblies.[19–21]

If the complexed metal M has a strong preference for 5-coordinate situations, M(A)(B) complexes should be strongly favoured *versus* symmetrical complexes of the $M(A)_2$ or $M(B)_2$ type. In the present paper, we would like to report the synthesis and the coordination properties of such a 2-chelate ligand, containing a terpy (terpy = 2,2′:6′,2″-terpyridine) unit attached to a phen (phen = 1,10-phenanthroline) nucleus.§ The rigid linker used (1,4-phenylene) has been chosen to be as short and rigid as possible, and connects the two chelates *via* appropriate positions (4′ position of terpy and 3 position of phen) so as for the coordination axes to be perpendicular to one another. The geometry of terpy is indeed very appropriate to an axial functionalization in the back (*via* the 4′ position). The terpy nucleus is functionalized at the 5 and 5″ positions with methyl groups. The phen unit bears an anisyl group, which will act as a ^{1}H NMR probe during the synthesis.

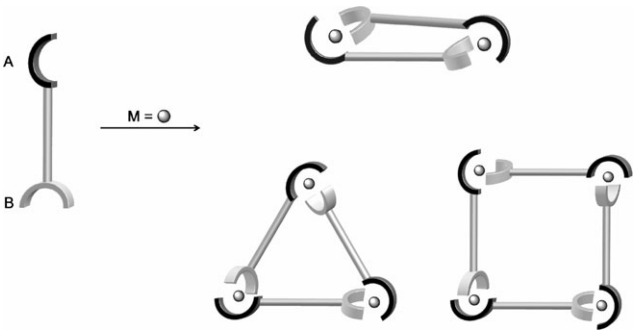


Fig. 1 Formation of M(A)(B) complexes should lead to oriented cyclic structures. Depending on the coordination sphere geometry of the transition metal used, various rings and nuclearities could be obtained. (A = bidentate; B = terdentate).‡

The aim of this full paper is to give extensive details on the synthetic procedure used to obtain the phen–terpy conjugate, whose coordination to zinc(II) metal centres was briefly revealed in a preliminary report.[24] The influence of the metal centres on the nuclearities of the structures obtained will be discussed through the study of coordination chemistry with copper(II).

Results and discussion

Synthesis of the acyclic phen–terpy conjugate

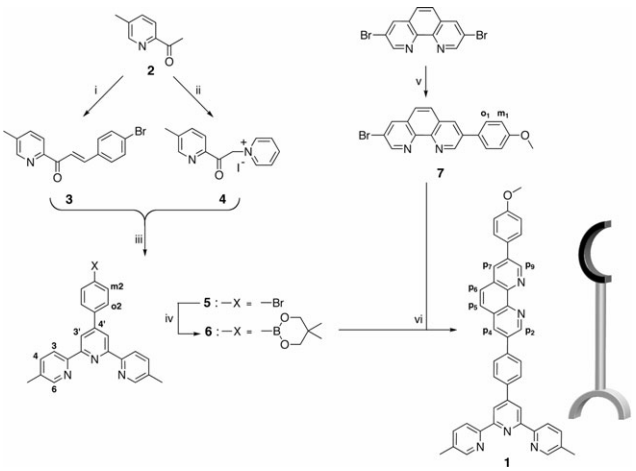
The strategy to obtain the desired molecule is straightforward: each chelate is introduced in a fragment, and both of them are

Laboratoire de Chimie Organo-Minérale, LC 3, UMR 7177 du CNRS, Université Louis Pasteur, Faculté de Chimie, 4 rue Blaise Pascal, 67070 Strasbourg Cedex, France. E-mail: sauvage@chimie.u-strasbg.fr; Fax: +33 (0)3 90 24 13 68; Tel: +33 (0)3 90 24 13 61

† Electronic supplementary information (ESI) available: Structures and atom numbering for all molecules; expanded isotopic distribution patterns for $[T + BF_4]^{5+}$ and $[D + BF_4]^{3+}$. See DOI: 10.1039/b713367g

‡ Recently, the synthesis of various metallamacrocycles using terpy-based ligands has been reported by Constable *et al.*[22]

§ It should be noted that recently, the synthesis of a ligand incorporating directly bonded phen and terpy nuclei has been reported by Gaviña and Tatay.[23] In that case, the phen unit is connected to the 5 position of the terpy.



Scheme 1 Synthesis of the 2-site ligand **1**. *Reagents and conditions*: (i) 4-bromobenzaldehyde, MeOH–$NaOH_{(aq)}$, 30 min; (ii) I_2, pyridine, reflux 1 h, rt 14 h; (iii) NH_4OAc, AcOH, reflux 7 h, rt 14 h; (iv) $Pd(dppf)Cl_2$, KOAc, B_2neo_2, dioxane, 80 °C, 18 h; (v) $Pd(PPh_3)_4$, Na_2CO_3, *p*-anisylboronic acid, toluene–H_2O, reflux, 14 h; (vi) $Pd(PPh_3)_4$, Na_2CO_3, reflux, 30 h.

coupled under Suzuki classical conditions (Scheme 1). The spacer between both chelates was decided to be incorporated in the terpy fragment using the Kröhnke synthesis. As far as the phen fragment is concerned, dissymmetry had to be introduced so as to have an anisyl unit on one side, and a precursor to the Suzuki coupling on the other side.

Synthesis of the terpy moiety. The Kröhnke synthetic pathway relies on the coupling of an azachalcone with a pyridinium iodide, and in our case, both of these building blocks are obtained from the same compound: 2-acetyl-5-methylpyridine **2** (Scheme 1). As the terpy moiety is a central building block, each step of the synthesis was optimized in order to obtain the highest possible yields and the largest amount of compound **5**.

Compound **2** had previously been made by reacting a Grignard reagent with the nitrile derivative.[25] We developed a new efficient route inspired by the procedure described by Holm *et al.*,[26] which afforded **2** in 52% yield.

Compound **3** was obtained thanks to a classical Claisen–Schmidt condensation between an aldehyde with no α-hydrogens (4-bromobenzaldehyde) and ketone **2** (Scheme 1). The crossed-coupling reaction was carried out in methanol in the presence of a strong base (NaOH, 1 M). The β-hydroxy ketone was thus formed, but the conditions used were sufficient to cause dehydration. The α,β-unsaturated ketone **3**, referred to here as *azachalcone* because of the presence of the pyridyl nucleus, was thus produced in good yield (86% after recrystallization),[27,28] and has been fully characterized by ^1H and ^{13}C NMR spectroscopy, and EI-MS.

