Synthesis and complexation characteristics of phenanthroline and bipyridine diols

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Dedicated to Professor Binne Zwanenburg on his 70th anniversary

(received 21 Oct 03; accepted 15 Jan 04; published on the web 20 Jan 04)

Abstract

Neocuproine (2,9-dimethyl-1,10-phenanthroline) **1** was converted to achiral and chiral tetradentate phenanthroline diols **3a-c** by addition to benzophenone, adamantanone and camphor, respectively. Analogously 6,6'-dimethyl-2,2'-bipyridine **2** was converted to diol **7a** on base-induced addition to benzophenone. Reactions with benzophenone and adamantanone proceeded smoothly although small amounts of mono adducts were also formed. Functionalization of **1** with (*R*)-camphor failed under the standard conditions. However, conversion of the lithio derivative **5** to the cerium chloride derivative **6** and subsequent reaction with (*R*)-camphor led to the phenanthroline diol **3c**. Complexes of the diols **3** and **7** with zinc and copper were prepared. X-ray analysis of the zinc complex **20** of diol **7a** revealed a five coordinate zinc ion that is firmly embedded in the ligand. X-ray analysis of the $Cu(acac)_2$ complex **21** of diol **7a** unexpectedly revealed this to be an acetate bridged di-copper species. This copper complex forms on recrystallization from ethyl acetate. The initial acac-complex apparently hydrolyses the ethyl acetate to provide the bridging acetate found in the di-copper complex **21**. From 4,7-dichloro-2,9-dimethyl-1,10-phenanthroline **13** a "doubly armed" derivative **18** was prepared by substitution with two tetraethylene glycol "arms" followed by suitable derivatisation. A bridged derivative **19** was prepared by ring closure with an amine of the ditosylated tetraethylene glycol derivative. Attempts to prepare copper complexes of **18** and **19** were inconclusive.

Keywords: Phenanthroline, bipyridine, neocuproine, zinc and copper complexes, benzophenone, adamantanone, camphor, diols, ligands, di-copper bridges, doubly armed ligands

Introduction

Both 1,10-phenanthroline and 2,2'-bipyridine are attractive building blocks that are often incorporated, usually as their metal complexes, into various host molecules. In addition the metal

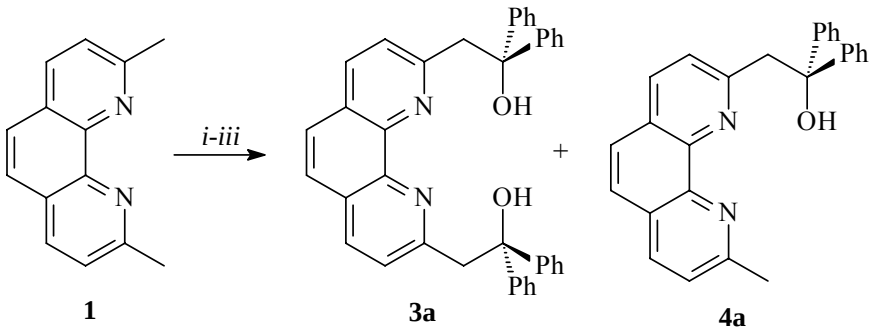
complexes of these two molecules are frequently employed for catalytic reactions. The two nitrogen atoms in each molecule are ideally placed for cooperative binding of many metal cations.[1] For example metal ion complexes with functionalised 1,10-phenanthrolines have been used as catalyst for the enantioselective hydrolysis of *N*-protected amino acid esters,[2] for the oxidative cleavage of DNA,[3] in palladium catalysed allylic substitutions[4] and in enantioselective reduction of acetophenone.[5,6] Metal complexes of 2,2'-bipyridines have also been widely used.[7] Functionalised 2,2'-bipyridines have been employed in the enantioselective alkylation of aldehydes,[8,9] in the enantioselective hydrosilylation of ketones,[10] in asymmetric allylation reactions,[11] in cyclopropanation of styrene,[12] in palladium catalysed allylic substitutions,[13] and as herbicides.[14] These building blocks have been used for, for example, the synthesis of (mixed) crown ethers,[15] catenates and catenands,[16] and for the formation of macromolecular structures and grids.[17]

In analogy to methodology that we have developed for the functionalisation of 2,6-dimethylpyridines to prepare tetradentate ligands [18] we have now prepared similar derivatives of 2,9-dimethyl-1,10-phenanthroline ("neocuproine", **1**) and the analogous 6,6'-dimethyl derivative **2** of 2,2'-bipyridine.

Results and Discussion

Synthesis

When **1** was deprotonated at the methyl groups with 2.5 equiv. of LDA at –80°C and subsequently quenched with benzophenone phenanthroline diol **3a** was obtained in 55% yield together with 15% of material judged to be the mono-adduct **4a** on the basis of the ^{1}H-NMR spectrum of the crude reaction mixture (Scheme 1).

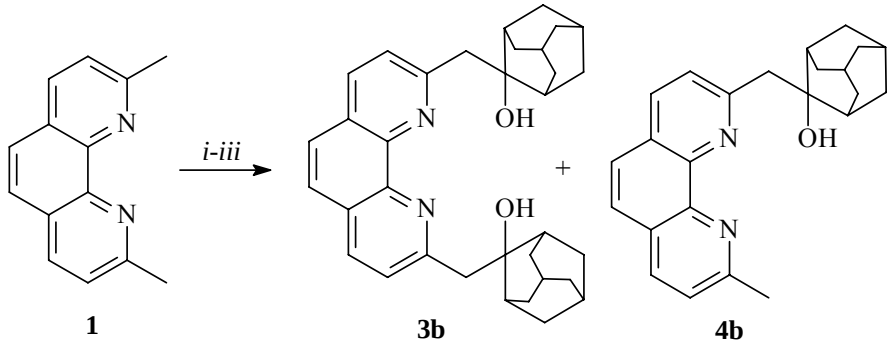


1 **3a** **4a**

Scheme 1. *Reagents and conditions*: *i*, LDA, -80°C; *ii* benzophenone; *iii* 2M NH_4Cl.

The bis-adduct **3a** was separated from the mono-adduct by washing with hot ethanol and was purified by recrystallization from chloroform/acetonitrile/hexane. Use of a smaller excess of LDA led to an increase in formation of the mono-adduct. Attempts to deprotonate **1** with *n*-butyllithium gave rise to undefined side products that probably result from addition of an n-butyl group to the ring system.

When adamantanone instead of benzophenone was used for the functionalization of **1** the bis-adduct **3b** was obtained on recrystallisation from ethyl acetate in 49% yield (Scheme 2). The mono-adduct **4b** was isolated but was not characterized further.

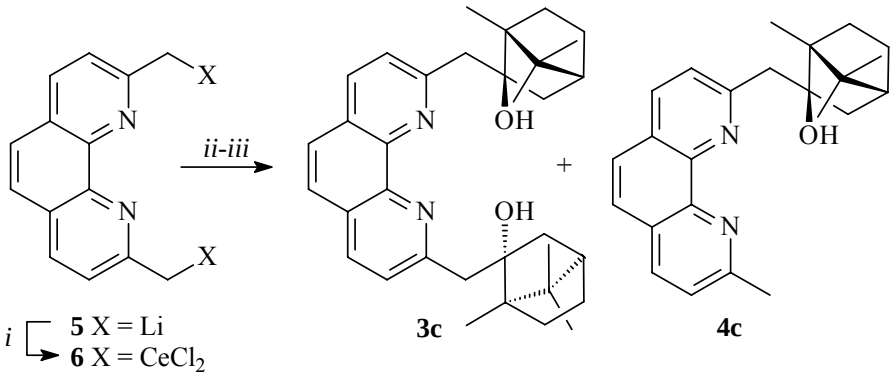


1 **3b** **4b**

Scheme 2. *Reagents and conditions*: *i*, LDA, -80°C; *ii* adamantanone; *iii* 2M NH_4Cl.

