Concave Reagents, 15[1]

New Concave 1,10-Phenanthrolines: Catalysts for the Alcohol Addition to Ketenes and Ligands in Transition Metal Complexes☆

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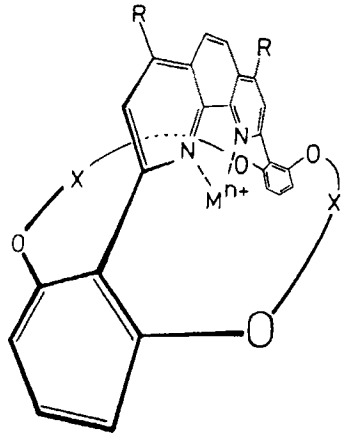
By bridging tetrahydroxy-1,10-phenanthrolines **9** by ditosylates **10** or diiodides **11** concave 1,10-phenanthrolines **1** were synthesized. Their concave shape was proven by X-ray analyses of **1a** and **1c**, their basicities were determined by photometric titrations. Compounds **1a–g** are active in the base-catalyzed addition of alcohols to ketenes and form stable metal ion complexes with transition metal salts.

The combination of a concave geometry with a basic center (e.g. a 1,10-phenanthroline system) gives concave bases[2,3,4] which exhibit increased selectivities in model reactions due to concave shielding. Besides the application of concave bases as proton transfer reagents[5], their use as base catalysts has been shown in ketene alcoholyses[6,7]. In this paper we demonstrate that concave 1,10-phenanthrolines **1**[4] also may be used as catalysts in this reaction, and we show that it is also possible to employ **1** as ligands for the complexation of transition metal ions. Due to the concave shape of the ligands, the stoichiometry between metal ion and ligand is strictly 1:1, and the complexed metal ion possesses free coordination site(s) (see Figure 1).

The synthesis of a concave 1,10-phenanthroline based on a 2,9-diaryl-1,10-phenanthroline system has already been published[4]. To change the size and the basicity of this system, two variations have now been made: (i) the bridges X have been varied (aliphatic, polyether, substituted polyether, chiral polyether) and (ii) a substituent R has been introduced into the 4- and 7-positions of the 1,10-phenanthroline system.

The latter substitution is feasible when 4,7-dichloro-1,10-phenanthroline (**2e**) is used as starting material[8,10]. Nucleophilic substitution of the chlorine atoms is possible with a variety of reagents[10,11], but the reaction sequence[4] for the synthesis of concave 1,10-phenanthrolines **1** allows only some substituents to be introduced because the following problems have to be overcome: (i) the substituents R may not exhibit a strongly electron-donating effect in order to still allow the nucleophilic addition of the aryllithium compound **3** to the 1,10-phenanthroline **2**, (ii) the substituents R themselves must not be displaced by nucleophiles, and



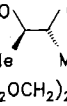
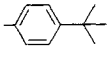
	–X–	R
1a	$-(CH_2)_8-$	H
1b	$-(CH_2)_{10}-$	H
1c	$-CH_2(CH_2OCH_2)_2CH_2-$	H
1d	$-CH_2(CH_2OCH_2)_3CH_2-$	H
1e	$-CH_2CH_2O$  OCH_2CH_2-	H
1f	$-CH_2CH_2O$  OCH_2CH_2- (Me, Me)	H
1g	$-CH_2(CH_2OCH_2)_2CH_2-$	O 

Figure 1. A transition metal ion M^{n+} is shielded from one side by the 1:1 binding into the cavity of a concave 1,10-phenanthroline **1**

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(iii) the substituents must survive the ether cleavage by BBr_3 (**8** → **9**). A class of substituents which fulfill these requirements are phenoxides. We have chosen an alkyl-substituted phenoxide (to increase the solubility of the concave 1,10-phenanthrolines **1**) and have introduced it into the 4- and 7-positions of the 1,10-phenanthroline system.

The bridges X in the concave 1,10-phenanthrolines **1** can be varied by using different di-*p*-tosylates **10** or diiodides **11** for the bis-macrocyclization of the tetraphenols **9** (see Scheme 1). Besides octa- and decamethylene bridges polyether chains have also been used (tri- and tetraethylene glycol derivatives).

The syntheses of the aliphatic and the unsubstituted polyether diiodides **11a–c** and ditosylates **10c** and **10d** are straightforward[12], but in the cases of **10e** and **11e** instead of the central ethylene unit a 1,2-phenylene unit is used, and in **11f** the central ethylene unit is (*R*,*R*)-dimethyl-substituted. These substituted derivatives, the ditosylate **10e** and diiodides **11e** and **11f**, have been synthesized by elongation of the corresponding 1,2-diol **12** or **15** with 2-chloroethanol (**13**) or its THP ether **16**, respectively (see Scheme 2).

The bis-macrocyclization of the tetraphenols **9** with the ditosylates **10** or diiodides **11** has been performed in two ways. In a cyclization according to the high-dilution principle (method A, see Experimental), a 1:2 mixture of the tetraphenol **9** and a ditosylate **10** is *slowly* added to a heated mixture of Cs_2CO_3 or K_2CO_3 in DMF. An alternative route is a batch reaction (method B, see Experimental) of one equivalent of the tetraphenol **9** with two equivalents of the diiodide **11** in the presence of an excess of K_2CO_3. Table 1 lists the yields of the macrocyclizations[13].

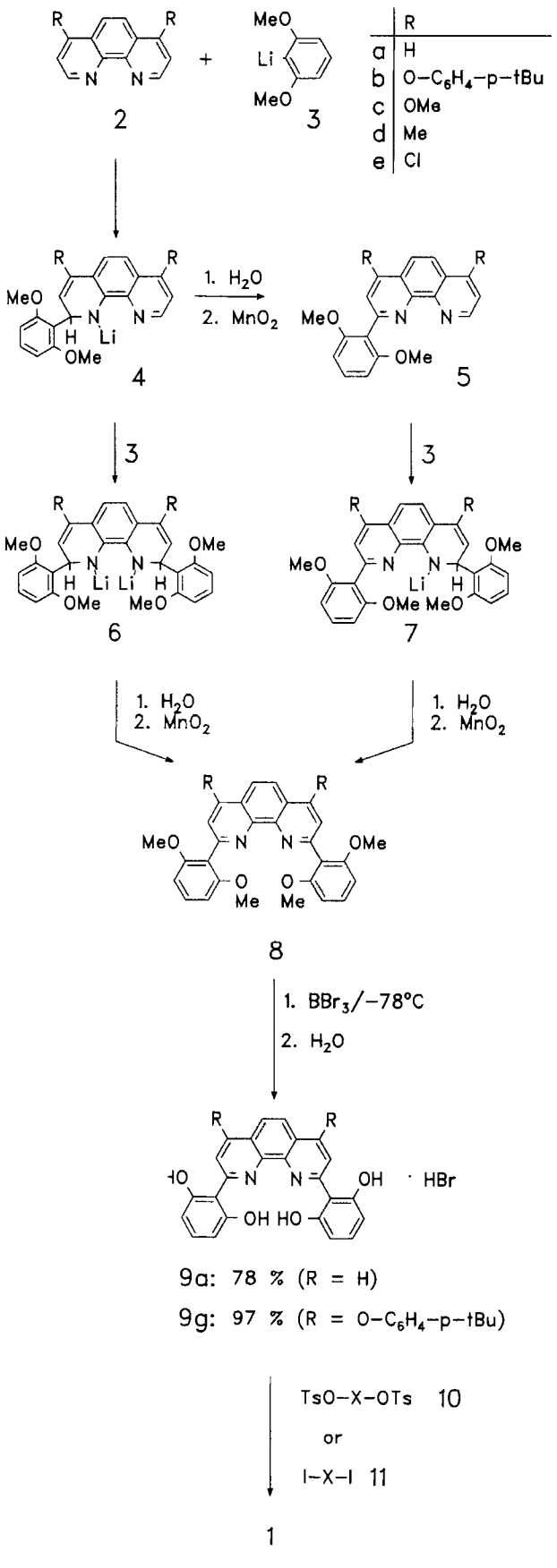
The structures of the new concave 1,10-phenanthrolines **1** have been elucidated by standard methods (IR, NMR, MS, elemental analysis). Then by ^{1}H-NMR spectroscopy the protonation of **1** has been investigated, and basicities were determined by photometric titrations in ethanol. Table 2 lists the relative basicities log *K*[14] for all concave 1,10-phenanthrolines **1** and some related compounds. On average, the basicity of the concave derivatives **1** is approx. 2 pK_a units larger than that of 1,10-phenanthroline itself.

The concave shape of the bis-macrocycles **1** has been proven by X-ray analyses (see Experimental, Figures 2, 3, 5, 6).