Compound **4** was obtained by reaction between **2** and 1.1 equivalents of iodine under argon in freshly distilled pyridine, which played here both the role of solvent and reagent.[29] The final product **4** precipitated out of the solution mixture and was obtained in a good yield (74%) after recrystallization (Scheme 1).

Terpyridine **5** was obtained following the Kröhnke procedure, between azachalcone **3** and pyridinium iodide **4** in acetic acid (Scheme 1). A Michael addition afforded in a first step a diketone intermediate, which was not isolated. After playing the role of a base in the first step, ammonium acetate enabled the central ring of the terpyridine to close and thus afforded the final compound **5** in 60% yield after column chromatography. This new compound has been fully characterized by ^1H and ^{13}C NMR spectroscopy, HMQC and HMBC 2D ^1H–^{13}C experiments, EI-MS and elementary analysis.

It should be noted that compound **5** could also be prepared *via* an alternative route, replacing acetic acid by methanol. In that case, terpy **5** spontaneously precipitated out of the solution mixture, and no further purification was needed. The overall yield was the same as in the first route. This optimized synthetic pathway afforded multigram quantities of terpyridine **5**.

In order to make a Suzuki coupling between the two chelating fragments, one of them should bear a boronic acid (or ester) function. In spite of the "synthetic price" of the terpy moiety **5**, we decided to modify the functionality at the back of the terpy by changing the bromine atom for a boronic ester function in presence of bis(neopentyl glycolato)diboron (B_2neo_2) according to the well described procedure[30] (Scheme 1). Remarkably, compound **6** was thus obtained in quantitative yield from **5**, and was fully characterized.

Synthesis of the phen building block. In order to incorporate the phen nucleus in a thread with axial symmetry, a phen substituted in the 3 and 8 positions was necessary. Synthesis of the dissymmetrical phen unit could be achieved in one step from 3,8-dibromo-1,10-phenanthroline.[31,32] In order to incorporate only one anisyl group, a statistical Suzuki coupling reaction[32,33] was performed under classical conditions, using 0.9 equivalents of *p*-anisylboronic acid, Na_2CO_3 as a base, and $Pd(PPh_3)_4$ as a catalyst (Scheme 1). The mono-coupled product **7** was isolated in 46% yield.

Connection of phen and terpy nuclei. A final Suzuki coupling reaction between **6** and **7** under classical conditions yielded the phen–terpy conjugate **1** (24%), containing 7 conjugated 6-membered aromatic rings.

Compound **1** has been fully characterized by ^1H and ^{13}C NMR spectroscopy, HMQC and HMBC 2D ^1H–^{13}C experiments, HR ES-MS and DOSY (diffusion-ordered spectroscopy).

Coordination studies on the phen–terpy conjugate

Zinc(II) assemblies. Zn^{2+} forms stable 5-coordinate complexes and most of the time it is sufficiently labile to allow formation of coordination compounds under thermodynamic control.[34] This metal was thus selected for complexation studies with ligand **1**.[24]

For entropic reasons, the reaction between Zn^{2+} and **1** is expected to lead to the smallest possible complex.¶ Nevertheless the size of the species obtained has to be compatible with the coordination constraints imposed by the metal and the ligand. If distortion of the Zn^{2+} coordination sphere and/or of the ligand backbone costs less than the entropic price

¶ Translational entropy would favour formation of the highest number of small particles, while conformational entropy would favour the formation of polymers.

needed to build the large ideal 4-metal species, lower nuclearities will be formed. This is the case in the present system. To our surprise, the dimer was the sole complex formed (78% yield), without formation of tetramer nor even trimer complexes. The chemical structure of $[Zn_2{\cdot}(\mathbf{1})_2]^{4+}$ (D = dimer) was proven by electrospray ionization mass spectroscopy (ES-MS) and ^{1}H NMR spectroscopies. HR ES-MS analysis of the yellow solid (Fig. 2) revealed three major peaks at mass-to-charge (m/z) ratios of 343.6, 507.8, and 836.1, corresponding to $[D]^{4+}$, $[D + \mathrm{OTf}]^{3+}$, and $[D + 2\mathrm{OTf}]^{2+}$, respectively (Fig. 2), a situation that is consistent with the proposed dimer compound $[Zn_2{\cdot}(\mathbf{1})_2]{\cdot}4\mathrm{OTf}$.

A DOSY experiment carried out on a solution of the yellow solid in MeOD (Fig. 3) revealed unambiguously the presence of a single species, characterized by its diffusion coefficient ($\mathscr{D}$ = 470 μm^2 s^{-1}; ligand **1** in CD_2Cl_2: $\mathscr{D}$ = 1000 μm^2 s^{-1}) and its hydrodynamic radius (r_H = 8.5 Å; monomer **1**: r_H = 5.3 Å). Computational simulation of the hydrodynamic radius of an ellipsoid object which matches the experimental value of the radius enabled us to predict the size of the product in solution: a = 14 Å and $b = c$ = 6 Å. The object is thus a prolate ellipsoid, which is consistent with the proposed dimer compound $[Zn_2{\cdot}(\mathbf{1})_2]{\cdot}4\mathrm{OTf}$. Considering both the results of ES-MS and DOSY experiments, we can tell that *the sole product formed during the complexation process is the dimer species* $[Zn_2{\cdots}(\mathbf{1})_2]{\cdots}4OTf$.

Moreover, ^{1}H NMR spectroscopy (Fig. 3) clearly shows what was expected for a dimer species: the geometry around the zinc centre is so distorted that the p_2 proton of the phen moiety of one terpy–phen conjugate points right in the shielding cone of the central ring of the terpy fragment of the other two-site ligand, and consequently the p_2 proton signal is strongly shifted upfield ($\Delta\delta$ = −2.82 ppm).

The present example tends to indicate that entropy is the prevailing factor in the complexation process: the reaction leads to the smallest possible complex in spite of probable distortion in the Zn^{2+} coordination sphere and constraints within the organic ligand **1**. Obviously, the use of transition metal centres other than Zn^{2+} with more demanding stereoelectronic requirements, making distortion more difficult, should favour formation of trimers or tetramers.

