Synthesis and Coordination Chemistry of Lower Rim Cavitand Ligands

Laura Pirondini,[a] Davide Bonifazi,[a] Edoardo Menozzi,[a] Elina Wegelius,[b] Kari Rissanen,[b] Chiara Massera,[c] and Enrico Dalcanale*[a]

Keywords: Cavitands / Coordination chemistry / Self-assembly

Four new cavitand ligands, modified at the lower rim with cyano and pyridyl functional groups, have been synthesized and their coordinative behaviour toward transition metal ions has been explored. The outcome of the self-assembly of these compounds in the presence of different metal precursors is biased toward the formation of intramolecular complexes, independent of the coordination geometry imposed by the metal centre. Dimeric species have been obtained by decreasing the number of ligands at the lower rim from four to two and by using a metal precursor capable of exchanging four ligands simultaneously.

Introduction

The use of transition metal ions to direct the self-assembly of supramolecular architectures has become a rapidly growing discipline.[1] The rich coordination chemistry of transition metals allows fine tuning of the self-assembly motifs in terms of coordination geometries, directionality and strength of bond energies. One possible means to steer the self-assembly towards the formation of the desired supramolecular structure is by controlling the coordinative behaviour of the molecular components, through preorganization of the ligands.

Among the several building blocks employed, resorcinarene-based cavitands have proven to be particularly interesting as multidentate ligands,[2] due to the presence of rigidly preorganized cavities of molecular dimensions and the possibility of introducing many different ligand moieties, at both the upper[3] and lower rims.[4] The use of these compounds, properly functionalized at the upper rim, has resulted in the formation of coordination cages[5] and metal complexes with peculiar anion complexation properties.[6] In contrast, the coordination chemistry at the lower rim has not so far been explored.

In this paper we report the syntheses and coordinative behaviour toward transition metal ions of four new lower rim cavitand ligands, and derive the structural and conformational features that direct the self-assembly toward the selective formation of various monomeric, dimeric or oligomeric complexes. Dimeric species are particularly attractive as building blocks for the formation of coordination polymers.[7]

[a] Dipartimento di Chimica Organica e Industriale, Università di Parma,
43100 Parma, Italy
Fax: (internat.) + 39-0521/905472
E-mail: enrico.dalcanale@unipr.it
[b] Department of Chemistry, University of Jyväskylä,
P. O. Box 35, 40351 Jyväskylä, Finland
[c] Dipartimento di Chimica Generale ed Inorganica, Chimica Analitica e Chimica Fisica, Università di Parma,
43100 Parma, Italy

Results and Discussion

Synthesis of the Cavitand Ligands

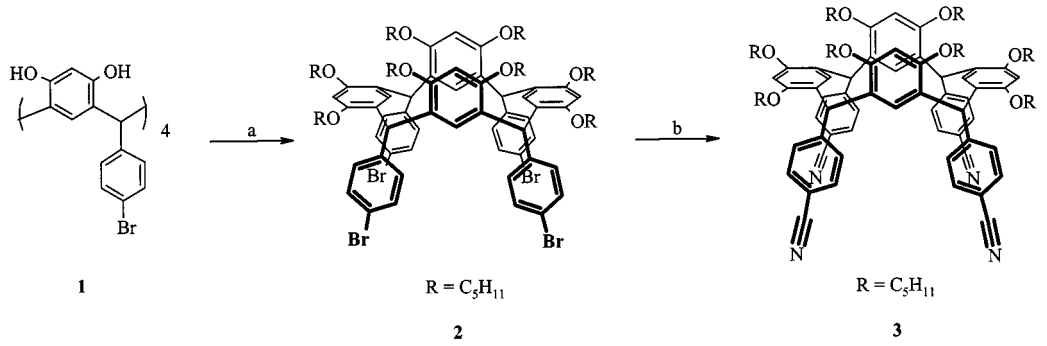
The preparation of tetracyanophenyl-resorcin[4]arene **3** is summarized in Scheme 1. The cyclic tetramer **1** was prepared from resorcinol and 4-bromobenzaldehyde according to a reported procedure.[8]

Alkylation of the hydroxy groups was carried out, in order to improve the solubility of the resorcin[4]arene and to protect the phenol groups in the subsequent nitrile insertion step. Octaalkylated resorcin[4]arene **2** was obtained in 29% isolated yield by treatment of **1** with 1-bromopentane in dry DMF at 60 °C in the presence of K_2CO_3. Tetrakis(4-bromophenyl)resorcin[4]arene **2** was converted in 46% yield into the corresponding tetracyano derivative **3** by the Rosenmund/von Braun reaction, heating **2** with CuCN in NMP at 200 °C.