In contrast to **1a**, the X-ray analysis of **1c** has been performed at low temperature (100 K). Four independent concave 1,10-phenanthrolines **1c** have been found in the unit cell. The main difference between the four molecules are the orientations of the triethylene glycol side chains X of **1c** which even differ for the left and the right chains X of each molecule. In two of the four conformers, one of the two bridges is disordered even at 100 K.

Because these eight different orientations of the triethylene glycol chain coexist in the crystal they have to be very similar in energy[19] explaining the difficulty in obtaining an X-ray structure for **1c** at ambient temperature. At room temperature and in solution, these (and possibly other) conformations can interconvert. Thus the structure in solution

Scheme 1



Scheme 2

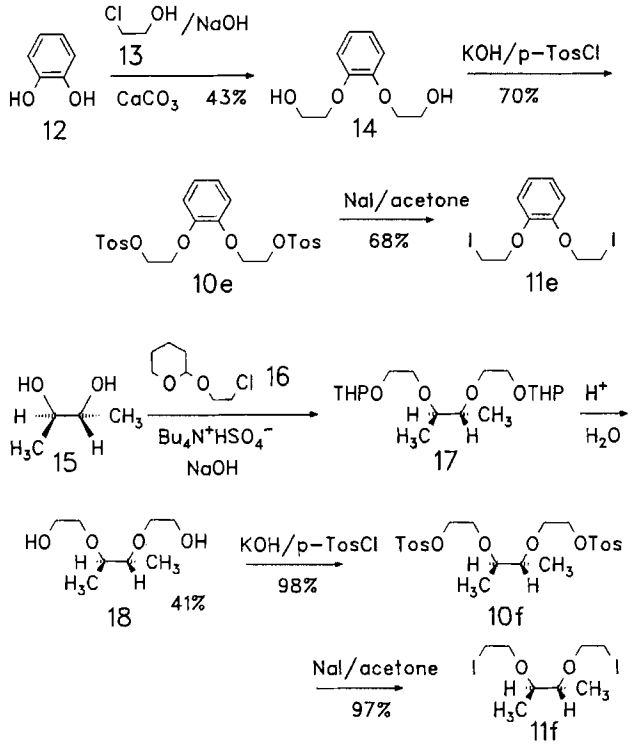


Table 1. Yields of the bis-macrocyclic concave 1,10-phenanthrolines **1** synthesized by high-dilution bis-macrocyclization (method A) and/or by batch bis-macrocyclization (method B)

Concave 1,10-phenanthroline **1**	-X-	method A (%)	method B (%)
1a (R = H)	$(CH_2)_8$	28	-
1b (R = H)	$(CH_2)_{10}$	19	-
1c (R = H)	$CH_2(CH_2OCH_2)_2CH_2$	13 [4]	24
1d (R = H)	$CH_2(CH_2OCH_2)_3CH_2$	-	11
1e (R = H)	CH_2CH_2O-(*o*-C_6H_4)-OCH_2CH_2	2.7	5
1f (R = H)	CH_2CH_2O-(*R*-CHMe)$_2$-OCH_2CH_2	-	13
1g (R = *p*-tBu-C_6H_4-O)	$CH_2(CH_2OCH_2)_2CH_2$	-	14

is mainly determined by the orientation of the aromatic rings.

The aromatic backbone of the concave 1,10-phenanthrolines **1** is very similar for **1a** and **1c**. The bis-alkoxy-substituted aryl rings are twisted against the 1,10-phenanthroline units. The dihedral angles of **1a** and the four conformers of **1c** are ca. 70° varying from 62 to 83°. Therefore, the four resorcinyl oxygen atoms of the concave 1,10-phenanthrolines form parallelograms whose sides consist of two aryl rings and two chains X. Due to the similar dihedral angles in **1a** and in the four conformers of **1c** this parallelogram is very similar for all molecules. It is best seen in Figure 3. Thus the major difference between the structures are the orientations of the side chains X which is best seen in Figure 6.

In Figure 2, **1a** is shown in two different orientations revealing its concave shape. While the nitrogen atoms of the 1,10-phenanthroline unit are hidden behind the side chains X in view A, view B shows how these basic centers are oriented in the concave pocket of **1a**.

Table 2. Basicities of concave 1,10-phenanthrolines **1** determined by photometric titrations in ethanol[3] and rates of the addition of ethanol to diphenylketene k_{obs} catalyzed by these bases

(Concave) 1,10-phenanthroline	-X-	log K a)	log K' b)	k_{obs} [10^{-3} s^{-1}] c)
2a (R = H)	-	0	-	451
2b (R = tBu-*p*-C_6H_4-O)	-	1.4	-	-
2c (R = OMe) [15]	-	(1.6)	-1.6 - -2.0	1330
2d (R = Me) [16]	-	(1.4)	-1.9 - -2.3	967
2,9-dimethyl-1,10-phenanthroline	-	0.15	-	121
8a (R = H)	-	(2.0)	-1.4	30.3
8b (R = tBu-*p*-C_6H_4-O)	-	(2.9)	-0.5	78.7
1h (R = H)	$(CH_2)_2OMe$ $MeO(CH_2)_2$	(2.5)	-0.9	63.6
1a (R = H)	$(CH_2)_8$	(1.9)	-1.2 - -1.8	31.1
1b (R = H)	$(CH_2)_{10}$	(2.5)	-0.9	80.0
1c (R = H)	$CH_2(CH_2OCH_2)_2CH_2$	1.5	-	8.3
1d (R = H)	$CH_2(CH_2OCH_2)_3CH_2$	(2.1)	-1.3	40.7
1e (R = H)	CH_2CH_2O-(*o*-C_6H_4)-OCH_2CH_2	(3.1)	-0.3	39.8
1f (R = H)	CH_2CH_2O-(*R*-CHMe)$_2$-OCH_2CH_2	(2.8)	-0.6	35.6
1g (R = tBu-*p*-C_6H_4-O)	$CH_2(CH_2OCH_2)_2CH_2$	(2.8)	-0.6	66.4

a) To determine log *K*, the equilibrium between thymol blue and the base was measured. For the definition of log *K* see ref.[3]. When log *K* appears in brackets, only log *K'* could be determined, and log *K* was calculated from log *K'* using the equation log *K'* + 3.4 = log *K*[17]. – b) Determined with bromophenol blue. – c) The rates of ethanol addition to diphenylketene were determined as described[6], with c_{ketene} = 4.0 mM, c_{EtOH} = 50.0 mM.

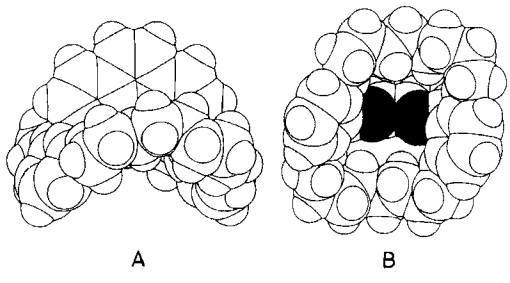


Figure 2. X-ray analysis of **1a**. – A: Side view of **1a**, the nitrogen atoms of the 1,10-phenanthroline system are hidden behind the $(CH_2)_8$ chains. – B: View from below, the black atoms represent the nitrogen atoms in 1- and 10-position of the 1,10-phenanthroline system

The basicity measurements and the X-ray analyses prove that **1a–g** indeed are *concave bases*: they possess a concave geometry *and* they are basic. The concave shape of **1** becomes obvious in the X-ray analyses and is best seen in Figure 2. Using the Connolly routine[20], we have investigated the accessibility of the nitrogen atoms in **1a**. Spheres with a radius up to 2.7–2.8 Å can still contact the N atoms. That means that molecules or parts of molecules with a diameter up to 5.5 Å should be able to react with the basic center. A molecule of this size is acetone which is incorporated into **1c** as its X-ray structure shows (see above).