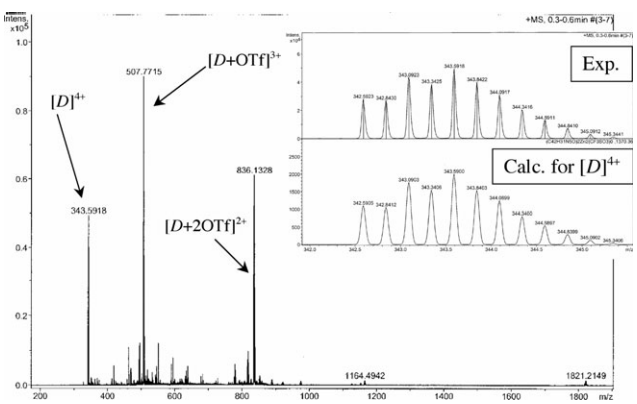


Fig. 2 HR ES-MS of the zinc(II) dimer complex and expanded isotopic distribution patterns for $[D]^{4+}$, which correlate well with the calculated distributions of the dimer $[Zn_2{\cdot}(\mathbf{1})_2]$.

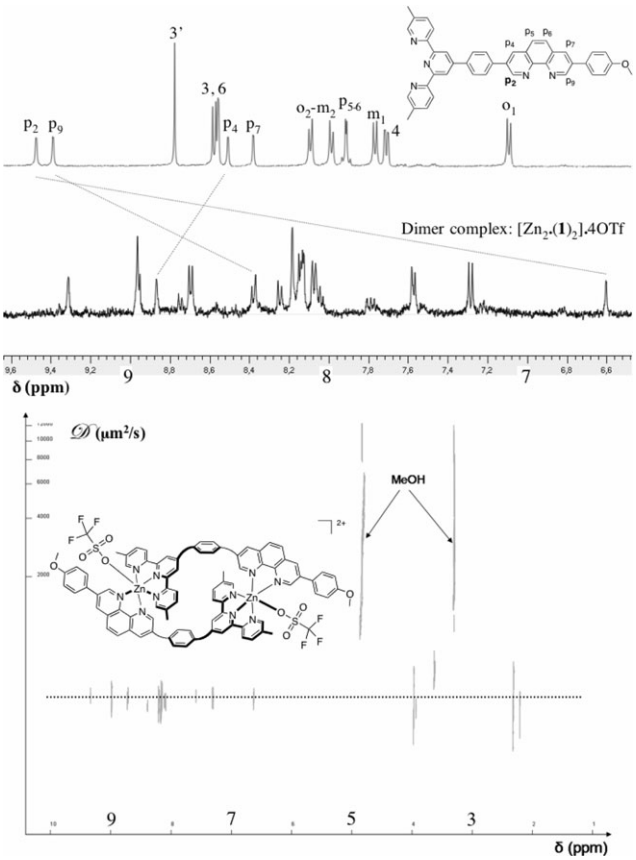
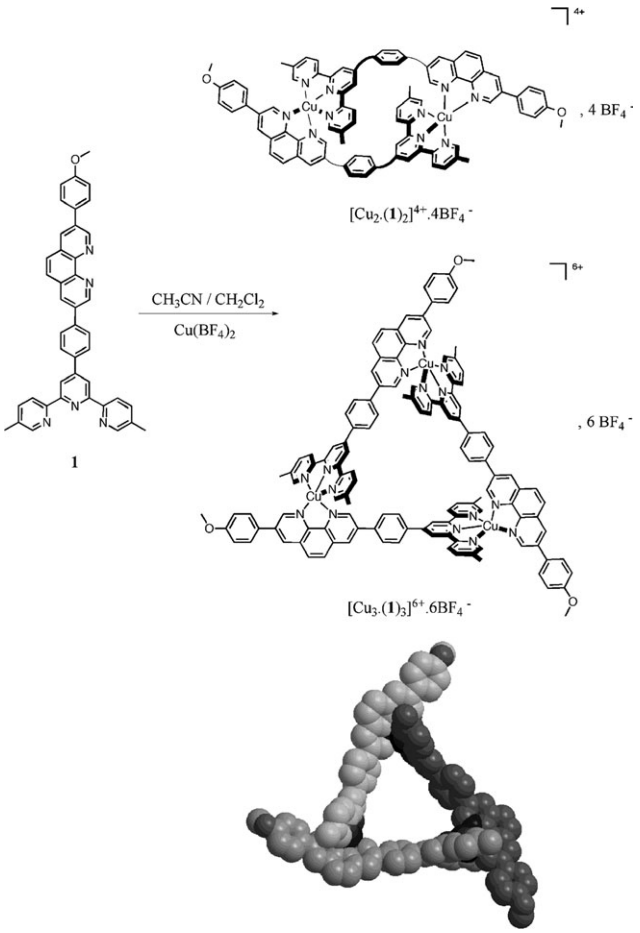


Fig. 3 (Top) ^{1}H NMR spectra (aromatic region) of **1** and its zinc dimer complex $[Zn_2{\cdot}(\mathbf{1})_2]{\cdot}4\mathrm{OTf}$. (Bottom) DOSY experiment on the dimer complex in MeOD. Apart from the MeOH broad signals, a single product is present.

Copper(II) complexes. The achievement of such complicated structures around metal centres is in our case carried out under thermodynamic control, thanks to labile coordination bonds between the ligands and the metal centre. Indeed the system has to have the possibility to create and break bonds at will, so that it can self-repair its own mistakes, and eventually converge to the most stable product, this one being hopefully the desired one. The most commonly encountered copper(II) complexes have a coordination number (CN) of 5 (square pyramidal or trigonal bipyramidal geometries) or 6 (octahedral arrangement, with Jahn–Teller distortion). In spite of its paramagnetic character, which prevents us from using NMR spectroscopy to identify species formed, copper(II) was thus an attractive candidate, especially considering its more demanding stereoelectronic requirements.

The choice of the counterion was again crucial: it should be as little coordinating as possible in order to avoid its coordination to the copper centre, which should remain 5-coordinate. Among the various copper(II) salts available, tetrafluoroborate copper(II) was selected. The coordination experiment was carried out by mixing equimolar amounts of ligand **1** in CH_2Cl_2 and $Cu(BF_4)_2$ in CH_3CN, respectively (Scheme 2). The solution turned instantaneously olive green, which is characteristic of Cu(II) complexes bearing phen and terpy units in their coordination sphere.[35–37] The solution was



Scheme 2 Formation of the dimer and trimer complexes, and molecular model of the trimer species (Chem 3D software), whose energy was minimized using MM2 software.

allowed to stir for 19 h at room temperature, and by addition of diethyl ether a green solid precipitated out. It was recovered in a good yield (89%).