The lower yield of **3b** related to the benzophenone adduct is probably due to the lower reactivity of the carbonyl functionality of adamantanone compared to that of benzophenone.

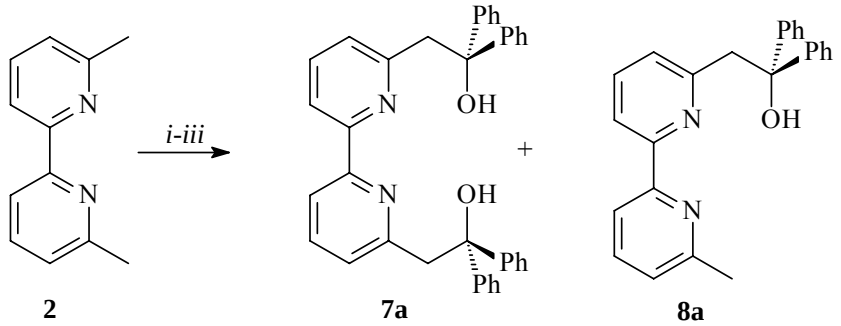
When (*R*)-camphor, which is even less reactive than adamantanone and which easily undergoes enolization, was allowed to react with the bislithiated **5** derived from **1** formation of neither the desired diol **3c** nor the mono-adduct **4c** was observed. At –80°C no reaction at all occurs. However, when the temperature was raised to –50°C decolorization occurred indicating the disappearance of the dilithio adduct. Workup afforded only starting material indicating that at –50°C (*R*)-camphor enolises rather than undergoing attack at the carbonyl functionality. In order to effect addition to (*R*)-camphor the more oxaphilic and less basic cerium derivative was generated by exchange with lithium.[19] The dilithio derivative **5** derived from **1** was converted to the $CeCl_2$ species **5** by addition of $CeCl_3$·THF after lithiation. When **5** was stirred with $CeCl_3$·THF for 1 hour at –78°C and quenched with (*R*)-camphor the chiral phenanthroline diol **3c** was formed in 65% yield (Scheme 3). Concentration of the mother liquor gave a small amount of the presumed mono-adduct **4c,** which was characterized only on the basis of the ^{1}H-NMR spectrum of the crude material.



3c **4c**

Scheme 3. *Reagents and conditions*: *i*, $CeCl_3$·THF, -80°C; *ii* (*R*)-camphor; *iii* 2M NH_4Cl.

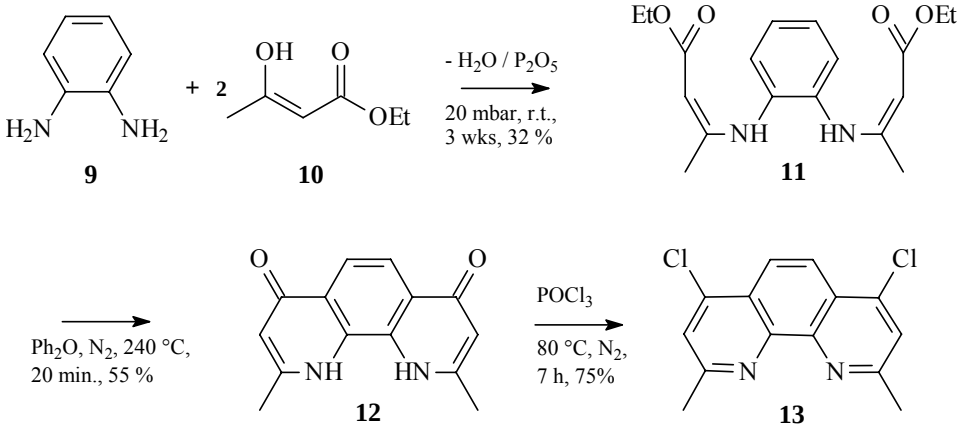
Functionalization of 6,6'-dimethyl-2,2'-bipyridine **2** was carried analogously to the procedure described for **1**. Lithiation of **2** with 2.5 equiv. of LDA and subsequent addition of benzophenone afforded the bipyridine diol **7a** in 49% yield along with 29% of the mono-adduct **8a**, which was characterized fully (Scheme 4). The mono and bis-adducts could be separated by making use of the lower solubility of the bis-adduct in methanol.



2 **7a** **8a**

Scheme 4. *Reagents and conditions*: *i*, LDA, -80°C; *ii* benzophenone; *iii* 2M NH_4Cl.