Base Catalysis

To investigate the catalytic power of the concave 1,10-phenanthrolines **1** in base catalyses they are applied in the

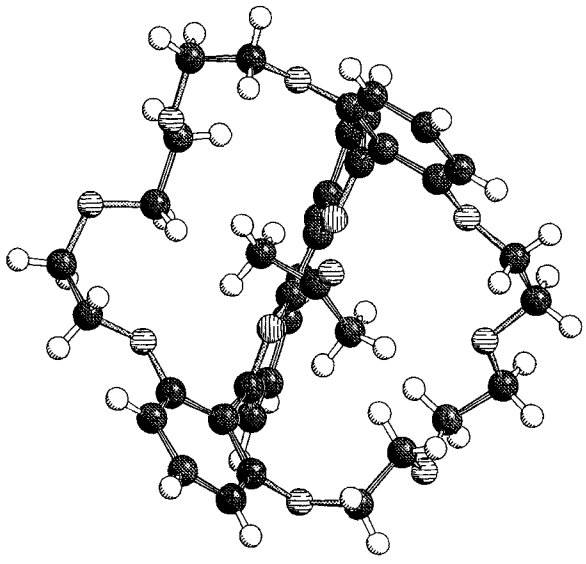


Figure 3. X-ray analysis of **1c** containing one molecule of acetone, view from below into the concave region of **1c**. Only one of four conformers is shown. The parallelogram formed by the four resorcinyl oxygen atoms is similar for all conformers. The differing orientations of their side chains are best seen in Figure 6

base-catalyzed addition of ethanol to diphenylketene. Comparable to concave pyridines[6], the concave 1,10-phenanthrolines **1** do catalyze this reaction.

$$Ph_2C{=}C{=}O + EtOH \rightarrow Ph_2CHCO_2Et$$

Observed rate constants k_{obs} for the catalysis by various 1,10-phenanthrolines under standardized conditions ([EtOH] = 50 mM, [base] = 50 mM) are listed in Table 2[21]. In a Brønsted plot (Figure 4), the logarithms of the observed rates log k_{obs} are plotted against the basicities log K[14] of the concave 1,10-phenanthrolines **1** and other 1,10-phenanthrolines **2** and **8**.

rate = $k \cdot$ [diphenylketene]$^1 \cdot$ [EtOH]$^x \cdot$ [base]^y
with [EtOH] = 50 mM and [base] = 50 mM:
rate = $k_{obs} \cdot$ [diphenylketene]

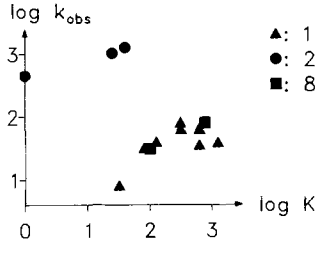


Figure 4. Brønsted plot for the addition of ethanol to diphenylketene catalyzed by concave and non-concave 1,10-phenanthrolines **1**, **2**, and **8**

Figure 4 reveals that the rates are not only determined by the basicity of a 1,10-phenanthroline. For three different classes of 1,10-phenanthrolines, the concave 1,10-phenanthrolines **1**, the 2,9-diaryl-1,10-phenanthrolines **8** and the 2,9-unsubstituted 1,10-phenanthrolines **2**, there exists a reactivity-basicity relationship. The slopes are 0.2 for the unsubstituted 1,10-phenanthrolines **2** and 0.3 for the 2,9-diaryl-1,10-phenanthrolines **8**. The vertical distances between these slopes at log K = 0 or 2 correspond to a difference in reactivity between 67 and 40, respectively. The data for concave 1,10-phenanthrolines **1**, however, are not forming a straight line but a cluster. But this cluster is located *on* the slope of the 2,9-diaryl-1,10-phenanthrolines **8**. The rate of addition of ethanol to diphenylketene catalyzed by concave 1,10-phenanthrolines **1** is therefore mainly determined by the 2,9-diaryl substitution which is similar for all concave 1,10-phenanthrolines **1** (see X-ray analyses).

For more voluminous alcohols than ethanol, additional interactions influence the reaction: When an asymmetric secondary alcohol is used, the chiral chains X of the concave 1,10-phenanthroline **1f** exhibit an influence on the rate of addition. When chiral (*R*,*R*,*R*,*R*)-**1f** is used as catalyst for the addition of phenylethanol to diphenylketene, (*R*)-phenylethanol is added 20% faster than the (*S*)-enantiomer.

Metal Ion Complexes

The well-known transition metal-complexing ability of the 1,10-phenanthroline moiety is still present in the concave 1,10-phenanthrolines as Table 3 shows for ions of the first transition metal period.

The formation of concave 1,10-phenanthroline transition metal complexes has been investigated by UV titration, and from the appearance of a shoulder at 350 nm association constants have been calculated. In most cases, strong binding occurs. Only for the concave 1,10-phenanthrolines with purely aliphatic side chains [especially $(CH_2)_8$], smaller association constants have been determined, indicating that the oxygen atoms in the chains X of the 1,10-phenanthrolines **1** contribute to the stronger binding in **1c**, **1d**, and **1e**.

The use of I^- instead of $C_4F_9SO_3^-$ for the same transition metal/bis-macrocycle system (**1a**, Co^{2+}, Cu^+) leads to comparable association constants.

For comparison, complex formation of the non-bis-macrocyclic 1,10-phenanthroline **8** and of 2,9-dimethyl-1,10-phenanthroline has been measured in the same way. But in contrast to **1**, a 1:1 stoichiometry of metal-to-1,10-phenanthroline has not been observed for all complexes with nonmacrocyclic 1,10-phenanthrolines. Isosbestic points have not been observed either. These findings are in agreement with results obtained for comparable non-bis-macrocyclic systems[22].

After mixing solutions of the organic ligands and the metal salts and evaporation of the solvents, for most metal salt/concave 1,10-phenanthroline combinations we have succeeded in isolating crystalline complexes. In some cases we have obtained analytically pure complexes by recrystallization in a 1:1 stoichiometry[23], whereas some complexes do not crystallize in a defined composition.

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Table 3. Logarithms of the association constants log K_{Ass} for complex formation between 1,10-phenanthrolines **1**, **8**, or 2,9-dimethyl-1,10-phenanthroline and transition metal nonafluorobutanesulfonates

Ligand	Mn^{2+}	Fe^{2+}	Fe^{3+} (log K_{Ass})	Co^{2+}	Ni^{2+}	Cu^{+}	Cu^{2+}
1a	4.7	5.9		4.7	4.7	5.1	
1c	> > 7	4.6		> > 7	> 6.5	5.1	
1d	> > 7	> 6.5	> 6.5	> > 7 > > 7 [a]	> 6.5 > 6.5 [a]	> 6.5	5.6
1e	> > 7	> 6.5		> > 7	5.4	5.9	
8	> > 7	- [b]		> > 7	> > 7	- [b]	
2,9-dimethyl-1,10-phenanthroline	> > 7	- [b]		> > 7	> > 7	- [b]	

[a] Iodide as counter ion. – [b] K_{Ass} values could not be estimated. It seems that complexes with stoichiometries differing from 1:1 were present.

Experimental

General Remarks: See ref.[3]. – Polarimeter: Perkin-Elmer 141, cell length 10 cm. – DMF was refluxed with calcium hydride and distilled (b.p. 153°C). – DMSO was refluxed with calcium hydride, distilled (b.p. 189°C), and filtered through basic alumina.

2-(2,6-Dimethoxyphenyl)-4,7-bis[4-(1,1-dimethylethyl)phenoxy]-1,10-phenanthroline (**5b**): 2,6-Dimethoxyphenyllithium (**3**) was prepared[4] from 0.96 g (138 mmol) of lithium powder and 13.7 g (63 mmol) of 2-bromo-1,3-dimethoxybenzene[4] in 200 ml of dry diethyl ether. Then 5.0 g (10 mmol) of 4,7-bis[4-(1,1-dimethylethyl)-phenoxy]-1,10-phenanthroline (**2b**)[10,11] in 250 ml of dry toluene was added, the mixture was stirred for 14 h at room temp. and for 4 h at reflux. After hydrolysis with 250 ml of water, the mixture was extracted four times with 200 ml of dichloromethane. 50 g (0.57 mol) of manganese dioxide[24] was added to the combined organic layers, and the mixture was heated to reflux for 4 h, water being removed by azeotropic distillation. After filtration at room temp. the solvents were distilled off, and the residue was purified by chromatography (silica gel; dichloromethane/ethanol, 10:1). The yellow product was recrystallized from ethanol yielding 4.08 g (64%) of **5b** as its monohydrate, m.p. 153°C. – IR (KBr): $\tilde{\nu}$ = 3410 cm^{-1} (H_2O), 1610, 1585, 1548 (arom.), 1248, 1108 (C–O). – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.34 (s, 9H), 1.39 (s, 9H), 2.01 (br. s, 2H, H_2O), 3.68 (s, 6H), 6.58 (d, *J* = 8 Hz, 2H), 6.83 (d, *J* = 5 Hz, 1H), 6.95 (s, 1H), 7.14 (d, *J* = 8 Hz, 2H), 7.17 (d, *J* = 8 Hz, 2H), 7.27 (t, *J* = 8 Hz, 1H), 7.43 (d, *J* = 8 Hz, 2H), 7.48 (d, *J* = 8 Hz, 2H), 8.38 (AB system, *J* = 8 Hz, 2H), 8.98 (d, *J* = 5 Hz, 2H). – MS (EI, 70 eV), *m/z* (%): 612 (50), 611 (56), 594 (100), 582 (17). – $C_{40}H_{40}N_2O_4 \cdot H_2O$ (612.7 + 18.0): calcd. C 76.17, H 6.71, N 4.44; found C 76.53, H 6.59, N 4.33.