The composition of the mixture was first investigated using ES-MS (Fig. 4 and ESI†). It clearly showed the presence of two species corresponding to the dimer (*D*) and the trimer (*T*). The respective amount of each compound could not be evaluated since intensity of peaks in the ES-spectrum is connected to the amount of product by a response factor, which is specific to each species.

The major peaks at mass-to-charge (*m*/*z*) ratios of 342.6, 428.5, 557.2 and 772.2 correspond to the trimer species $[Cu_3\cdot(\mathbf{1})_3]^{6+}$ (*T*), with, respectively, no BF_4^- as counterion $[T]^{6+}$, one counterion $[T + BF_4]^{5+}$, two counterions $[T + 2BF_4]^{4+}$, and three counterions $[T + 3BF_4]^{3+}$. The other peaks at 342.6, 485.8 and 772.2 correspond to the dimer species $[Cu_2\cdot(\mathbf{1})_2]^{4+}$ (*D*), with, respectively, no BF_4^- as counterion $[D]^{4+}$, one counterion $[D + BF_4]^{3+}$, and two counterions $[D + 2BF_4]^{2+}$. The *m*/*z* ratio regions at 342.6 and 772.2 are thus superpositions of the isotopic patterns of both the dimer and the trimer species, as shown in Fig. 4.

The EPR spectrum of the frozen solution obtained at 100 K was also consistent with a mixture of two species, although further work will be needed to fully understand the EPR data.

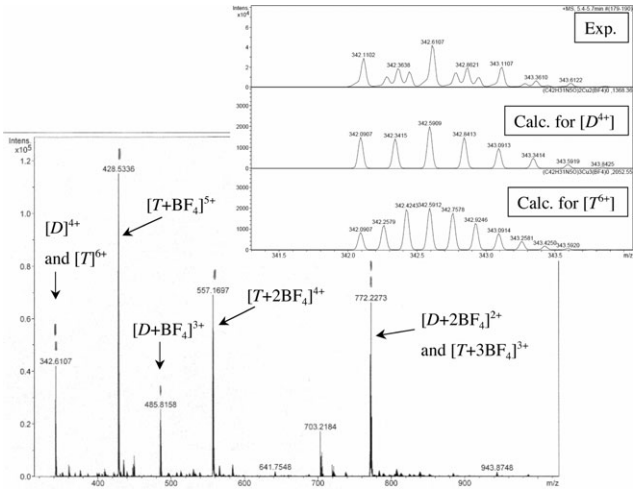


Fig. 4 HR ES-MS of the mixture of copper(II) dimer and trimer complexes $[Cu_2(\mathbf{1})_2]^{4+}$ and $[Cu_3(\mathbf{1})_3]^{6+}$ (*D* and *T*, respectively). Inset: the *m*/*z* ratio experimental region (1st line) at 342.6 is a superposition of the calculated isotopic patterns of the dimer (2nd line) and the trimer complexes (3rd line).

Moreover, cyclic voltammetry of a DCM–MeCN (80 : 20) solution of the olive-green solid showed two reversible reduction waves at, respectively, +0.15 V and −0.05 V (*vs.* SCE). These values are reminiscent of the ones obtained for 5-coordinate copper species.[35–37] Nevertheless, it should be noted that the sole results of respectively the EPR and CV study can not be fully conclusive. But considering the ES-MS analysis of the solution that proved unambiguously the formation of both the dimer and the trimer species, the EPR and CV results corroborate these conclusions.

Hence, changing the nature of the metal centre cause a noteworthy modification of the assembly process and yields once again the dinuclear, but also, for the first time with this ligand, the trinuclear complex. As expected, the copper(II) centre managed to impose a more controlled geometry in its inner coordination sphere than the d^{10} metal centre zinc(II), thus disfavouring the formation of the highly distorted dimer and enabling the trimer to exist.

Conclusions

In this paper, we present the synthesis of a new highly rigid ditopic ligand whose chelate coordination axes are perpendicular to one another. The synthesis has been optimized and a sequence of several Suzuki C–C coupling reactions afforded the desired product, which was fully characterized. Coordination chemistry of such a ditopic ligand with zinc(II) afforded in good yield a dimeric structure as the sole product. Contrary to what was expected from the ideal geometries of the ligand and of the zinc(II) coordination sphere, neither the trimer nor the tetramer species could be observed. Formation of the dimer has been proven by ES-MS, ^{1}H NMR and diffusion-ordered spectroscopies. By changing the nature of the metal ion to copper(II), we obtained in a good yield a mixture of trimer and dimer structures, as shown by ES-MS, EPR and CV.

It thus appears that translational entropy is a very important factor in such complexation processes, leading to the

smallest possible structure, in spite of the enthalpic cost of the probable distortion in the zinc(II) coordination sphere and constraints within the ligand. Such behaviour could be moderated by introducing a metal with more stereoelectronic requirements, making distortion more difficult. These results should enable preparation of multi-rotaxanes by adapting the presently reported methodology to a cyclic derivative of ligand **1**.

Experimental

General points

Instrumentation. Nuclear Magnetic Resonance (NMR) spectra for ^{1}H and ^{13}C were acquired on either a Bruker AVANCE 300 (300 MHz), a Bruker AVANCE 400 (400 MHz) or a Bruker AVANCE 500 (500 MHz) spectrometer. Carbons were assigned using HMQC and HMBC 2D ^{1}H–^{13}C HETCORR experiments. Mass spectra were obtained using a VG ZAB-HF (FAB) spectrometer, a VG-BIOQ triple quadrupole, positive mode or a Bruker MicroTOF spectrometer (ES-MS). Cyclic voltammetry experiments were performed using an EG&G Princeton Applied Research 273A potentiostat, a Pt working electrode, a Pt counter electrode, a KCl-saturated calomel electrode (SCE) or a silver wire as reference, and 0.1 M Bu_4NPF_6 as the supporting electrolyte. The EPR spectra were recorded on an X-band Bruker spectrometer (ESP-300-E) equipped with a rectangular TE 102 cavity. The static field was measured with an NMR Gaussmeter (Bruker ER035) while the microwave frequency was simultaneously recorded with a frequency counter (HP-5350 B). Solutions were degassed by bubbling argon directly into the EPR tube prior to measurements. Temperature was measured with a thermocouple (AuFe/Chromel) introduced inside the tube 1.5 cm from the bottom. An ESR900 cryostat (Oxford Instruments) was used for the low-temperature measurements. Computer simulations of the EPR spectra were performed with the help of Simfonia (BRUKER) and WINEPR softwares. UV-visible absorption spectra were performed using a Kontron UVIKON 860 spectrophotometer.