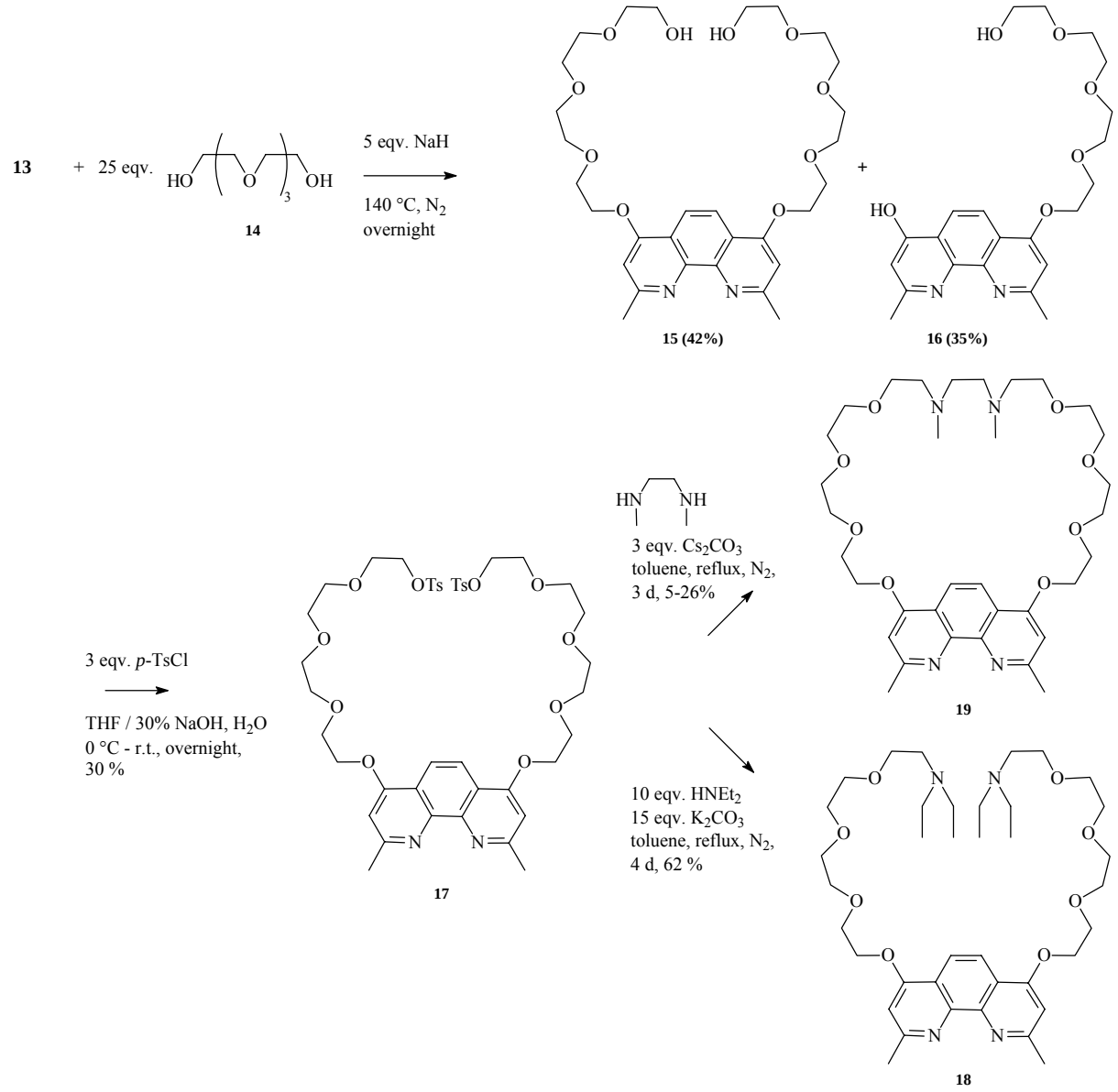
We have also briefly examined the possibilities of incorporation of extra complexation possibilities not through the methyl groups but through macrocyclic rings that bridge the diaza coordination system. These investigations have been confined to the phenanthroline nucleus. The starting point was 4,7-dichloro-2,9-dimethylphenanthroline **13** prepared by the method of Schmittel et al [20] as shown in Scheme 5. We made numerous attempts to speed up or to increase the scale (in our hands maximally 0.1 mol) of this extremely useful reaction but with limited success. The conversion of **10** to **11** is very slow but works well, and can be carried out on reasonable (20-30 g) scale. The bottleneck is the conversion of **12** to **13**. Schmittel et al describe this conversion in quantitative yield on 1 g scale. In our hands increase of scale to 2-3 g led to yields of **13** between 63-95%. The greatest problem is the work-up procedure for the isolation of **13**. The hot reaction mixture is poured into an ice:water mixture and the water layer is subsequently brought to pH 14 with conc. NaOH, which has to be added *very slowly* ensuring that the reaction temperature does not exceed 45-50°C. We mention these details for the benefit of others who may want to use this valuable reaction.



9 **10** **11** **12** **13**

Scheme 5. Synthesis of 4,7-dichloro-2,9-dimethylphenanthroline.

Two derivatives have been prepared, one with two arms and the other bridged. The syntheses of the "armed" derivative **18** and the "closed" derivative **19** are shown in Scheme 6.



Scheme 6. Synthesis of phenanthroline derivatives.

The doubly armed tosylate **17** is the key intermediate for preparation of both compounds. Ring closure to **19** proceeded in 7-26% yield. Both end products were characterized by NMR spectroscopy and ES-MS. It was not possible to obtain exact mass spectra for either **18** or **19**.

Complexations with metals

Ligands with a phenanthroline or bipyridine moiety are usually strong metal chelating agents. The phenanthroline and bipyridine based tetradentate diols were also expected to form stable complexes with zinc and copper. Of particular interest was whether the hydroxy groups would

also participate in coordination. When zinc perchlorate heptahydrate was added to a suspension of phenanthroline diol **3c** in a mixture of $CD_3CN/CDCl_3$ (9:1) a complex was formed as deduced from ^1H NMR spectroscopy. A downfield shift of 0.5 ppm for the aromatic protons (referred to the free ligand in the same solvent mixture) was observed indicating complexation of the phenanthroline moiety. The benzylic protons gave a set of 4 signals, which indicates that these protons are diastereotopic and that the complex has a locked conformation on the NMR scale. This observation is consistent with coordination of the hydroxy groups. Furthermore a signal for the hydroxy groups was observed at δ 5.40, which suggests strongly that the hydroxy groups, despite coordination, are not deprotonated. Although a crystalline complex with a correct elemental analysis (no water) was isolated, attempts to determine the structure by X-ray methods were unsuccessful.

After addition of zinc perchlorate heptahydrate to a suspension of the bipyridyl diol **7a** in a mixture of CD_3CN and $CDCl_3$ (9/1) the material slowly dissolved and a complex **20** was formed. Again complexation gave rise to a downfield shift of the pyridine protons, though to a smaller extent than observed for the phenanthroline system **3c**. Furthermore the benzylic protons are shifted 0.4 ppm downfield (referred to the free ligand). The benzylic protons in this complex appear as a singlet, which could indicate some flexibility in the complex as a consequence of the possibility of torsion about the bipyridine bond. Also a signal for the hydroxy groups is observed at δ 7.48, indicative of the fact that deprotonation did not take place. More structural information for **20** was obtained from the X-ray structure. [21] Crystals for X-ray were grown from ethyl acetate/acetonitrile and isothermal distillation of hexane into the solution.

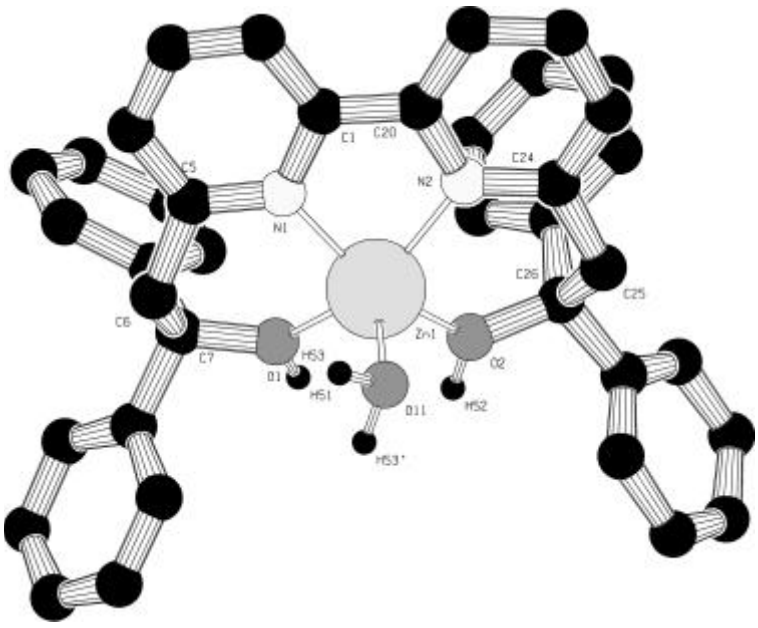


Figure 1. X-ray structure of **20** without the perchlorate counter ions.

Although an X-ray structure determination was severely hindered by persistent weakly scattering crystals and also broad reflections, ultimately a data set was gathered from which a successful structure determination was obtained (Figure 1). The crystal structure reveals a pentacoordinated zinc atom in a square pyramidal surrounding. The two hydroxy groups, the two nitrogen groups and an additional water molecule are involved in the binding of the zinc in a square pyrimidal fashion. The zinc is situated in the middle of the molecule, which roughly has a symmetry axis through the zinc, the water molecule and the bipyridine bond. The bipyridine bridge moiety is almost flat and the hydroxy groups are directed towards the zinc ion.