2,9-Bis(2,6-dimethoxyphenyl)-4,7-bis[4-(1,1-dimethylethyl)-phenoxy]-1,10-phenanthroline (**8b**): 2,6-Dimethoxyphenyllithium (**3**) was prepared[4] from 0.88 g (129 mmol) of lithium powder and 12.7 g (58 mmol) of 2-bromo-1,3-dimethoxybenzene[4] in 250 ml of dry diethyl ether. Then 5.71 g (9.3 mmol) of **5b** in 350 ml of dry toluene was added, the mixture was stirred for 16 h at room temp. and then for 4 h at reflux. Hydrolysis, rearomatization with 50 g (0.57 mmol) of manganese dioxide[10] and workup were carried out as described for **5b**. Recrystallization from ethanol yielded 1.72 g (25%) of **8b**, m.p. 273°C. – IR (KBr): $\tilde{\nu}$ = 3400 cm^{-1} (H_2O), 1578, 1460 (arom.), 1100 (C–O). – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.37 (s, 18H), 3.11 (br. s, H_2O), 3.61 (s, 12H), 6.67 (br. d, *J* = 8 Hz, 4H), 7.13–7.57 (br. m with d at 7.20, *J* = 8 Hz, and d at 7.51, *J* = 8 Hz, ca. 12H), 8.47 (br. s, 2H). – ^1H NMR (250 MHz, $CDCl_3$, 2.6 equivalents of picric acid): δ = 1.38 (s, 18H), 3.74 (s, 12H), 5.30 (br. s, H_2O), 6.67 (d, *J* = 8 Hz, 4H), 7.25 (d, *J* = 8 Hz, 4H), 7.40 (s, 2H), 7.44 (t, *J* = 8 Hz, 2H), 7.57 (d, *J* = 8 Hz, 4H), 8.59 (s, 2H), 8.89 (s, 5.2H, picric acid). – MS (EI, 70 eV), *m/z* (%): 749 (29), 748 (62), 730 (100). – MS (high resolution): calcd. 748.3512; found 748.3461. – $C_{48}H_{48}N_2O_6 \cdot H_2O$ (748.9 + 18.0): calcd C 75.17, H 6.57, N 3.65; found C 75.25, H 6.44, N 3.72.

2,9-Bis(2,6-dihydroxyphenyl)-4,7-bis[4-(1,1-dimethylethyl)phenoxy]-1,10-phenanthroline Hydrobromide (**9b**): Under N_2 1.7 g (2.3 mmol) of **8b** was dissolved in 150 ml of dry dichloromethane, and the solution was cooled to −78°C. 5.1 g (20.4 mmol) of boron tribromide was added. The mixture was stirred for 48 h at room temp. and after hydrolysis with 70 ml of water it was filtered. To remove boron in the form of its methyl ester, the precipitate was heated to reflux with 70 ml of methanol, and the solvent was distilled off in vacuo (three times). Recrystallization of the residue from methanol yielded 1.73 g (97%) of **9b**, m.p. >220°C (dec.). – IR (KBr): $\tilde{\nu}$ = 3365 cm^{-1} (br., OH), 2940 (C–H), 1605, 1566, 1480 (arom.), 1204 (C–O). – ^1H NMR (250 MHz, [D$_6$]DMSO): δ = 1.36 (s, ca. 18H), 6.43 (d, *J* = 9 Hz, 4H), 7.10 (t, *J* = 9 Hz, 2H), 7.34 (d, *J* = 9 Hz, 4H), 7.59 (d, *J* = 9 Hz, 4H), 8.09 (s, 2H), 8.39 (s, 2H). – MS (EI, 70 eV), *m/z* (%): 693 (13), 692 (30). – The microanalysis of **9b** was not satisfactory (the material did not crystallize as a defined monohydrobromide) and a high-resolution MS could not be obtained. But its structure is proven by conversion of **9b** into **1g**.

2,9-Bis[2,6-bis(1,4-dioxapentyl)phenyl]-1,10-phenanthroline (**1h**): 3.3 g (6.9 mmol) of 2,9-bis(2,6-dihydroxyphenyl)-1,10-phenanthroline hydrobromide (**9a**), 6.6 g (70 mmol) of 2-chloroethyl methyl ether, and 14.3 g (103 mmol) of K_2CO_3 were stirred under N_2 in 150 ml of dry DMSO at 65°C for 120 h. After evaporation of the solvent in vacuo the residue was dissolved in dichloromethane, the solution filtered and concentrated to dryness. The resulting solid was extracted with hot petroleum ether (b.p. 100–140°C) (six times 100 ml), the solvents were evaporated, and the residue was recrystallized from toluene yielding 810 mg (19%) of **1h**, m.p. 139–140°C. – IR (KBr): $\tilde{\nu}$ = 1610, 1588 cm^{-1} (arom.), 1245, 1102 (C–O). – ^1H NMR (250 MHz, $CDCl_3$): δ = 3.07 (s, 12H), 3.54 (m_c, 8H), 4.19 (m_c, 8H), 6.81 (d, *J* = 9 Hz, 4H), 7.50 (t, *J* = 9 Hz, 2H), 8.45 (d, *J* = 9 Hz, 2H), 8.47 (s, 2H), 9.13 (d, *J* = 9 Hz, 2H). – MS (EI, 70 eV), *m/z* (%): 628 (33), 597 (100), 583 (54), 570 (17), 539 (22). – $C_{36}H_{40}N_2O_8$ (628.7): calcd. C 68.77, H 6.41, N 4.45; found C 68.23, H 6.22, N 4.40.

1,2-Bis(2-hydroxyethoxy)benzene (**14**): Under N_2 10.0 g (91 mmol) of 1,2-dihydroxybenzene (**12**), 14.5 g (360 mmol) of sodium hydroxide, 22.7 g (230 mmol) of calcium carbonate, and 140 ml of water were heated to reflux. During 30 min 60 g (0.7 mmol) of 2-chloroethanol was added. After refluxing for 4 h the mixture was carefully hydrolyzed with 2 N HCl at room temp. After extraction with dichloromethane (4 × 120 ml) the combined organic layers were washed (3 × 40 ml of 2 N NaOH, 2 × 40 ml of water), dried with $MgSO_4$, and evaporated to dryness. Recrystallization of the residue from ethanol yielded 7.76 g (43%) of **14**, m.p. 74°C. – IR (KBr): $\tilde{\nu}$ = 3600–3000 cm^{-1} (OH), 1580, 1495 (arom.), 1100 (C–O). – ^1H NMR (250 MHz, $CDCl_3$): δ = 3.24 (s, 2H), 3.43 (m_c, 4H), 4.11 (m_c, 4H), 6.96 (s, 4H). – MS (EI, 70 eV), *m/z* (%): 198 (23), 154 (16), 110 (100). – $C_{10}H_{14}O_4$ (198.2): calcd. C 60.59, H 7.11; found C 60.23, H 7.09.

1,2-Bis[2-(p-tosyloxy)ethoxy]benzene (**10e**): A solution of 20.7 g (100 mmol) of **14** and 49.1 g (250 mmol) of *p*-toluenesulfonyl chloride in 250 ml of dry THF was cooled to 0°C. With cooling and vigorous stirring, 72.4 g (1.29 mol) of freshly powdered KOH was added in portions. The mixture was stirred for 2 h, poured into

1 l of ice/water, the THF was distilled off in vacuo, and the resulting solid was filtered off. The aqueous layer was extracted three times with 100 ml of dichloromethane, the combined organic layers were concentrated to dryness, the residue was added to the filtered solid and recrystallized from acetone/water (4:1). Yield: 36.2 g (71%) of **10e**, m.p. 92°C. – IR (KBr): $\tilde{\nu}$ = 1595, 1495 cm^{-1} (arom.), 1210, 1180 (SO_2O), 1040 (C–O). – ^1H NMR (250 MHz, $CDCl_3$): δ = 2.42 (s, 6H), 4.11 (m_c, 4H), 6.83 (m_c, 4H), 7.32 (d, J = 7.3 Hz, 4H), 7.78 (d, J = 7.3 Hz, 4H). – MS (EI, 70 eV), *m/z* (%): 506 (7), 199 (100), 155 (30), 91 (75). – $C_{24}H_{26}O_8S_2$ (506.6): calcd. C 56.90, H 5.17; found C 56.64, H 5.09.