Chromatographic supports. Thin-layer chromatography was performed using glass or plastic sheets coated with silica or neutral alumina. They were examined after dipping in an aqueous iron(II) solution (terpyridines), after oxidation with iodine (other organic compounds) or under a UV lamp. Column chromatography was carried out on silica gel (Kieselgel 60 (0.063–0.200 mm), Merck) or alumina (Aluminoxid 90 standardized (0.060–0.200 mm), Merck).

Solvents and chemicals. Some solvents were dried in the laboratory by distillation under argon, over the appropriate drying agent: diethyl ether and dioxane over sodium–benzophenone, dichloromethane over CaH_2, and pyridine over KOH. All other anhydrous solvents used are commercially available (“analytical grade”): dimethylformamide (dried with molecular sieves) and methanol. All commercial chemicals were of the best commercially available grade, and were used without further purification, except *n*-BuLi which was titrated using the double titration method described by Gilman and Cartledge[38]

Synthesis of compounds

2-Acetyl-5-methylpyridine: 2. 2-Bromo-5-methylpyridine (10 g; 58 mmol) in anhydrous diethyl ether (150 mL) was cooled to −78 °C under argon. *n*-butyllithium (38 mL; 64 mmol) was added dropwise to the solution mixture. After addition was complete, the reaction mixture was allowed to warm to −40 °C for 30 min; a dark-red solution resulted. *N*,*N*-Dimethylacetamide (6 mL; 64 mmol) was added dropwise and cautiously at −78 °C. The mixture was then allowed to warm to −40 °C for 2.5 h, and hydrolysed with saturated aqueous NH_4Cl solution. The aqueous layer was separated, washed with diethyl ether, and the united ether extracts were washed with water, dried over anhydrous $MgSO_4$, and evaporated to give a brown oil (4.5 g). Chromatography (silica, CH_2Cl_2–MeOH 100% to 98%) gave 4.12 g (30 mmol; 52%) of **2** as a yellow oil. δ_H (300 MHz, $CDCl_3$): 2.40 (s, 3H, CH_3); 2.69 (s, 3H, CH_3CO); 7.61 (dd, 1H, H_4, J = 8.0 Hz, J' = 0.6 Hz); 7.93 (d, 1H, H_3, J = 8.0 Hz); 8.47 (dd, 1H, H_6, J = 0.6 Hz).

4-Bromo-2′-azachalcone: 3. 4-Bromobenzaldehyde (6.25 g; 33.8 mmol) was dissolved in 80 mL methanol and 25 mL NaOH (1 M). 2-Acetyl-5-methylpyridine **2** (4.56 g; 33.8 mmol) dissolved in methanol was added and a precipitate appeared after 5 min. The reaction mixture was stirred for 30 more minutes. The resulting precipitate was filtered off, dissolved in CH_2Cl_2 and washed once with water. The organic phase was dried over Na_2SO_4, filtered, and evaporated to dryness. The residue was recrystallized from methanol to give **3** as a light-yellow solid. Yield 8.76 g (29 mmol; 86%). δ_H (300 MHz, $CDCl_3$): 2.44 (s, 3H, CH_3); 7.56 (m, 4H, H_{arom}); 7.66–7.69 (dm, 1H, H_4, J = 8.2 Hz); 7.81–7.86 (d, 1H, H_a, J = 16.1 Hz); 8.08–8.11 (dm, 1H, H_3, J = 8.2 Hz); 8.26–8.31 (d, 1H, H_b, J = 16.1 Hz); 8.55 (m, 1H, H_6); δ_C (75 MHz, $CDCl_3$): 121.6; 122.7; 129.9; 130.1; 132.0; 134.5; 137.4; 142.8; 149.3; 153.7; 155.6; 158.0; 196.1; m/z (EI-MS): 301.0 (**3**, calc. for $C_{15}H_{12}BrNO$: 301.0).

1-(5-Methyl-2-pyridylacetyl)pyridinium iodide: 4. To a solution of iodine (10.50 g; 41.4 mmol) in freshly distilled pyridine (50 mL) was added 2-acetyl-5-methylpyridine **2** (5.08 g; 37.6 mmol). The mixture was refluxed under argon for 1 h, and then stirred at room temperature overnight. The resulting green precipitate was filtered off, washed with pyridine and recrystallized from absolute ethanol. Yield 9.479 g (27.9 mmol; 74%). δ_H (300 MHz, DMSO-d_6): 2.47 (s, 3H, CH_3); 6.48 (s, 2H, CH_2); 7.97 (m, 2H, H_3-H_4); 8.24–8.29 (dd, 2H, $H_{2'}$, J = 7.8 Hz, J' = 6.7 Hz); 8.71 (m, 1H, H_6); 8.70–8.75 (tt, 1H, $H_{3'}$, J = 7.8 Hz, J' = 1.4 Hz); 8.99–9.02 (dd, 2H, $H_{1'}$, J = 5.5 Hz, J' = 1.2 Hz).

4′-(4-Bromophenyl)-5,5″-dimethyl-2,2′:6′,2″-terpyridine: 5. 4-Bromo-2′-azachalcone **3** (6.04 g; 20 mmol), 1-(5-methyl-2-pyridylacetyl)pyridinium iodide **4** (6.80 g; 20 mmol) and ammonium acetate (39.3 g; 35 mmol) were dissolved in 50 mL of glacial acetic acid and refluxed for 7 h. The reaction mixture was kept at room temperature for 14 h and was then made alkaline with NaOH (10 M). The reaction mixture was

extracted with CH_2Cl_2. The combined organic phases were dried with anhydrous $MgSO_4$ and evaporated on aluminium oxide. Chromatography (400 g aluminium oxide, pentane–CH_2Cl_2–EtOAc (8 : 2 : 1)) gave 4.98 g (12 mmol; 60%) of **5** as a light-yellow solid. δ_H (300 MHz, $CDCl_3$): 2.43 (s, 6H, CH_3); 7.61–7.64 (dm, 2H, H_{m2}); 7.67–7.69 (dm, 2H, H_4-$H_{4''}$, J = 8.0 Hz); 7.76–7.79 (dm, 2H, H_{o2}); 8.53–8.56 (d, 2H, H_3-$H_{3''}$, J = 7.9 Hz); 8.54 (m, 2H, H_6-$H_{6''}$); 8.63 (s, 2H, $H_{3'}$-$H_{5'}$); δ_C (125 MHz, $CDCl_3$): 18.43 (*CH*$_3$); 117.96 (*3′*); 120.92 (*3*); 123.34 (*x*); 128.93 (*o2*); 132.02 (*m2*); 133.61 (*5*); 137.43 (*4*); 137.63 (*y*); 148.93 (*4′*); 149.56 (*6*); 153.65 (*2*); 156.17 (*2′*); *m*/*z* (EI-MS): 414.9 (**5**, calc. for [M]: 415.1); anal. calc. for $C_{23}H_{18}BrN_3$: C, 66.36; H, 4.36; N, 10.09. Found: C, 66.38; H, 4.52; N, 10.01%.