Complexes with copper were also easily formed. Addition of Cu(I)triflate.benzene complex to 2,2'-bipyridyl diol **7a** in acetonitrile under argon immediately afforded a red solution that turned blue after a few seconds of stirring indicating that the Cu(I) is converted to more stable Cu(II). This conclusion is also supported by the observation of a paramagnetic nucleus (by NMR) in solution. Since elemental Cu is not observed it is most probable that the Cu(I) is oxidized by the ligand. Complexation of $Cu(acac)_2$ with 2,2'-bypyridine diol **7a** in acetonitrile was more successful and a blue crystalline precipitate was formed. The ^{1}H NMR of this complex in chloroform revealed the presence of a paramagnetic nucleus and complexation with the ligand. Whether or not the alcohol functionalities are deprotonated is unclear from the ^{1}H NMR spectra. Suitable crystals for X-ray diffraction were grown by recrystallization from hot ethyl acetate. Surprisingly X-ray analysis showed a di-copper complex **21** in which the copper ions are bridged by acetate groups and the hydroxylates.[21] The asymmetric unit of the crystals consisted of two di-Cu complexes and four heavily disordered acetate molecules (Figure 2).

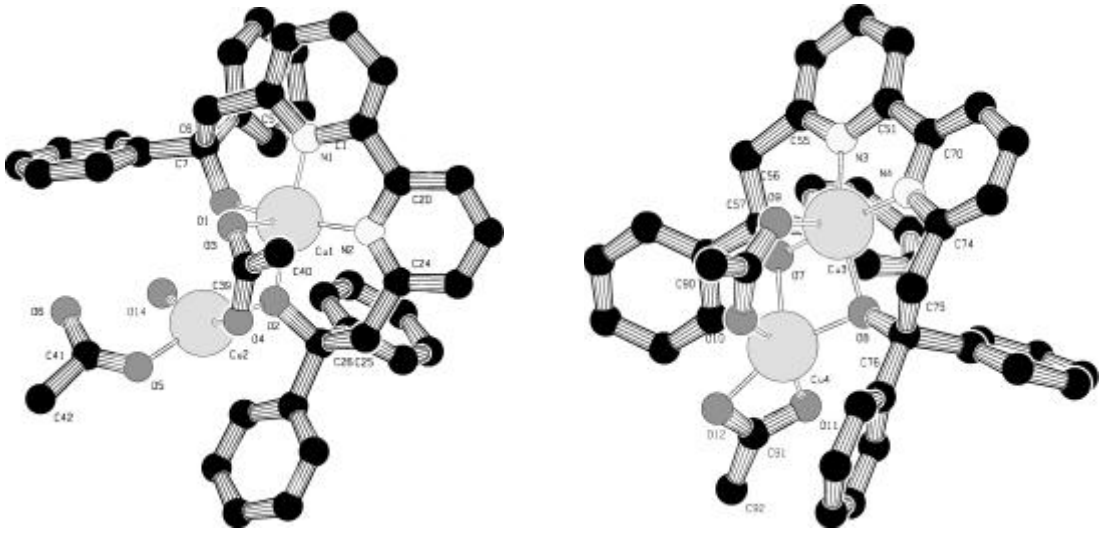


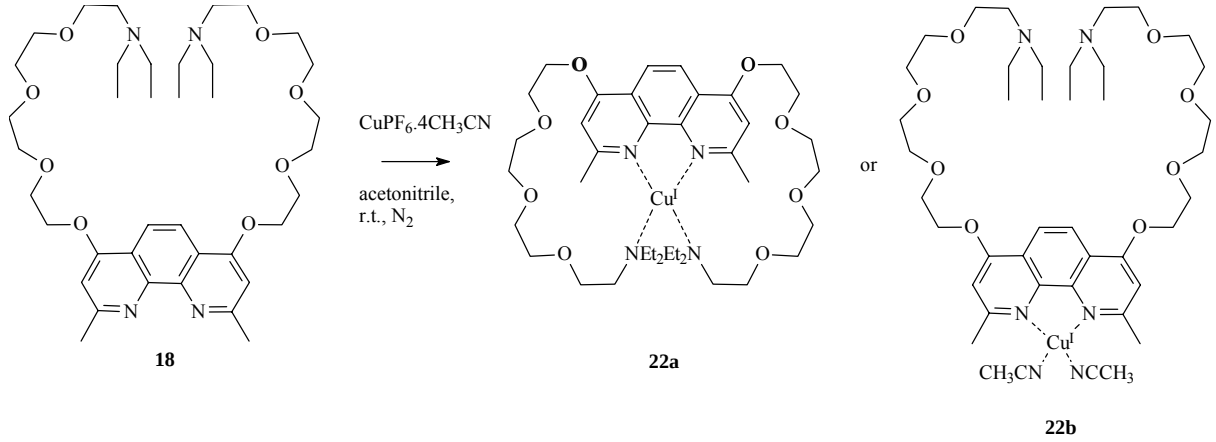
Figure 2. X-ray structure of residues 1(left) and 2 of complex **21**.

In the first residue (left) one copper ion is symmetrically bond to the bipyridine nitrogens, an acetate oxygen and the hydroxylates of the ligand to form square pyramidal surroundings (Cu(1)…N(1) 1.954 Å; Cu(1)…N(2) 2.000 Å; Cu(1)…O(3) 2.342 Å; Cu(1)…O(1) 1.913 Å;

Cu(1)…O(2) 1.913 Å). The second copper ion also coordinates to one of the hydroxylates and is bridged to the other copper ions through the acetate molecule. A second acetate molecule is coordinated to this copper. The fourth coordination site of this copper is occupied by a water molecule. The distance between the two copper ions Cu(1) and Cu(2) is 3.151 Å, which is comparable to the distances found for other di-copper complexes.[22] The ligand backbone is slightly twisted; a torsion angle of -5.1° is observed. The second residue (right) embeds, analogously to the first residue, two copper ions. These ions are bridged by both hydroxylates and by an acetate molecule. The distance between the two copper ions in this structure is somewhat shorter (Cu(3)…Cu(4) 2.8861 Å). The first copper ion is embedded in the ligand and is square pyramidal coordinated. The second copper ion coordinates to both hydroxylate groups (Cu(3)…O(7) 2.225 Å; Cu(3)…O(8) 1.932 Å). No coordination of water is found in this residue. The bipyridine backbone is nearly flat, a torsion angle of -4.2 ° being observed.

Although the synthesis of this complex began with free ligand and $Cu(acac)_2$ the inclusion of the acetate molecules in the X-ray structure can be explained by the hydrolysis of ethyl acetate upon heating. Probably water present in the complex gives rise to the hydrolysis.

Attempts to form copper complexes with bridged phenanthroline **19** using either Cu^{+1} or Cu^{+2} salts were inconclusive. Marginally more success was obtained with the "armed" derivative **18**. Attempts to form complexes with $CuCl_2$ led to complex mixtures, which, on the basis of ES-MS appeared to consist of Cu^{+} complexes. We were surprised to observe reduction. In view of these observations we examined complexation of **18** by the copper(I) salt $CuPF_6$. In principle two types of complex, **22a** or **22b**, might be formed as indicated in Scheme 7.