1,2-Bis(2-iodoethoxy)benzene (**11e**): 20.0 g (40 mmol) of **10e** and 33.0 g (200 mmol) of sodium iodide in 500 ml of dry acetone were heated to reflux for 24 h. After evaporation of the acetone, 800 ml of ice/water was added to the residue, the mixture was stirred for 30 min, and the solid was filtered off, dried in vacuo, and recrystallized from 900 ml of dry cyclohexane yielding 11.5 g (68%) of **11e**, m.p. 49–50°C. – IR (KBr): $\tilde{\nu}$ = 1580, 1490 cm^{-1} (arom.), 1100 (C–O). – ^1H NMR (250 MHz, $CDCl_3$): δ = 3.46 (t, J = 7 Hz, 4H), 4.30 (t, J = 7 Hz, 4H), 6.95 (s, 4H). – MS (EI, 70 eV), *m/z* (%): 418 (11), 263 (23), 155 (100), 136 (54), 105 (24). – $C_{10}H_{12}I_2O_2$ (418.0): calcd. C 28.73, H 2.89; found C 29.19, H 2.89.

(4R,5R)-4,5-Dimethyl-1,8-bis(p-tosyloxy)-3,6-dioxaoctane (**10f**): Under N_2 a solution of 4.5 g (25 mmol) of (4*R*,5*R*)-4,5-dimethyl-3,6-dioxaoctane-1,8-diol (**18**)[25] and 19.3 g (101 mmol) of *p*-toluenesulfonyl chloride in 150 ml of dry THF was cooled to 0°C, and 11.3 g (200 mmol) of powdered KOH was added in portions. After 3 h the mixture was poured on 150 ml of ice/water, the THF was distilled off in vacuo, and the residue was extracted four times with 100 ml of dichloromethane. The combined organic layers were washed twice with 100 ml of water and dried with $MgSO_4$. Evaporation of the solvent and drying of the residue in vacuo yielded 12.1 g (98%) of colorless, highly viscous analytically pure **10f**: $[\alpha]_D^{20}$ = −7.9 (*c* = 1.081, ethanol). – IR (KBr): $\tilde{\nu}$ = 1580 cm^{-1} (arom.), 1340, 1160 (SO_2), 1110, 1080 (C–O). – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.98 (d, J = 7 Hz, 6H), 2.43 (s, 6H), 3.29 (m_c, 2H), 3.63 (m_c, 4H), 4.07 (t, J = 7 Hz, 4H), 7.32 (d, J = 8.2 Hz, 4H), 7.76 (d, J = 8.2 Hz, 4H). – MS (CI, NH_3), *m/z* (%): 504 [M^+ + NH_3] (100), 332 (60). – $C_{22}H_{30}O_8S_2$ (486.6): calcd. C 54.30, H 6.21; found C 54.01, H 5.95.

(4R,5R)-1,8-Diiodo-4,5-dimethyl-3,6-dioxaoctane (**11f**): 12.1 g (24.8 mmol) of **10f** and 22.4 g (150 mmol) of sodium iodide in 350 ml of dry acetone were refluxed for 3 h. After evaporation to dryness the residue was dissolved in 200 ml of dichloromethane and 150 ml of water. The phases were separated, and the aqueous layer was extracted three times with 100 ml of dichloromethane. The combined organic layers were washed (100 ml of a diluted solution of sodium thiosulfate, 3 × 100 ml of water) and dried with $MgSO_4$. Evaporation of the solvent yielded 9.58 g (97%) of a slightly red oil. An analytically pure sample was obtained by chromatography (silica gel, ethyl acetate/*n*-hexane, 1:2): $[\alpha]_D^{25}$ = −3.32 (*c* = 1.002, ethanol). – IR (KBr): $\tilde{\nu}$ = 2940, 2840 cm^{-1} (C–H), 1100 (C–O). – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.14 (d, J = 7 Hz, 6H), 3.22 (t, J = 7 Hz, 4H), 3.44 (m_c, 2H), 3.65–3.85 (m, 4H). – MS (CI, NH_3), *m/z* (%): 416 [M^+ + NH_4] (100), 415 [M^+ + NH_3] (78). – $C_8H_{16}I_2O_2$ (398.0): calcd. C 24.12, H 4.05; found C 24.39, H 4.02.

General Procedure for the Synthesis of **1**. – *Method A: High-Dilution Cyclization:* One equivalent of 2,9-bis(2,6-dihydroxyphenyl)-1,10-phenanthroline hydrobromide (**9a**) and two equivalents of a di-*p*-toluenesulfonate **10** were dissolved in 600–800 ml of dry DMF. Under N_2 during 8.5–12 h this solution was slowly dropped into a well stirred (1000 rpm) mixture of Cs_2CO_3 or K_2CO_3 and 400–800 ml of dry DMF which was warmed to 65°C. After the addition was complete, the mixture was stirred for additional 60 min, then filtered, and the solvent was distilled off. The residue was dissolved in 400 ml of dichloromethane and 200 ml of water. The aqueous layer was extracted with dichloromethane (three times 100 ml each), and the combined organic extracts were dried with $MgSO_4$. After evaporation of the solvent the crude product was purified by chromatography.

Method B: Batch Cyclization: To a solution of one equivalent of a tetraphenol **9** and two equivalents of a diiodide **11** in 150 ml of dry DMSO, 8–10 equivalents of K_2CO_3 was added, and the mixture was stirred under N_2 for 66–96 h at 65°C. After evaporation of the solvent the product was isolated as described in method A.

6,15,33,42-Tetraoxa-43,46-diazaheptacyclo[18.12.10.4^{22,31}.0^{5,32}.0^{16,21}.0^{25,45}.0^{28,44}]hexatetraconta-1,3,5(32),16,18,20,22,24,26,28,30,43,45-tridecaene (**1a**): According to method A during 9 h a solution of 3.0 g (6.3 mmol) of **9a** and 5.71 g (12.6 mmol) of **10a** in 600 ml of dry DMF was dropped into a mixture of 8.5 g (25 mmol) of Cs_2CO_3 and 6.9 g (50 mmol) of K_2CO_3 in 800 ml of dry DMF. The workup yielded 4.63 g of a dark-red solid which was purified by chromatography on neutral alumina (eluent: dichloromethane). The resulting yellow solid was recrystallized from petroleum ether (b.p. 60–70°C) yielding 1.08 g (28%) of **1a**, m.p. 249°C. – IR (KBr): $\tilde{\nu}$ = 2915, 2840 cm^{-1} (C–H), 1585 (arom.), 1100 (C–O). – ^1H NMR (250 MHz, [D$_6$]DMSO): δ = 0.61–0.98 (br. m, 16H), 1.11–1.45 (br. m, 8H), 3.74 (m_c, 4H), 3.84–3.94 (m, 4H), 6.67 (d, J = 8 Hz, 4H), 7.30 (t, J = 8 Hz, 2H), 7.45 (d, J = 8 Hz, 2H), 7.98 (s, 2H), 8.40 (d, J = 8 Hz, 2H). – ^1H NMR (250 MHz, $CDCl_3$, 1.3 equivalents of picric acid): δ = 0.73–1.09 (br. m, 16H), 1.50 (m_c, 8H), 3.90–4.08 (m, 8H), 6.68 (d, J = 9 Hz, 4H), 7.47 (t, J = 9 Hz, 2H), 8.16 (d, J = 9 Hz, 2H), 8.45 (s, 2H), 8.99 (s, 2.6 H, picric acid), 9.10 (d, J = 9 Hz, 2H). – MS (EI, 70 eV), *m/z* (%): 616 (16), 585 (6), 40 (100). – $C_{40}H_{44}N_2O_4$ (616.8): calcd. C 77.89, H 7.19, N 4.54; found C 77.99, H 7.27, N 4.48.

X-Ray Analysis of **1a**[26] (see also Figures 2 and 5): Empirical formula $C_{40}H_{44}N_2O_4 \cdot CH_2Cl_2$, molecular mass 701.73, $a = b$ = 1766.5(2), c = 2438.7(5) pm, V = 7610(2) · 10^6 pm^3, Z = 8, d(calcd) = 1.225 g · cm^{-3}, crystal system: tetragonal, space group $I4_1/a$. – Siemens R3m/V diffractometer, Mo-K_α radiation, graphite monochromator, crystal size [mm]: 0.4 × 0.4 × 0.6, data collection mode: Wyckoff scan, theta range [deg]: 1.75–27.5, reciprocal lattice segment: $h = k$ = 0–22, l = 0–31, no. of reflections measured: 4766, no. of unique reflections: 4373, no. refl. $F > 3\sigma(F)$: 2119, line absorption coefficient: 0.06 mm^{-1}, absorption correction: ψ scan. – Solution by direct phase determination, method of refinement: full matrix LSQ. Hydrogen positions of riding model with fixed isotropic U, data-to-parameter ratio: 9.55, R, R_W: 0.147, 0.129, weighting scheme $w = 1/\sigma^2(F)$, largest difference peak 0.56 $eÅ^{-3}$, largest difference hole: 0.53 $eÅ^{-3}$, program used: Siemens SHELXTL PLUS (MicroVAX II).