4′-(4-(Neopentyl glycolatoboron)phenyl)-5,5″-dimethyl-2,2′:6′,2″-terpyridine: 6. A round-bottom flask was charged with Pd(dppf)Cl_2 (6 mg; 0.007 mmol), KOAc (70.7 mg; 0.721 mmol), bis(neopentyl glycolato)diboron (B_2neo_2, 57 mg; 0.252 mmol) and 4′-(4-bromophenyl)-5,5″-dimethyl-2,2′:6′,2″-terpyridine (**5**, 100 mg; 0.240 mmol) and flushed with nitrogen. Freshly distilled dioxane (10 mL) was then added and the mixture was heated at 80 °C for 18 h. It was then diluted with toluene and the resulting solution washed with water. The toluene layer was dried over Na_2SO_4 and the solvent removed by rotary evaporation. The residue was dried overnight on a vacuum pump giving **6** as a brownish white solid (quantitative yield). It was used directly for the next step without further purification. δ_H (300 MHz, $CDCl_3$): 1.05 (s, 6H, CH_{3neo}); 2.43 (s, 6H, CH_3); 3.81 (s, 4H, CH_{2neo}); 7.65–7.69 (ddd, 2H, H_4-$H_{4''}$, J = 8.2 Hz, J' = 2.2 Hz, J'' = 0.7 Hz); 7.88–7.94 (dm, 4H, H_{m2}-H_{o2}); 8.54–8.56 (d, 2H, H_3-$H_{3''}$, J = 7.5 Hz); 8.54–8.56 (dt, 2H, H_6-$H_{6''}$, J = 2.2 Hz, J' = 0.7 Hz); 8.69 (s, 2H, $H_{3'}$-$H_{5'}$); δ_C (75 MHz, $CDCl_3$): 18.44 (*CH*$_3$); 21.95 (*CH*$_{3neo}$); 31.92 (*C*$_{neo}$); 72.35 (*CH*$_{2neo}$); 118.29 (*3′*); 120.90 (*3*); 126.46 (*o2*); 132.77 (*x*); 133.41 (*5*); 134.38 (*m2*); 137.36 (*4*); 140.55 (*y*); 149.55 (*6*); 150.13 (*4′*); 153.88 (*2*); 155.97 (*2′*); *m*/*z* (ES-MS): 450.24 (**6**, calc. for [M]: 450.23).

3-Bromo-8-(4-methoxyphenyl)-1,10-phenanthroline: 7. To a degassed solution of 3,8-dibromo-1,10-phenanthroline (100 mg; 0.296 mmol) and Pd(PPh_3)$_4$ (18 mg; 0.015 mmol) in 5 mL of toluene were added, under argon, 1.5 mL of a degassed solution of 2 M aqueous Na_2CO_3 and a solution of *p*-anisylboronic acid (45 mg; 0.296 mmol) in 2 mL of toluene with a few drops of methanol. It is very important to respect the following sequence in the additions: (a) dibromophenanthroline in toluene, (b) 3 vacuum–argon cycles, (c) addition of the catalyst, (d) 3 vacuum–argon cycles, (e) addition of the degassed solution of Na_2CO_3, (f) 3 vacuum–argon cycles, (g) addition of the degassed solution of the boronic acid. The reaction was monitored by TLC, and after 14 h of reflux, the reaction mixture was allowed to cool to room temperature. The solvent was removed by rotary evaporation and chromatography (aluminium oxide, pentane–$CHCl_3$ (1 : 1)) gave 50 mg (0.137 mmol; 46%) of pure product as a slightly yellow solid. δ_H (300 MHz, $CDCl_3$): 3.90 (s, 3H, OCH_3); 7.06–7.11 (dm, 2H, H_{o1}, J = 8.8 Hz); 7.70–7.75 (dm, 2H, H_{m1}, J = 8.9 Hz); 7.72–7.89 (dd, 2H, $H_{p5,p6}$, J = 9.0 Hz); 8.33–8.34 (d, 1H, H_{p7}, J = 2.4 Hz); 8.40–8.41 (d, 1H, H_{p4}, J = 2.3 Hz); 9.18–9.19 (d, 1H, H_{p2}, J = 2.4 Hz); 9.40–9.41 (d, 1H, H_{p9}, J = 2.4 Hz).