18 **22a** **22b**

Scheme 7. Complexation of Cu(I).

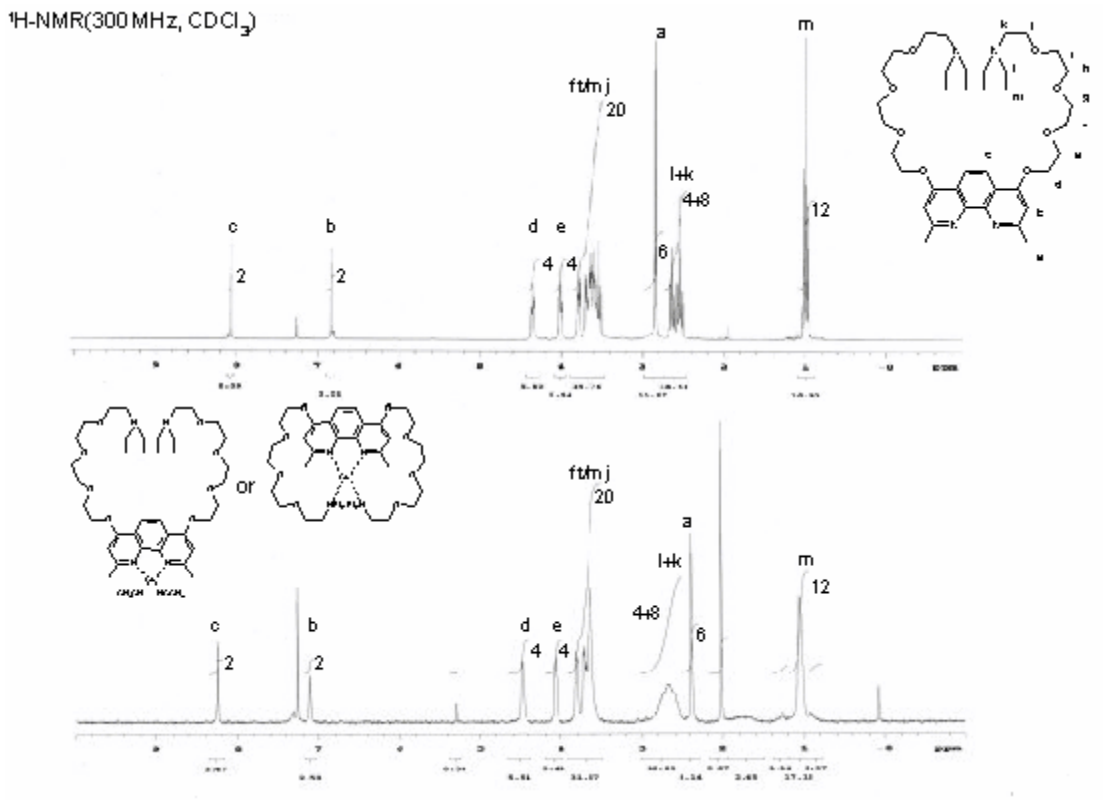


Figure 3. 300 MHz ^{1}H-NMR spectra of free ligand 18 (top) and of the Cu(I) complex of this ligand (bottom) in $CDCl_3$.

The ^{1}H-NMR spectrum (Figure 3) is consistent with complexation between the Cu^+ and the ligand. Protons H_b and H_c show a downfield shift of δ 0.27 and δ 0.17 ppm, respectively, relative to the free ligand. The protons H_a of the methyl group showed a large upfield shift from δ 2.84 to δ 2.38 ppm. The signals of the protons of the methylene group adjacent to the nitrogens of the arms (H_k and H_l) showed extensive line broadening, although the signals for these protons did not show a large shift. The signals of the other protons showed also some line broadening, but little up of downfield shifts.

Based on the observed shifts of the protons from the phenanthroline moiety it can be concluded that the Cu^+ cation is bound to the ligand via its phenanthroline nitrogens. Whether the third and fourth coordination sites of the Cu+ are occupied by the nitrogens of the arms of the ligand, by two solvent molecules or by another ligand is not clear.

Conclusions

Phenanthroline diols **3** and bipyridine diols **7** have been prepared using the methodology described previously for the synthesis of pyridine diols.[18] Monoadducts **4** and **8**, respectively, were formed as a side products but can easily be removed. Although the nucleophilicity of the dilithiated **1** and **2** is most likely less than that of lithiated 2,6-lutidine, reactions with

benzophenone and adamantanone occur smoothly. Reaction with (*R*)-camphor, however, was thwarted by the lower nucleophilicity and the possibility of the ketone to enolise. These problems can be neatly solved by conversion to the cerium derivative.

It is clear that the hydroxyl groups of these ligands also readily participate in coordination to metal ions.

Experimental Section

General Procedures. All reactions were carried out under an Ar atmosphere. The following solvents were distilled prior to use: THF, diethyl ether and toluene were distilled from Na wire, acetonitrile was distilled over CaH_2, and dichloromethane, ethyl acetate, and hexane were distilled over P_2O_5. Column chromatography was performed on alumina (Merck 90, II/III, 0.063-0.200 mm) or silica gel (Aldrich 60, 230-400 mesh). Elemental microanalyses were carried out in the analytical department of the University of Groningen. X-ray diffraction studies were carried out in the Crystal Structure Center of the university. ^{1}H and ^{13}C spectra were recorded using a Varian Unity Plus Varian 500, a Varian VXR 300 instrument or a Genuine 200 Instrument. The chemical shifts are expressed relative to TMSCl for ^{1}H NMR and to $CDCl_3$ for ^{13}C NMR. *NOESY* [23], and *COSY* [24] spectra were performed using standard Varian pulse programs. Deuterated solvents were dried over an Al_2O_3 (activity 1) column just prior to use. Melting points (uncorrected) were determinated on a Mettler FP-2 melting point apparatus, equipped with a Mettler FP-21 microscope. Reagents and starting materials used were obtained from Aldrich, Fluka or Acros Chimica and used as received, unless noted otherwise. Anhydrous neocuproine was obtained by recrystallization from benzene. $CeCl_3 \cdot 7H_2O$ was dried according to the literature.[25]

2-[9-(2-Hydroxy-2,2-diphenylethyl)-1,10-phenanthrolin-2-yl]-1,1-diphenyl-1-ethanol (3a). To a stirred solution of neocuproine **1**[26] (0.25 g, 1.2 mmol) in 50 mL of THF at –80°C was added LDA (2.0 M solution in THF/*n*-heptane, 1.5 mL, 3.0 mmol). After stirring for 1h a solution of benzophenone (0.54 g, 3.0 mmol) in 5 mL of THF was added. Stirring was continued overnight and the reaction mixture was allowed to reach room temperature. The solution was quenched with 2M NH_4Cl and chloroform/acetonitrile (1:1) 100 mL was added. The solution was sonicated for 1 h and the layers were separated. The aqueous layer was washed with chloroform twice. The combined organic layers were dried over Na_2SO_4. After evaporation of the solvent the solid was washed with hot ethanol to yield the bis-adduct, which was crystallized from chloroform/acetonitrile/hexane to afford the bis-adduct **3a** as a hydrate (0.47 g, 0.8 mmol, 55%): mp 208-209 °C; ^{1}H NMR (300 MHz, CD_3CN): δ 1.53 (br, H_2O), 4.00 (s, 4H), 7.07 (m, 4H), 7.19 (m, 10H), 7.29 (d, *J* = 8.05 Hz, 2H), 7.57 (m, 8H), 7.95 (d, *J* = 8.05 Hz, 2H). δ; HRMS calcd 572.246; no proper HRMS could be obtained, CI(NH_3) gave a molecular ion at *m/e* 573. Anal. Calcd for $C_{80}H_{66}N_4O_5$: C, 82.59; H, 5.72; N, 4.82. Found C, 82.94; H, 5.84; N, 4.81.