6,17,23,34-Tetraoxa-47,50-diazaheptacyclo[20.12.12.4^{36,45}.0^{5,35}.0^{18,46}.0^{39,48}.0^{42,49}]pentaconta-1,3,5(35),18,20,22(46),36,38,40,42,44,47,49-tridecaene (**1b**): According to method A during 12 h a solution of 3.0 g (6.3 mmol) of **9a** and 6.06 g (12.6 mmol) of 1,10-decanediyl bis-(*p*-toluenesulfonate) (**10b**) in 600 ml of dry DMF was dropped into a mixture of 8.5 g (25 mmol) of Cs_2CO_3 and 6.9 g (50 mmol) of K_2CO_3 in 800 ml of dry DMF. Chromatography (silica gel, dichloromethane/ethanol, 50:1) and recrystallization from petroleum ether (b.p. 60–70°C) yielded 810 mg (19%) of a slightly yellow solid, m.p. 186°C. – IR (KBr): $\tilde{\nu}$ = 2910, 2840 cm^{-1} (C–H), 1586 (arom.), 1100 (C–O). – ^1H NMR (250 MHz, [D$_6$]DMSO): δ = 0.46 (br. s, 8H), 0.61–0.96 (br. m, 16H), 1.30

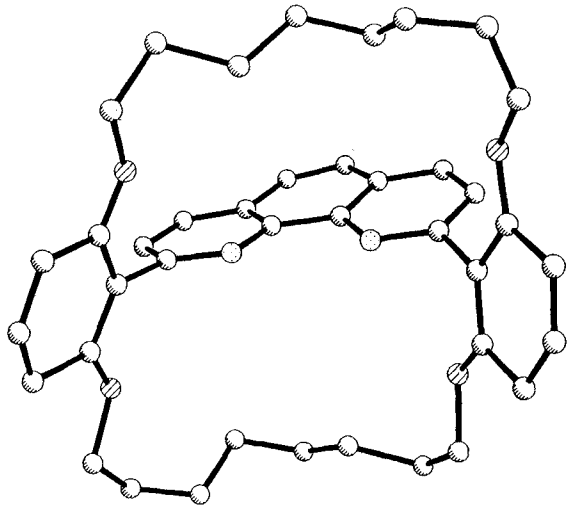

Figure 5. X-ray structure of **1a**

(br. m_c, 8H), 3.81 (m_c, 8H), 6.72 (d, J = 8 Hz, 4H), 7.30 (t, J = 8 Hz, 2H), 7.50 (d, J = 8 Hz, 2H), 7.96 (s, 2H), 8.39 (d, J = 8 Hz, 2H). – ^{1}H NMR (250 MHz, $CDCl_3$, 3 equivalents of picric acid): δ = 0.56–1.09 (br. m, 24H), 1.47–1.70 (m, 8H), 4.06 (m_c, 8H), 6.74 (d, J = 9 Hz, 4H), 7.50 (t, J = 9 Hz, 2H), 8.35 (s, 2H), 8.45 (d, J = 9 Hz, 2H), 8.96 (d, J = 9 Hz, 2H), 9.07 (s, 6H, picric acid). – MS (EI, 70 eV), *m/z* (%): 672 (100), 629 (14), 559 (28). – $C_{40}H_{44}N_2O_4$ (672.9): calcd. C 78.53, H 7.78, N 4.16; found C 78.41, H 7.93, N 4.20.

6,9,12,15,33,36,39,42-Octaoxa-43,46-diazaheptacyclo-[18.12.10.4^{22,31}.0^{5,32}.0^{16,21}.0^{25,45}.0^{28,44}]hexatetraconta-1,3,5(32),16,18,20,22,24,26,28,30,43,45-tridecaene (**1c**): Method A: ref.[3]. – Method B: Under N_2 1.62 g (3.40 mmol) of **9a** and 2.74 g (6.90 mmol) of 1,8-diiodo-3,6-dioxaoctane (**11c**) were dissolved in 100 ml of dry DMSO. Then 7.6 g (55 mmol) of powdered K_2CO_3 was added to the clear yellow solution which was subsequently heated to 65°C for 94 h. The workup[3] yielded 510 mg (24%) of **1c**.

X-Ray Analysis of **1c**[26] (see also Figures 3 and 6): Empirical formula $C_{36}H_{36}N_2O_8 \cdot C_3H_6O$, molecular mass 682.75, temp. 100 K, wavelength 1.54178 Å, crystal system: monoclinic, space group $P2_1/n$, No. 14, a = 1674.1(2), b = 2444.4(2), c = 3327.7(5) pm, β = 90.92(1)°, V = 13616(3) · 10^6 pm^3, Z = 16, d_{calcd} = 1.332 g · cm^{-3}. – Enraf Nonius CAD4 diffractometer, Cu-K_α radiation, graphite monochromator, crystal size [mm]: 0.35 × 0.70 × 0.39, data collection mode: ω-2Θ scan, theta range [deg]: 2.24–75.08, index ranges: $-20 \le h \le 20$, $0 \le k \le 30$, $0 \le l \le 41$, reflections collected: 28507, independent reflections: 28006 (R_{int} = 0.0335), refl. observed [$I > 2\sigma(I)$]: 22490, F(000): 5792, no absorption correction applied. – Solution by direct phase determination, method of refinement: full-matrix block least-squares on F^2. Hydrogen positions were calculated and not refined, data-to-parameter ratio: 12.5, R indices [$I > 2\sigma(I)$]: $R1$ = 0.0685, $wR2$ = 0.2014, R indices (all data): $R1$ = 0.0841, $wR2$ = 0.2136, extinction coefficient: 0.00007(2), largest diff. peak and hole 1.159 and −0.734 eÅ^{-3}, programs used: MOLEN (Enraf-Nonius, 1990), SHELXS-86 (Sheldrick, 1990), SHELXL-93 (Sheldrick, 1993).

6,9,12,15,18,24,27,30,33,36-Decaoxa-49,52-diazaheptacyclo-[21.13.12.4^{38,47}.0^{5,37}.0^{19,48}.0^{41,50}.0^{44,51}]dopentaconta-1,3,5(37),19,21,23(48),38,40,42,44,46,49,51-tridecaene (**1d**): According to method B 2.65 g (5.5 mmol) of **9a**, 4.87 g (11.0 mmol) of 1,11-diiodo-3,6,9-trioxaundecane (**11d**), and 11.4 g (83 mmol) of K_2CO_3 were heated in 100 ml of dry DMSO to 65°C for 66 h. The workup yielded 2.07 g of a dark-brown, viscous oil which was purified by chromatography (silica gel, methanol) giving a slightly yellow solid which was recrystallized from acetone/petroleum ether (b.p. 30–50°C). Yield: 430 mg (11%) of **1d**, m.p. 200–204°C. Even after 5 d in a vacuum-drying oven at 20 Torr and 60–80°C, the compound still contained water. – IR (KBr): ṽ = 1588, 1460, 1450 cm^{-1} (arom.), 1245, 1098 (C–O). – ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 2.6–2.7 (m, 4H), 2.8–2.9 (m, 4H), 3.06 (t, J = 6 Hz, 8H), 3.5–3.7 (m, 4H), 3.7–3.8 (m, 4H), 3.95 (s, ca. 4H, H_2O), 4.2–4.3 (m, 4H), 6.73 (d, J = 8 Hz, 4H), 7.35 (t, J = 8 Hz, 2H), 7.78 (d, J = 8 Hz, 2H), 7.82 (s, 2H), 8.39 (d, J = 8 Hz, 2H). – ^{1}H NMR ($CDCl_3$, 250 MHz, 1 equivalent of picric acid): δ = 2.78–2.89 (m, 4H), 3.02–3.21 (m, 12H), 3.49–3.60 (m, 4H), 3.67–3.77 (m, 4H), 4.06–4.25 (m, 8H), 6.72 (d, J = 8 Hz, 4H), 7.46 (t, J = 8 Hz, 2H), 8.29 (d, J = 8 Hz, 2H), 8.35 (s, 2H), 9.02 (d, J = 8 Hz, 2H), 9.06 (s, 2H, picric acid). – MS (EI, 70 eV), *m/z* (%): 713 (49), 712 (100), 711 (21), 682 (16), 594 (38), 593 (39), 566 (28). – $C_{40}H_{44}N_2O_{10} \cdot 2\ H_2O$ (712.8 + 36.0): calcd. C 64.16, H 6.45, N 3.74; found C 63.89, H 6.01, N 3.48.