Acyclic phen–terpy conjugate: 1. To a degassed solution of 3-bromo-8-(4-methoxyphenyl)-1,10-phenanthroline (**7**, 49 mg; 0.134 mmol) and Pd(PPh_3)$_4$ (7.8 mg; 0.007 mmol) in 10 mL of toluene were added, under argon, 1 mL of a degassed solution of 2 M aqueous Na_2CO_3 and a solution of 4′-(4-(neopentyl glycolatoboron)phenyl)-5,5″-dimethyl-2,2′:6′,2″-terpyridine (**6**, 62 mg; 0.138 mmol) in 5 mL of toluene. It is very important to respect the following sequence in the additions: (a) bromophenanthroline in toluene, (b) 3 vacuum–argon cycles, (c) addition of the catalyst, (d) 3 vacuum–argon cycles, (e) addition of the degassed solution of Na_2CO_3, (f) 3 vacuum–argon cycles, (g) addition of the degassed solution of the boronic ester. The reaction was monitored by TLC, and after 30 h of reflux, the reaction mixture was allowed to cool to room temperature. The solvent was removed by rotary evaporation and the crude mixture was taken in CH_2Cl_2 and washed with water. The combined organic layers were dried over Na_2SO_4 and the solvent evaporated. Chromatography (aluminium oxide, CH_2Cl_2 to CH_2Cl_2–MeOH (99 : 1)) gave 20 mg (0.032 mmol; 24%) of pure product **1** as a white solid. δ_H (300 MHz, $CDCl_3$): 2.44 (s, 6H, CH_3); 3.90 (s, 3H, OCH_3); 7.08–7.11 (dm, 2H, H_{o1}, J = 8.8 Hz); 7.67–7.71 (dm, 2H, H_4-$H_{4''}$, J = 8.1 Hz, J' = 2.0 Hz, J'' = 0.5 Hz); 7.72–7.75 (dm, 2H, H_{m1}, J = 8.8 Hz); 7.88 (d, 2H, $H_{p5,p6}$, J = 1.5 Hz); 7.91–8.11 (dd, 4H, H_{m2}-H_{o2}, J = 8.3 Hz); 8.34 (d, 1H, H_{p7}, J = 2.3 Hz); 8.46 (d, 1H, H_{p4}, J = 2.3 Hz); 8.57 (m, 2H, H_6-$H_{6''}$); 8.56–8.58 (d, 2H, H_3-$H_{3''}$, J = 7.4 Hz); 8.75 (s, 2H, $H_{3'}$-$H_{5'}$); 9.42 (d, 1H, H_{p9}, J = 2.25 Hz); 9.50 (d, 1H, H_{p2}, J = 2.25 Hz); δ_C (75 MHz, $CDCl_3$): 18.48 (*CH*$_3$); 55.47 (*OCH*$_3$); 114.78 (*o1*); 118.16 (*3′*); 120.96 (*3*); 127.06 (*p5*); 127.24 (*p6*); 127.97 (*m2*); 128.21 (*o2*); 128.37 (*p13*); 128.67 (*p14*); 128.69 (*m1*); 130.00 (*p*); 132.59 (*p7*); 133.41 (*p4*); 133.57 (*5*); 134.92 (*x*); 135.46 (*p8*); 137.44 (*4*); 138.68 (*y*); 144.72 (*p11*); 145.40 (*p3*); 146.02 (*p12*); 149.30 (*p2*); 149.36 (*p9*); 149.43 (*4′*); 149.62 (*6*); 153.80 (*2*); 156.19 (*2′*); 160.07 (*i*); *m*/*z* (HR ES-MS): 622.254 (**1**, calc. for [M + H]: 622.260); DOSY NMR (500 MHz, CD_2Cl_2): $\mathscr{D}$ = 1000 μm^2 s^{-1}; r_h = 5.3 Å.

Dimer complex with zinc(II): [Zn_2·(1**)$_2$]·4OTf.** Phen–terpy conjugate **1** (10 mg; 0.016 mmol) was dissolved in 0.25 mL of CD_2Cl_2. A solution of $Zn(OTf)_2$ in CD_3OD (23.8 mg in 1 mL) was prepared, and 0.25 mL (0.016 mmol) was added to the ligand solution, which became clear and orange. The solution was transferred to an NMR tube and the reaction was monitored by ^{1}H NMR spectroscopy. After 6 h at room temperature and 22 h at 30 °C, the NMR spectrum remained the same as after 1 h of reaction. The solvent was then evaporated and the crude mixture taken in methanol, filtered, and the filtrate evaporated to dryness yielding [Zn_2·(**1**)$_2$]·4OTf as a yellow solid (10.5 mg; 78%). δ_H (500 MHz, CD_3OD): 2.37 (s, 6H, CH_3); 4.02 (s, 3H, OCH_3); 6.68 (s, 1H, H_{p2}); 7.35–7.37 (d, 2H, H_{o1}, J = 8.85 Hz); 7.64–7.66 (dm, 2H, H_{m2}, J = 8.0 Hz); 8.12 (m, 2H, H_4); 8.14–8.16 (dm, 2H, H_{o2}, J = 8.0 Hz); 8.20 (m, 4H, H_{p5}-H_{p6}-H_{m1}); 8.25 (m, 2H, H_6-$H_{6''}$); 8.44–8.46 (d, 1H, H_{p9}); 8.76–8.78 (d, 2H, H_3-$H_{3''}$, J = 8.1 Hz); 8.94 (m, 1H, H_{p4}); 9.04 (s, 2H, $H_{3'}$-$H_{5'}$); 9.39 (s, 1H, H_{p7}); *m*/*z*

(HR ES-MS): 342.592 (calc. for $[Zn_2(\mathbf{1})_2]^{4+}$: 342.590); 506.439 (calc. for $[Zn_2(\mathbf{1})_2, OTf]^{3+}$: 506.438); 834.681 (calc. for $[Zn_2(\mathbf{1})_2, 2OTf]^{2+}$: 834.637); DOSY NMR (500 MHz, CD_3OD): $\mathscr{D} = 470\ \mu m^2\ s^{-1}$; $r_h = 8.5$ Å; ellipsoid parameters: $a = 14$ Å; $b = c = 6$ Å.

Dimer and trimer complexes with copper(II): $[Cu_2(\mathbf{1})_2]\cdot 4BF_4$ and $[Cu_3(\mathbf{1})_3]\cdot 6BF_4$. Phen–terpy conjugate **1** (12.5 mg; 0.020 mmol) was dissolved in 2 mL of CH_2Cl_2. A solution of $Cu(BF_4)_2$ in CH_3CN (47.7 mg in 10 mL) was prepared, and 1 mL was added to the ligand solution, which turned instantaneously clear and olive green. The solution was left to stir for 19 h at room temperature, and by addition of diethyl ether, a green solid precipitated out, which was then filtered, washed, dissolved again in an acetone–acetonitrile–methylene chloride mixture, and recovered as a solid by addition of diethyl ether in a good yield (13.8 mg; 89%). *m*/*z* (HR ES-MS): 342.6107 (calc. for $[Cu_2(\mathbf{1})_2]^{4+}$: 342.5909; calc. for $[Cu_3(\mathbf{1})_3]^{6+}$: 342.5912); 428.5336 (calc. for $[Cu_3(\mathbf{1})_3, BF_4]^{5+}$: 428.5102); 485.8158 (calc. for $[Cu_2(\mathbf{1})_2, BF_4]^{3+}$: 485.7893); 557.1697 (calc. for $[Cu_3(\mathbf{1})_3, 2BF_4]^{4+}$: 557.1386); 772.2273 (calc. for $[Cu_2(\mathbf{1})_2, 2BF_4]^{2+}$: 772.1861; calc. for $[Cu_3(\mathbf{1})_3, 3BF_4]^{3+}$: 772.1864); UV-Vis ($CH_2Cl_2$ + *n*-Bu_4NPF_6 0.1 M) λ_{max} (ε): 292 (1.2×10^5); 359 (9.2×10^4); 573 (560).