2-({9-[(2-Hydroxy-2-adamantyl)methyl]-1,10-phenanthrolin-2-yl}methyl)-2-adamantanol (3b). A solution of neocuproine **1** (0.30g, 1.44 mmol) in 50 mL of THF was cooled to –80°C and LDA (2.0 M solution in THF/*n*-heptane, 1.8 mL, 3.6 mmol) was slowly added. After stirring for 1h adamantanone (0.54 g, 3.6 mmol) in 5 mL of THF was added. The mixture was quenched with 2M NH_4Cl and extracted with dichloromethane twice. The combined organic layers were washed with brine and dried over Na_2SO_4. The bis-adduct **3b** was recrystallized from ethyl acetate to afford colorless needles (0.36 g, 0.71 mmol, 49%): mp 221-223 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.42 (m, 4H), 1.71 (m, 10H), 1.78 (m, 4H), 1.90 (m, 2H), 2.01 (m, 4H), 2.43 (m, 4H), 3.48 (s, 4H), 7.50 (d, *J* = 8.3 Hz, 2H), 7.73 (s, 2H), 8.16 (d, *J* = 8.3 Hz, 1H). ^{13}C NMR: δ 27.42 (d), 27.50 (d), 32.75 (t), 34.72 (t), 37.28 (d), 38.51 (t), 44.56 (t), 75.42 (s), 124.56 (d), 125.50 (d), 126.94 (s), 136.27 (d), 160.40 (s); HRMS calcd 508.309; found 508.309. Anal. Calcd for $C_{34}H_{40}N_2O_2$: C, 80.28; H, 7.93; N, 5.51. Found C, 80.28; H, 7.77; N 5.46.

(1*R*,2*S*)-2-[(9-{[(1*R*,2*S*)-2-Hydroxy-1,7,7-trimethylbicyclo[2.2.1]hept-2-yl]methyl}-[1,10]phenanthrolin-2-yl)methyl]-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol (3c). A solution of $CeCl_3$ [25] (1.61 g, 6.5 mmol) in 150 mL of THF was sonicated overnight and cooled to –80°C. Subsequently a previously prepared solution of lithiated neocuproine **5** (0.03N solution in THF, 1.6 mmol, 53 mL) was slowly added. The solution was stirred remained at –80°C for 1h after which time (*R*)-camphor (0.87 g, 5.7 mmol) in 5 mL of THF was added. Stirring was continued for 3h allowing the mixture to reach –10°C. Subsequently the mixture was quenched with 2M NH_4Cl and extracted with dichloromethane twice. The combined organic layers were washed with brine and dried over Na_2SO_4. After removal of the solvent under reduced pressure the product was flushed over a short column (silica, ethyl acetate/hexane (1:3)). The obtained solid **3c** was recrystallized from ethyl acetate (0.53 g, 1.0 mmol, 65%): mp 199-201 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.51 (s, 6H), 0.77 (s, 6H), 1.09 (m, 2H), 1.17 (s, 6H), 1.42 (m, 6H), 1.66 (m, 4H), 2.35 (m, 2H), 3.28 (m, 4H), 6.6 (br, 2OH), 7.45 (d, *J* = 8.05 Hz, 2H), 7.67 (s, 2H), 8.11 (d, *J* = 8.05 Hz, 2H); ^{13}C NMR: δ 11.21 (q), 21.05 (q), 21.58 (q), 27.21 (t), 30.92 (t), 45.13 (d), 45.84 (t), 47.28 (t), 49.40 (s), 52.46 (s), 81.05 (s), 124.46 (d), 125.54 (d), 126.95 (s), 129.12 (s), 136.35 (d), 161.31 (s); HRMS calcd 512.340; found 512.340. Anal. Calcd for $C_{34}H_{44}N_2O_2$: C, 79.65; H, 8.65; N, 5.46. Found C, 79.24; H, 8.79; N, 5.44.

2-[3'-(2-Hydroxy-2,2-diphenylethyl)[2,2'-bipyridyl]-6-yl]-1,1-diphenyl-1-ethanol (7a). The 2,2'-bipyridyl **2**[27] (0.16 g, 0.87 mmol) was dissolved in 25 mL of THF and lithiated at –80°C with LDA (2.0 M solution in THF/*n*-heptane, 1.1 mL, 2.2 mmol). After stirring for 1h at –80°C a solution of benzophenone (0.40 g, 2.2 mmol) in 5 mL of THF was added. The mixture was allowed to reach ambient temperature in 3 h and was quenched with 2M NH_4Cl. The mixture was extracted with dichloromethane twice and the combined organic layers were washed with brine and dried over Na_2SO_4. After removal of the solvent the solid was washed with methanol and recrystallized from chloroform/hexane to afford the bis-adduct **7a** as hydrate (0.23 g, 0.43 mmol, 49 %): mp > 230 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.56 (br, H_2O), 3.78 (s, 4H), 7.04 (m, 2H), 7.11 (m, 4H), 7.20 (m, 8H), 7.40 (m, 8H), 7.52 (br, 2OH), 7.60 (t, *J* = 7.69 Hz, 2H), 7.86 (d, *J* = 8.06 Hz, 2H). ^{1}H NMR (300 MHz, $CD_3CN/CDCl_3$): δ 3.53 (s, 4H), 6.82 (m, 4H), 6.94 (m, 8H), 7.00 (d, *J* = 7.32 Hz, 2H), 7.22 (m, 8H), 7.50 (m, 4H); ^{13}C NMR: δ 46.92 (t),

78.32 (s), 118.91 (d), 124.91 (d), 128.98 (d), 126.48 (d), 127.90 (d), 138.07 (d), 146.94 (s), 153.77 (s), 158.57 (s); HRMS calcd 548.246; found 548.246 Anal. Calcd for $C_{38}H_{34}N_2O_3$: C, 80.54; H, 6.05; N, 4.94. Found C, 80.85; H, 5.83; N 4.99.

The methanolic solution was concentrated and the solid was recrystallized from ethanol to afford the mono-adduct **8a** as a white solid, (0.09 g, 0.25 mmol, 29%): mp 194-195 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.55 (s, 3H), 3.74 (s, 2H), 7.00 (d, *J* = 7.7 Hz, 1H), 7.11 (m, 3H), 7.19 (m, 4H), 7.43 (m, 4H), 7.62 (m, 2H), 7.87 (br, OH), 7.93 (d, *J* = 8.1 Hz, 1H), 8.14 (d, *J* = 7.5 Hz, 1H); ^{13}C NMR: δ 24.52 (q), 46.87 (t), 78.35 (s), 117.85 (d), 119.07 (d), 123.39 (d), 124.49 (d), 126.03 (d), 126.40 (d), 127.87 (d), 137.18 (d), 137.81 (d), 147.05 (s), 154.90 (s), 157.92 (s), 158.31 (s); HRMS calcd 366.173; found 366.173 Anal. Calcd for $C_{25}H_{22}N_2O$: C, 81.94; H, 6.05; N, 7.64. Found C, 81.44; H, 6.07; N, 7.46.