6,9,16,19,25,28,35,38-Octaoxa-51,54-diazanonacyclo-[22.14.12.4^{40,49}.0^{5,39}.0^{10,15}.0^{20,50}.0^{29,34}.0^{43,52}.0^{46,53}]tetrapentaconta-1,3,5(39),10,12,14,20,22,24(50),29,31,33,40,42,44,46,48,51,53-nonadecaene (**1e**)

Method A: According to method A, during 10 h a solution of 3.0 g (6.3 mmol) of **9a** and 6.3 g (12.6 mmol) of 1,2-bis[2-(*p*-tolylsulfonyloxy)ethoxy]benzene (**10e**) in 600 ml of dry DMF was dropped into a mixture of 8.2 g (25 mmol) of Cs_2CO_3 and 6.9 g (50 mmol) of K_2CO_3 in 800 ml of dry DMF. Workup according to method A and chromatography (silica gel, methanol) yielded a slightly yellow solid which was recrystallized from toluene. Yield: 120 mg (2.7%) of **1e**, m.p. 326°C. – IR (KBr): ṽ = 2905, 2880 cm^{-1} (C–H), 1583, 1490 (arom.), 1245, 1105 (C–O). – ^{1}H NMR (250 MHz, [D$_6$]DMSO): δ = 3.79–4.24 (br. m, 16H), 6.57 (m_c, 8H), 6.81 (d, J = 8 Hz, 4H), 7.37 (t, J = 8 Hz, 2H), 7.49 (d, J = 8 Hz, 2H), 7.92 (s, 2H), 8.38 (d, J = 8 Hz, 2H). – ^{1}H NMR (250 MHz, $CDCl_3$, 2 equivalents of picric acid): δ = 3.81–4.47 (m, ca. 16H), 5.93 (m_c, 8H), 6.86 (d, J = 9 Hz, 4H), 7.56 (t, J = 9 Hz, 2H), 8.12 (s, 2H), 8.27 (d, J = 9 Hz, 2H), 8.95 (d, J = 9 Hz, 2H), 9.08 (s, 4H, picric acid). – MS (EI, 70 eV), *m/z* (%): 720 (100), 584 (73), 449 (60), 422 (46), 147 (60). – $C_{44}H_{36}N_2O_8$ (720.8): calcd. C 73.32, H 5.03, N 3.89; found C 73.14, H 5.14, N 3.76.

Method B: Under N_2 3.0 g (6.3 mmol) of **9a** and 5.3 g (12.6 mmol) of 1,2-bis(2-iodoethoxy)benzene (**11e**) were dissolved in 150 ml of dry DMSO. 13.0 g (94.0 mmol) of K_2CO_3 was added to the clear solution which then was heated to 65°C for 96 h. The workup yielded a residue which was extracted twice with 100 ml of hot methanol (TLC control). The solvent was evaporated, and the crude product was purified by two chromatographies (1. silica gel, methanol; 2. silica gel, dichloromethane/ethanol, 20:1). Yield: 210 mg (5%) of **1e**.

(10R,11R,37R,38R)-10,11,37,38-Tetramethyl-6,9,12,15,33,36,39,42-octaoxa-43,46-diazaheptacyclo[18.12.10.4^{22,31}.0^{5,32}.0^{16,21}.0^{25,45}.0^{28,44}]hexatetraconta-1,3,5(32),16,18,20,22,24,26,28,30,43,45-tridecaene (**1f**): Under N_2 3.0 g (6.3 mmol) of **9a**, 5.0 g (12.6 mmol) of (4*R*,5*R*)-1,8-diiodo-4,5-dimethyl-3,6-dioxaoctane (**11f**), and 18.0 g (0.10 mol) of K_2CO_3 in 150 ml of dry DMSO were heated to 65°C for 90 h. The workup yielded 4.31 g of a dark-red viscous oil which was purified by chromatography (silica gel, methanol). The resulting slightly red solid was recrystallized from ca. 800 ml of petroleum ether (b.p. 60–70°C). Yield: 570 mg (13%) of **1f**, m.p. 171–172°C. – IR (KBr): ṽ = 3400 cm^{-1} (br., OH), 2945, 2905, 2850 (C–H), 1580, 1440 (arom.), 1245, 1100

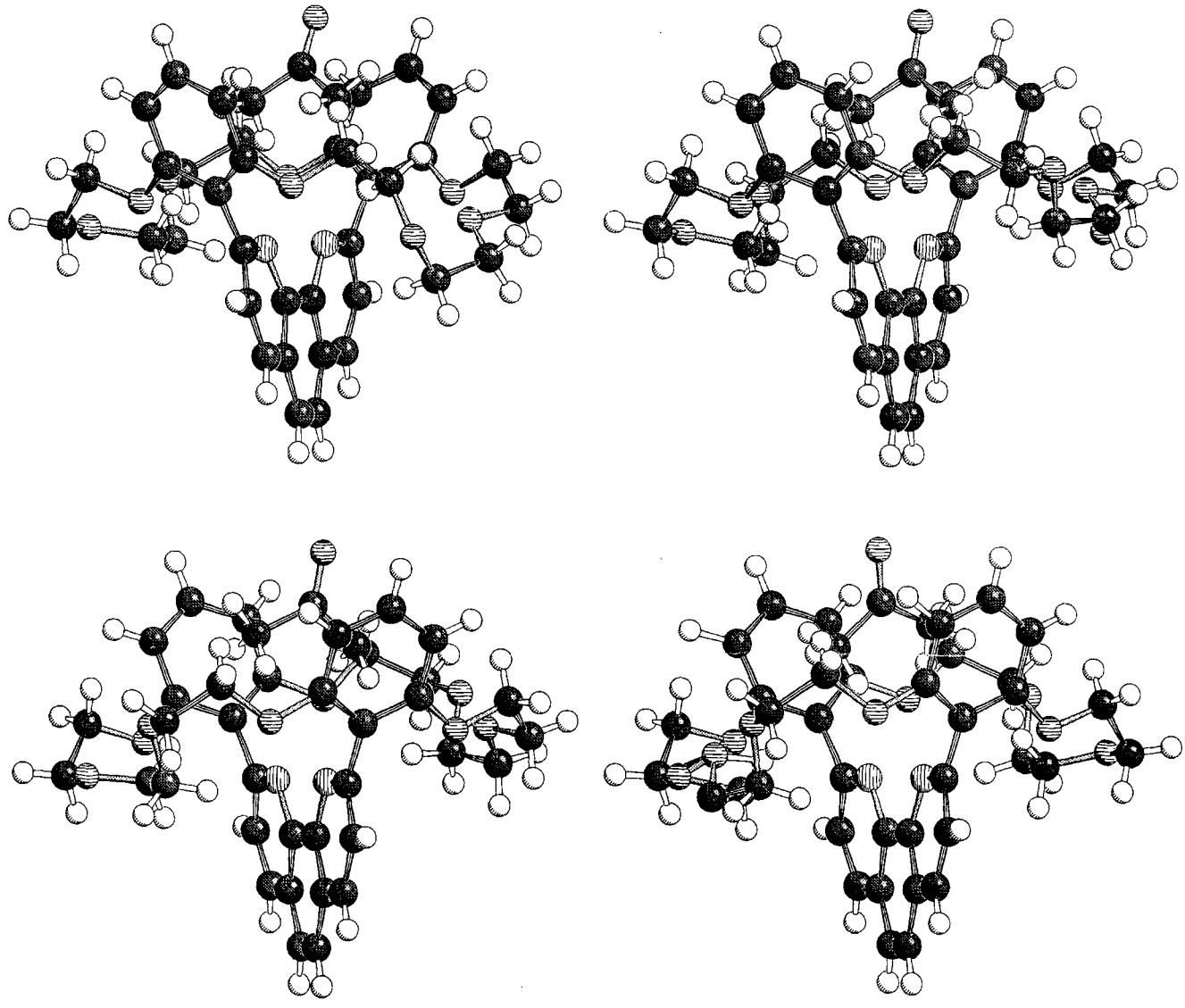

Figure 6. X-ray structure of the four conformers of **1c**

(C–O). – ^{1}H NMR (250 MHz, [D$_6$]DMSO): δ = 0.04 (d, *J* = 6 Hz, 6H), 0.45 (d, *J* = 6 Hz, 6H), 2.74 (m$_c$, 4H), 3.00–3.19 (m, 4H), 3.36 (s, H$_2$O), 3.46–3.62 (br. m, 4H), 3.80–4.06 (br. m, 8H), 6.66, 6.68 (2 d, *J* = 8 Hz, 4H), 7.31 (t, *J* = 8 Hz, 2H), 7.46 (d, *J* = 8 Hz, 2H), 7.91 (s, 2H), 8.38 (d, *J* = 8 Hz, 2H). – ^{1}H NMR (250 MHz, CDCl$_3$, 5.1 equivalents of picric acid): δ = –0.25 (d, *J* = 6.8 Hz, 6H), 0.9 (d, *J* = 6.8 Hz, 6H), 2.76 (m$_c$, 4H), 3.13–3.31 (m, 4H), 3.63 (br. t, *J* = 9 Hz, 4H), 3.81–4.18 (m, 8H), 6.09 (br. s, H$_2$O), 6.57 (d, *J* = 8 Hz, 2H), 6.61 (d, *J* = 8 Hz, 2H), 7.38 (t, *J* = 9 Hz, 2H), 8.51 (d, *J* = 9 Hz, 2H), 8.99 (s, 2H), 9.15 (s, 10.2H, picric acid), 9.34 (d, *J* = 9 Hz, 2H). – MS (EI, 70 eV), *m/z* (%): 680 (39), 565 (23), 564 (81). – $[\alpha]_D^{22}$ = +6.26 (*c* = 1.105 in ethanol). – $C_{40}H_{44}N_2O_8 \cdot 0.5\ H_2O$ (680.8 + 9.0): calcd. C 69.64, H 6.57, N 4.06; found C 69.62, H 6.68, N 3.96.