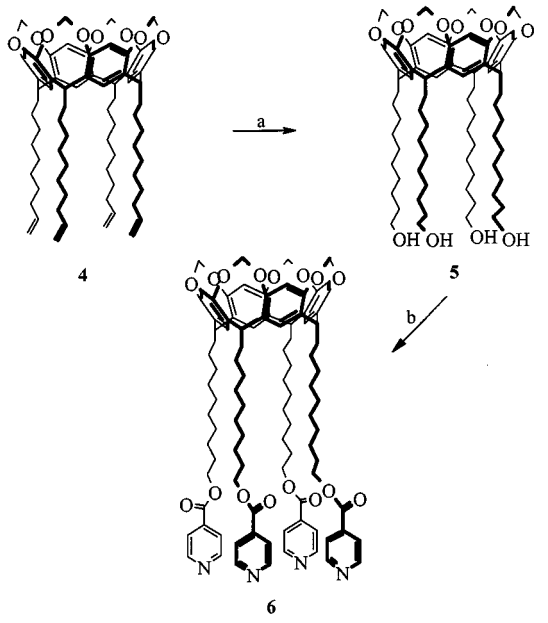
Introduction of pyridine moieties at the lower rim of resorcin[4]arenes was accomplished by acylation of ω-hydroxyalkyl cavitands with isonicotinoyl chloride hydrochloride (Scheme 2 and Scheme 3). To achieve such hydroxy-footed cavitands **5** and **8**, two different synthetic routes were pursued. In the first case, we started from cavitand **4** with ω-decenyl tails;[9] hydroboration of the terminal double bonds was performed using BH_3·THF in THF. The addition was carried out at room temperature, followed by in situ oxidation with $NaOH/H_2O_2$ to give tetrahydroxy cavitand **5** in 94% yield. The reaction was completely regioselective, as expected. The four hydroxy groups of cavitand **5** were then acylated with isonicotinoyl chloride hydrochloride in DMF in the presence of NEt_3, giving tetraisonicotinate cavitand **6** in 95% yield.

The synthesis of propanol-footed cavitand **8** was carried out in a totally different manner from the decanol-footed one: Dodecol **7** was prepared directly in 69% yield from 2-methylresorcinol and 2,3-dihydrofuran.[10] In the subsequent step, bridging of the phenol OH group with CH_2BrCl was accomplished in improved yields by applying the method reported by Kaifer:[11] The reaction was con-

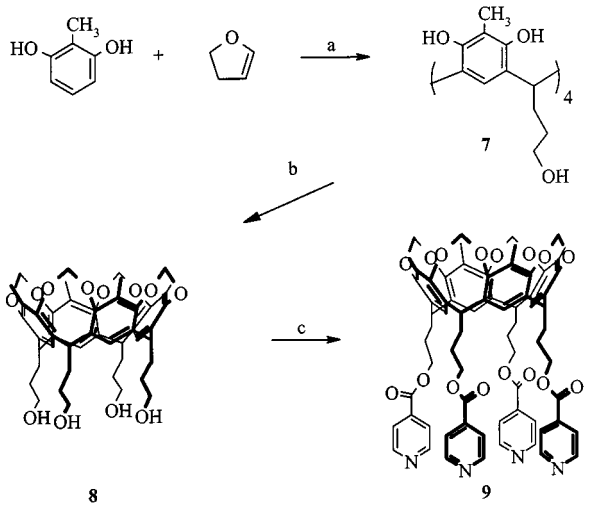
  1434−193X/01/0612−2311 $ 17.50+.50/0



Scheme 1. Synthesis of tetrakis(4-cyanophenyl)resorcin[4]arene octapentyl ether **3**: (a) 1-bromopentane, K_2CO_3, 60 °C, DMF; (b) CuCN, 200 °C, NMP; $FeCl_3$, H_2O/HCl (12 N) 2:1, 90 °C



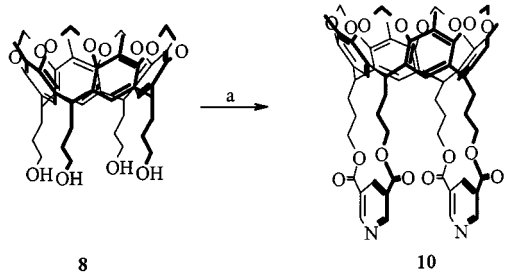
Scheme 2. Synthesis of ω-isonicotinoyldecyl cavitand **6**: (a) BH_3·THF, THF; NaOH aq./H_2O_2, 50 °C; (b) isonicotinoyl chloride hydrochloride, NH_3, DMF, room temp. for 2 d, 70 °C for 8 h