2-[2-(2-{2-[7-(2-{2-[2-(2-Hydroxy-ethoxy)-ethoxy]-ethoxy}-ethoxy)-2,9-dimethyl-1,10-phenanthrolin-4-yloxy]-ethoxy}-ethoxy)-ethoxy]-ethanol (16) and 7-(2-{2-[2-(2-hydroxy-ethoxy)-ethoxy]-ethoxy}-ethoxy)-2,9-dimethyl-[1,10]phenanthrolin-4-ol (15). 1.18 g (29.5 mmol NaH) sodium hydride (60% dispersion in oil) was washed twice with 10 ml of hexanes and was then added carefully to 26.3 g (135 mmol) tetraethyleneglycol **14**. The mixture was stirred for one hour at room temperature. 1.50 g (5.41 mmol) 4,7-dichloro-2,9-dimethyl-1,10-phenanthroline **13** was added and the resulting mixture was stirred at 140 ºC for 18 hours. The reaction mixture was allowed to cool to room temperature and was subsequently poured onto 150 ml of ice-water and 50 ml of CH_2Cl_2 was added. The organic layer was separated and the water layer was extracted three times with 50 ml of CH_2Cl_2. The combined organic layers were washed once with 50 ml of brine. After drying on Na_2SO_4, the solvents were evaporated *in vacuo*. The di- and mono-substituted products (**15** and **16**) could be isolated by two successive flash column chromatographic separations (silica; $CHCl_3$/MeOH 9:1) yielding **15** (1.40 g, 2.36 mmol, 43 %) as a viscous, colorless oil and **16** (35 %) as a colorless solid respectively. **15** ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 2.49 (br s, 2H), 2.86 (s, 6H), 3.56-3.59 (m, 4H), 3.63-3.72 (m, 16H), 3.79-3.83 (m, 4H), 4.01-4.04 (m, 4H), 4.36-4.39 (m, 4H), 6.85 (s, 2H), 8.09 (s, 2H). ^{13}C-NMR ($CDCl_3$, 50.3 MHz): δ 26.44 (q), 61.55 (t), 67.81 (t), 69.34 (t), 70.20 (t), 70.52 (t), 70.57 (t), 70.93 (t), 72.40 (t), 103.39 (d), 117.97 (d), 119.31 (s), 145.83 (s), 160.08 (s), 161.34 (s). **16** ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 2.49 (s, 3H), 2.65 (s, 3H), 3.59-3.82 (m, 12H), 3.98-4.01 (m, 2H), 4.29-4.32 (m, 2H), 6.28 (s, 1H), 6.69 (s, 1H), 7.80 (d, 1H, J = 9.0 Hz), 8.12 (d, 1H, J = 9.0 Hz). ^{13}C-NMR ($CDCl_3$, 50.3 MHz): δ 20.26 (q), 25.44 (q), 61.55 (t), 68.09 (t), 69.19 (t), 70.22 (t), 70.51 (t), 70.58 (t), 70.95 (t), 72.45 (t), 103.73 (d), 111.99 (d), 115.74 (d), 119.79 (s), 120.64 (d), 123.43 (s), 135.86 (s), 138.67 (s), 147.17 (s), 159.31 (s), 161.70 (s), 178.53 (s). HRMS: calcd. for $C_{22}H_{28}N_2O_6$: 416.195; found 416.196.

2-{2-[2-(2-{[2,9-Dimethyl-7-(2-{2-[2-(2-{[(4-methylphenyl)-sulfonyl]-oxy}-ethoxy)-ethoxy]-ethoxy}-ethoxy)-1,10-phenanthrolin-4-yl]-oxy}-ethoxy)-ethoxy]-ethoxy}-ethyl 4-methylbenzenesulfonate (17). 1.20 g (2.02 mmol) diol **15** was dissolved in 10 ml of THF and 40 ml of CH_2Cl_2. To this stirred mixture 25 ml of 30% aqueous NaOH was added and the resulting biphasic system was cooled to 0 °C. A solution of 1.16 g (6.08 mmol) 4-methylbenzenesulfonyl chloride in 12 ml of THF was added dropwise keeping the temperature of the reaction mixture at 0 °C (circa 30 minutes). The

mixture was stirred for an additional 30 minutes at 0 °C and was then allowed to reach room temperature. Stirring was continued overnight. The organic layer was separated and the water layer was extracted three times with 30 ml portions of CH_2Cl_2. The combined organic layers were washed once with 50 ml brine. After drying on Na_2SO_4 the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography (silica; CH_2Cl_2/EtOAc/Et_3N 40:55:5) and a clear yellow oil was obtained (0.55 g, 0.61 mmol, 30%). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 2.40 (s, 6H), 2.87 (s, 6H), 3.56-3.69 (m, 16H), 3.78-3.81 (m, 4H), 4.01-4.05 (m, 4H), 4.12-4.15 (m, 4H), 4.36-4.39 (m, 4H), 6.86 (s, 2H), 7.30 (d, 4H, J = 8.2 Hz), 7.77 (d, 4H, J = 8.2 Hz), 8.08 (s, 2H). ^{13}C-NMR ($CDCl_3$, 50.3 MHz): δ 21.56 (q), 26.51 (q), 67.89 (t), 68.60 (t), 69.18 (t), 69.38 (t), 70.51 (t), 70.68 (t), 70.95 (t), 103.43 (d), 118.00 (d), 119.35 (s), 127.88 (d), 129.76 (d), 132.86 (s), 144.75 (s), 145.87 (s), 160.15 (s), 161.40 (s).

{2-[2-(2-{2-[7-(2-{2-[2-(2-Diethylamino-ethoxy)-ethoxy]-ethoxy}-ethoxy)-2,9-di-methyl-[1,10]phenanthrolin-4-yloxy]-ethoxy}-ethoxy)-ethoxy]-ethyl}-diethyl-amine (18). 0.40 g (0.44 mmol) ditosylate **17** was added to a mixture of 0.92 g (6.7 mmol) potassium carbonate and 0.33 g (4.5 mmol) diethylamine in 10 ml of toluene. The reaction mixture was refluxed for 4 days and was then allowed to cool to room temperature. The suspension was filtered with suction on a glass filter P4 and the residue was washed three times with 10 ml of CH_2Cl_2. The filtrate and the washings were combined and the solvents were evaporated *in vacuo*. The crude product was purified by column chromatography (silica; CH_3CN/MeOH/Et_3N 18:1:1) yielding **18** as a pale brown, clear oil (192 mg, 0.273 mmol, 62%). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 0.99 (t, 12H, J = 7.0 Hz), 2.54 (q, 8H, J = 7.0 Hz), 2.63 (t, 4H), 2.84 (s, 6H), 3.52-3.70 (m, 16H), 3.77-3.80 (m, 4H), 4.01 (t, J = 4.8 Hz, 4H), 4.35 (t, J = 4.8 Hz, 4H), 6.83 (s, 2H), 8.07 (s, 2H). ^{13}C-NMR ($CDCl_3$, 75.4 MHz): δ 11.44 (q), 26.46 (q), 47.47 (t), 52.13 (t), 67.84 (t), 69.36 (t), 69.51 (t), 70.32 (t), 70.48 (t), 70.61 (t), 70.96 (t), 103.36 (d), 117.99 (d), 119.35 (s), 145.91 (s), 160.07 (s), 161.38 (s). A correct r HRMS could not be obtained, although EI-MS gave *m/e* 703 (M+H).