24,29-Bis[4-(1,1-dimethylethyl)phenoxy]-6,9,12,15,33,36,39,42-octaoxa-43,46-diazaheptacyclo[18.12.10.4^{22,31}.0^{5,32}.0^{16,21}.0^{25,45}.0^{28,44}]hexatetraconta-1,3,5(32),16,18,20,22,24,26,28,30,43,45-tridecaene (**1g**): Under N$_2$ 1.7 g (2.2 mmol) of **9b**, 1.92 g (4.8 mmol) of 1,8-diiodo-3,8-dioxaoctane (**11c**), and 7.5 g (54 mmol) of K$_2$CO$_3$ in 100 ml of dry DMSO were heated to 65°C for 75 h. After evaporation of the solvent the residue was extracted three times with 250 ml of boiling methanol. After evaporation of the solvent from the combined extracts the residue was extracted three times with 350 ml of boiling petroleum ether (b.p. 60–70°C).

Table 4. Elemental analyses for transition metal nonafluorobutanesulfonates

Metal ion	formula (molecular weight)	yield (%)	m. p. (°C)	C (calcd) (found)	H	N	solvent content
Mn^{2+}	$C_8F_{18}MnO_6S_2 \cdot 2\ H_2O$ 653.13 + 36.02	82	>330	13.94 13.91	0.58 0.41	- 0.00	2 H_2O
Fe^{2+}	$C_8F_{18}FeO_6S_2$ 654.03	2 [a]	>350	14.69 14.52	- 0.00	- 0.00	-
Co^{2+}	$C_8F_{18}CoO_6S_2 \cdot 3\ H_2O$ 657.12 + 54.03	79	>330	13.51 13.37	0.84 0.65	- 0.00	3 H_2O
Ni^{2+}	$C_8F_{18}NiO_6S_2 \cdot 4\ H_2O$ 656.90 + 72.04	67	>350	13.18 13.08	1.10 0.95	- 0.00	4 H_2O
Cu^{+}	$C_4F_9CuO_3S \cdot CH_3CN$ 362.64 + 41.05	71	oil	17.85 18.00	0.74 1.23	3.46 3.31	1 CH_3CN

[a] Non-optimized.

Evaporation of the solvent from the combined extracts and drying of the residue in vacuo yielded 660 mg of a slightly yellow solid which was purified by chromatography (silica gel, dichloromethane/ethanol, 10:1). Yield: 280 mg (14%) of **1g**, m.p. 186°C. – IR (KBr): $\tilde{\nu}$ = 2930, 2825 cm^{-1} (C–H), 1575, 1560, 1460 (arom.), 1208, 1095 (C–O). – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.36 (s, 18H), 1.62 (br. s, H_2O), 2.68–2.80 (m, 4H), 3.27–3.42 (m, 8H), 3.76–3.87 (m, 4H), 3.94–4.15 (m, 8H), 6.50 (d, *J* = 9 Hz, 4H), 6.90 (s, 2H), 7.12–7.25 [m, with d at 7.16 (*J* = 9 Hz), and t at 7.20 (*J* = 9 Hz), 6H], 7.44 (d, *J* = 9 Hz, 4H), 8.41 (s, 2H). – ^1H NMR (250 MHz, $CDCl_3$, 6 equivalents of picric acid): δ = 1.36 (s, 18H), 3.03 (br. m_c, 8H), 3.39 (br. m_c, 4H), 3.64–3.77 (m, 4H), 3.91–4.03 (m, 4H), 4.13 (br. m_c, 4H), 5.16 (H_2O), 6.58 (d, *J* = 9 Hz, 4H), 7.10 (s, 2H), 7.21 (d, *J* = 9 Hz, 4H), 7.36 (t, *J* = 9 Hz, 2H), 7.54 (d, *J* = 9 Hz, 4H), 8.64 (s, 2H), 9.12 (s, picric acid, ca. 12H). – ^1H NMR (250 MHz, [D$_6$]DMSO): δ = 1.31 (s, 18H), 2.60–2.71 (m, 4H), 2.84–2.96 (m, 4H), 3.11–3.24 (br. m, ca. 4H), 3.33 (br. s, H_2O), 3.54–3.65 (br. m, 4H), 3.84–4.02 (br. m, 8H), 6.64 (d, *J* = 9 Hz, 4H), 6.69 (s, 2H), 7.20 (d, *J* = 9 Hz, 4H), 7.29 (t, *J* = 9 Hz, 2H), 7.53 (d, *J* = 9 Hz, 4H), 8.33 (s, 2H). – MS (EI, 70 eV), *m/z* (%): 921 (8), 832 (13). – $C_{56}H_{60}N_2O_{10} \cdot 2\,H_2O$ (921.1 + 36.0): calcd. C 70.27, H 6.73, N 2.92; found C 70.17, H 6.30, N 2.77.

Titration of 1,10-Phenanthrolines in Ethanol with Acids: The general procedure for the determination of the relative basicity of a concave base by photometric titration in ethanol has already been described[3]. Since the basicity of many concave 1,10-phenanthrolines **1** and their non-macrocyclic analogues **8** which usually can be measured against thymol blue exceeded the range of log *K*[3], bromophenol blue had to be used as indicator. Its pK_a in ethanol is 3.4 pK_a values larger than that of thymol blue[18]. Therefore, higher basicities can be determined by measuring the equilibrium constants *K'* of the reaction of bromophenol blue with bases. Unfortunately, during the titrations with bromophenol blue the calculated basicities did not converge asymptotically to a final value as in the case of thymol blue. Therefore the determined basicities must have a larger error than those determined by titration against thymol blue.

Determination of Association Constants K_{Ass} for Complexes **1** · M^{n+} *between Transition Metal Salts and Concave 1,10-Phenanthrolines* **1** *in Acetonitrile:* To 2 ml of a 45 μM solution of the concave 1,10-phenanthroline **1** in dry acetonitrile a 2 mM solution of the transition metal salt in dry acetonitrile was added in 9-μl aliquots. The titration was followed by UV, and from a shoulder at 350 nm the association constants were calculated. With concave 1,10-phenanthrolines **1**, isosbestic points at 270–290 nm were observed in contrast to 2,9-dimethyl-1,10-phenanthroline (neocuproine) and the noncyclic 1,10-phenanthroline **8**. Due to the detection limits and errors (<10%), association constants larger than $10^{6.5}$ could not be determined accurately. Therefore, log K_{Ass} is then listed as >6.5 in Table 3. When very strong binding occurred (i.e. the titration "curve" showed a straight line up to 1:1 stoichiometry) log K_{Ass} is listed as ≫ 7.

Generation of Transition Metal Nonafluorobutanesulfonates: To a solution of 1.5–4 mmol of nonafluorobutanesulfonic acid (prepared by reaction of potassium nonafluorobutanesulfonate with a conc. aqueous solution of hydrogen chloride) in 50–80 ml of dry acetonitrile a metal carbonate was added in a 2:1 excess. After refluxing for 4 h the mixture was cooled down, filtered, and the solvent was distilled off. The aqueous solution of the residue was washed three times with diethyl ether. Then the water was evaporated. The solid residue was recrystallized from acetone/dichloromethane and characterized by IR and microanalyses (see Table 4). The metal could be analyzed qualitatively according to standard methods[27]. The IR spectra were identical. Typical IR (nickel salt, KBr): $\tilde{\nu}$ = 3400 cm^{-1} (H_2O), 1605, 1340, 1170 (S=O), 1240, 1050 (C–F).

☆ Dedicated to Prof. *C. Rüchardt* on the occasion of his 65th birthday.

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