Acknowledgements

Funding by the Région Alsace and the CNRS (fellowship to B. C.) is gratefully acknowledged. We warmly thank Dr Lionel Allouche for the DOSY NMR experiments and explaining the ins and outs of this technique, and Patrick Wehrung for his professionalism and efficiency in the ES-MS measurements.

References

1 J. P. Sauvage, J. P. Collin, J. C. Chambron, S. Guillerez, C. Coudret, V. Balzani, F. Barigelletti, L. De Cola and L. Flamigni, *Chem. Rev.*, 1994, **94**(4), 993.
2 S. Encinas, F. Barigelletti, A. M. Barthram, M. D. Ward and S. Campagna, *Chem. Commun.*, 20013), 277.
3 C. Ringenbach, A. De Nicola and R. Ziessel, *J. Org. Chem.*, 2003, **68**(12), 4708.
4 E. C. Constable, R. W. Handel, C. E. Housecroft, A. F. Morales, B. Ventura, L. Flamigni and F. Barigelletti, *Chem.–Eur. J.*, 2005, **11**(13), 4024.
5 S. Ghumaan, B. Sarkar, S. Patra, K. Parimal, J. van Slageren, J. Fiedler, W. Kaim and G. K. Lahiri, *Dalton Trans.*, 2005,(4), 706.
6 S.-H. Hwang, C. N. Moorefield, F. R. Fronczek, O. Lukoyanova, L. Echegoyen and G. R. Newkome, *Chem. Commun.*, 2005,(6), 713.
7 P. Wang, C. N. Moorefield and G. R. Newkome, *Angew. Chem., Int. Ed.*, 2005, **44**(11), 1679.
8 E. C. Glazer, D. Magde and Y. Tor, *J. Am. Chem. Soc.*, 2005, **127**(12), 4190.
9 P. N. W. Baxter, J. M. Lehn, J. Fischer and M.-T. Youinou, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 2284.
10 J. M. Lehn, A. Rigault, J. Siegel, J. Harrowfield, B. Chevrier and D. Moras, *Proc. Natl. Acad. Sci. U. S. A.*, 1987, **84**(9), 2565.
11 T. M. Garrett, U. Koert, J. M. Lehn, A. Rigault, D. Meyer and J. Fischer, *J. Chem. Soc., Chem. Commun.*, 19907), 557.
12 G. S. Hanan, C. R. Arana, J.-M. Lehn and D. Fenske, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**(10), 1122.
13 P. N. Baxter, G. S. Hanan and J.-M. Lehn, *Chem. Commun.*, 199617), 2019.
14 J. P. Sauvage, *Acc. Chem. Res.*, 1990, **23**(10), 319.
15 C. O. Dietrich-Buchecker and J. P. Sauvage, *New J. Chem.*, 1992, **16**, 277.
16 M. C. Jimenez-Molero, C. O. Dietrich-Buchecker, J. P. Sauvage and A. De Cian, *Angew. Chem., Int. Ed.*, 2000, **39**, 1295.
17 M. C. Jimenez-Molero, C. Dietrich-Buchecker and J. P. Sauvage, *Chem.–Eur. J.*, 2002, **8**(6), 1456.
18 T. Kraus, M. Budesinksy, J. Cvacka and J.-P. Sauvage, *Angew. Chem., Int. Ed.*, 2006, **45**(2), 258.
19 M. Fujita, M. Tominaga, A. Hori and B. Therrien, *Acc. Chem. Res.*, 2005, **38**(4), 371.
20 S. Leininger, B. Olenyuk and P. J. Stang, *Chem. Rev.*, 2000, **100**(3), 853.
21 F. Wurthner, C.-C. You and R. Saha-Moller Chantu, *Chem. Soc. Rev.*, 2004, **33**(3), 133.
22 E. C. Constable, E. L. Dunphy, C. E. Housecroft, W. Kylberg, M. Neuburger, S. Schaffner, E. R. Schofield and C. B. Smith, *Chem.–Eur. J.*, 2006, **12**(17), 4600.
23 P. Gaviña and S. Tatay, *Tetrahedron Lett.*, 2006, **47**(20), 3471.
24 B. Champin, V. Sartor and J. P. Sauvage, *New J. Chem.*, 2006, **30**, 22.
25 T. A. Crabb and G. C. Heywood, *Org. Magn. Reson.*, 1982, **20**(4), 242.
26 J. E. Parks, B. E. Wagner and R. H. Holm, *J. Organomet. Chem.*, 1973, **56**, 53.
27 P. Korall, A. Borje, P. O. Norrby and B. Akermark, *Acta Chem. Scand.*, 1997, **51**(6–7), 760.
28 G. W. V. Cave and C. L. Raston, *J. Chem. Soc., Perkin Trans. 1*, 200124), 3258.
29 P. Baret, J. Einhorn, G. Gellon and J. L. Pierre, *Synthesis*, 19984), 431.
30 J. A. G. Williams and C. J. Aspley, *New J. Chem.*, 2001, **25**(9), 1136.
31 Y. Saitoh, T.-A. Koizumi, K. Osakada and T. Yamamoto, *Can. J. Chem.*, 1997, **75**(10), 1336.
32 C. Dietrich-Buchecker, M. C. Jimenez and J.-P. Sauvage, *Tetrahedron Lett.*, 1999, **40**(17), 3395.
33 N. Miyaura and A. Suzuki, *Chem. Rev.*, 1995, **95**(7), 2457.
34 K. S. Chichak, S. J. Cantrill, A. R. Pease, S.-H. Chiu, G. W. V. Cave, J. L. Atwood and J. F. Stoddart, *Science*, 2004, **304**(5675), 1308.
35 A. Livoreil, C. O. Dietrich-Buchecker and J.-P. Sauvage, *J. Am. Chem. Soc.*, 1994, **116**(20), 9399.
36 A. Livoreil, J.-P. Sauvage, N. Armaroli, V. Balzani, L. Flamigni and B. Ventura, *J. Am. Chem. Soc.*, 1997, **119**(50), 12114.
37 F. Durola and J.-P. Sauvage, *Angew. Chem., Int. Ed.*, 2007, **46**(19), 3537.
38 H. Gilman and F. K. Cartledge, *J. Organomet. Chem.*, 1964, **2**(6), 447.