7,22,25,40-Tetramethyl-10,13,16,19,28,31,34,37-octaoxa-6,22,25,41-tetraazatetra-cyclo[36.4.0.0^{4,9}.0^{5,42}]dotetraconta-1(42),2,4,6,8,38,40-heptaene (19). 46 mg (0.52 mmol) *N*,*N*'-dimethylethylenediamine was added to a suspension of 0.52 g (1.6 mmol) cesium carbonate in 450 ml of toluene. 0.48 g (0.53 mmol) of ditosylate **17** in 10 ml toluene was added and the mixture was refluxed for 3 days. The mixture was allowed to cool to r.t. The suspension was filtered with suction on a glass filter P3 and the residue was washed three times with 20 ml of CH_2Cl_2. The filtrate and the washings were combined and the solvents were evaporated *in vacuo*. The crude oil was purified by preparative HPLC separation (silica; CH_3CN/MeOH/Et_3N 8:1:1; 0.3 ml/min) or by two successive flash column chromatographic separations (silica; CH_3CN/MeOH/Et_3N 18:1:1), yielding **19** in variable yield (5-26%). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 2.33 (s, 6H), 2.65 (s, 4H), 2.69 (t, 4H), 2.86 (s, 6H), 3.58-3.59 (m, 8H), 3.65-3.73 (m, 8H), 3.81-3.85 (m, 4H), 4.03 (dd, 4H), 4.36 (dd, 4H), 6.83 (s, 2H), 8.12 (s, 2H). ^{13}C-NMR ($CDCl_3$, 50.3 MHz): δ 26.52 (q), 42.70 (q), 54.48 (t), 56.70 (t), 68.26 (t), 68.64 (t), 69.45 (t), 70.44 (t), 70.66 (t), 71.25 (t), 103.35 (d), 118.13 (d), 119.41 (s), 144.30 (s), 160.18 (s), 161.40 (s). HRMS: calcd. 644.379; no proper HRMS could be obtained, but ES-MS gave molecular ions at *m/e* 645 $[M+H]^+$ and 323.5 $[M+2H]^{2+}$.

Zinc complex of 3c

The diol **3c** (30 mg, 59 μmol) was suspended in 1 mL of CD_3CN and zinc perchlorate heptahydrate (22 mg, 59 μmol) was added. The solution became clear. The ^1H NMR spectrum showed quantitative conversion to the complex. The solvent was evaporated and the solid was crystallized from chloroform/acetone (1:1) with isothermal distillation of hexane into the solution affording zinc-**3c** as colorless crystals (37 mg, 47 μmol, 80%): ^1H NMR (300 MHz, $CD_3CN/CDCl_3$): δ 0.37 (s, 6H), 0.28 (s, 6H), 0.78 (s, 6H), 0.93 (m, 2H), 1.28 (m, 6H), 1.54 (m, 4H), 1.94 (m, 2H), 2.2 (br, H_2O), 3.30 (d, *J* = 16.48 Hz, 2H), 3.43 (d, *J* = 16.48 Hz, 2H), 5.40 (s, 2OH), 7.79 (d, *J* = 8.43 Hz, 2H), 7.89 (s, 2H), 8.50 (d, *J* = 8.43 Hz, 2H). ^{13}C NMR: δ 9.92 (q), 19.31 (q), 20.09 (q), 24.96 (t), 30.20 (t), 43.42 (t), 43.76 (d), 45.61 (s), 48.72 (t), 52.66 (s), 88.14 (s), 125.73 (d), 126.91 (s), 127.19 (d), 133.05 (s), 140.88 (d), 160.01 (s); HRMS calcd 774.166; no proper HRMS could be obtained. Anal. Calcd for $C_{34}H_{44}N_2O_{10}ZnCl_2$: C, 52.56; H, 5.71; N, 3.61; Zn, 8.41. Found C, 52.46; H, 5.64; N, 3.63; Zn, 8.54.

Zinc complex of 7a

To a suspension of the ligand **7a** (48 mg, 88 μmol) in 1 mL of CD_3CN + 0.1 mL $CDCl_3$ was added zinc perchlorate heptahydrate (33 mg, 90 μmol). The ligand slowly dissolved within 5 min. and the reaction was analyzed by means of ^1H NMR, which indicated quantitative formation of the complex **20**. The solvent was removed under reduced pressure and the mixture was recrystallized from ethyl acetate/acetonitrile (1:1) by slow distillation of hexane into the solution (67 mg, 83 μmol, 95%): ^1H NMR (300 MHz, $CD_3CN/CDCl_3$): δ 2.2 (br, H_2O), 3.93 (s, 4H), 7.11 (m, 20H), 7.24 (d, *J* = 8.06 Hz, 2H), 7.48 (br, 2OH), 7.76 (dd, *J* = 8.06 Hz, *J* = 8.06 Hz, 2H), 7.87 (d, *J* = 8.06 Hz, 2H).). ^{13}C NMR: δ 45.03 (t), 82.87 (s), 119.94 (d), 125.56 (d), 127.55 (d), 127.66 (d), 128.55 (d), 140.95 (s), 142.00 (d), 146.76 (s), 157.50 (s).

Copper complex of 7a

The free ligand **7a** (50 mg, 91 μmol) was suspended in 3 mL of a mixture of acetonitrile and chloroform (2:1). $Cu(acac)_2$ (26 mg, 99 μmol) was added and stirring continued overnight. The solvents were removed and the product recrystallized from ethyl acetate to afford the di copper complex **21** (35 mg, 36 μmol, 40%): ^1H NMR (300 MHz, $CD_3CN/CDCl_3$): δ -7.5, -1.3, 1.2, 2.0, 4.1, 6.6, 9.5, 10.5, 34.7, 61.2.

Complexation of 18 with $CuPF_6.4CH_3CN$ (1:1 complex). A colorless solution of 6.7 mg (18 μmol) $Cu(PF_6).4CH_3CN$ in 1 ml of acetonitrile was added to solution of 12.6 mg (18 μmol) ligand **18** in 1.26 ml of acetonitrile via a canula. Immediately upon addition the solution turned bright orange. Two samples were taken: one was kept under N_2, the other was exposed to air. The samples gave comparable mass spectra. ES-MS of a sample showed a lot of signals, among them: *m/z* 383 $[Cu^I + ligand + H]^{2+}$, 703.5 $[ligand + H]^+$, 765.6 $[Cu^I + ligand]^+$ and 1467.8 $[Cu^I + 2\ ligands]^+$. The solvent of the rest of the reaction mixture was evaporated *in vacuo* yielding a orange oil. ^1H-NMR (300 MHz, $CDCl_3$): δ 1.05 (br, 12H), 2.01 (s, CH_3CN), 2.38 (s, 6H), 2.67 (br, 12H), 3.63-3.81 (m, 20H), 4.07 (br, 4H), 4.48 (br, 4H), 7.10 (s, 2H), 8.24 (s, 2H).

Acknowledgements

We are grateful to Mr. J. Buter for initial experiments with the phenanthrolines.

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