Scheme 3. Synthesis of the ω-butylisonicotinate cavitand **9**: (a) CH_3OH/HCl, 50 °C for 7 d; (b) CH_2BrCl, K_2CO_3, 88 °C, DMF; (c) isonicotinoyl chloride hydrochloride, pyridine, 100 °C

ducted in a sealed tube, enabling heating at temperatures (88 °C) higher than the low normal boiling point of CH_2BrCl (68 °C). This procedure resulted in a much shorter reaction time (3 h) and an increased yield of cavitand **8** (86%), compared to the standard procedure in an open vessel. The isonicotinic groups were introduced by adding cavitand **8** to a solution of isonicotinoyl chloride hydrochloride in pyridine at 100 °C; quenching with water after only 3 h afforded tetrapyridyl cavitand **9** in 67% yield.

The same synthetic method was applied to afford ligand **10**, with only two pyridyl groups at the lower rim (Scheme 4). In this case, 3,5-bis(chlorocarbonyl)pyridine was prepared immediately before use, by treatment of 3,5-pyridinedicarboxylic acid with $SOCl_2$ (8.5 mL) at 50 °C; a few drops of DMF were added to catalyse the reaction. After solvent removal, pyridine was added, the solution was heated at 100 °C for 30 min, and then cavitand **8** was added. The reaction resulted in the formation of **10** in 21% isolated yield, after purification by column chromatography.



Scheme 4. Synthesis of bis(ω-dinicotinoylpropyl)methylene-bridged cavitand **10**: (a) 3,5-bis(chlorocarbonyl)pyridine, pyridine, 100 °C

Complexation Properties of the Cavitand Ligands

Tetracyanophenylresorcin[4]arene **3** was designed and synthesized in order to study the formation of linear Ag^I complexes at the lower rim: Either dimers or polymers might be formed through coordination of the nitrile moieties to the metal centre.[12] Two different experiments were carried out, adding $AgCF_3SO_3$ and $AgBF_4$, respectively, to toluene solutions of resorcin[4]arene **3** in 2:1 molar ratios. The metal-induced self-assembly was monitored by ^1H NMR spectroscopy and ESI-MS. The first technique showed a broadening and a downfield shift

(0.22−0.32 ppm) of the signals of the protons *ortho* to the cyano groups, due to coordination to the metal centre. ESI-MS showed $[\mathbf{3}\cdot Ag]^+$ and $[\mathbf{3}\cdot 2AgX - X]^+$ peaks (X^- = $CF_3SO_3^-$ and BF_4^-), attributable to fragmentation of an oligomeric form. The same peaks could result from doubly charged $[2(\mathbf{3})\cdot 2AgX - 2X]^{2+}$ and $[2(\mathbf{3})\cdot 4AgX - 2X]^{2+}$ ions, which would fit better with the hypothesis of dimer formation, but the isotopic pattern of each ion shows a 1 a.m.u. separation between each peak, compatible only with singly charged ions. Evidence of polymeric assembly was obtained from a preliminary X-ray crystal structure of **11** in benzene.[13] Despite the high *R* factor found, the crystal structure was sufficiently resolved to rule out dimer formation and to support the polymeric assembly. As shown in Figure 1, the aromatic groups at the lower rim are not parallel to each other, as required for dimerization, but slightly tilted, favouring polymeric self-assembly to give **11** and **12** (Scheme 5).

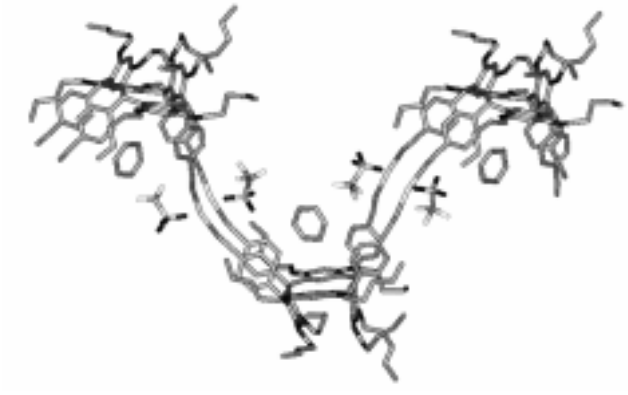
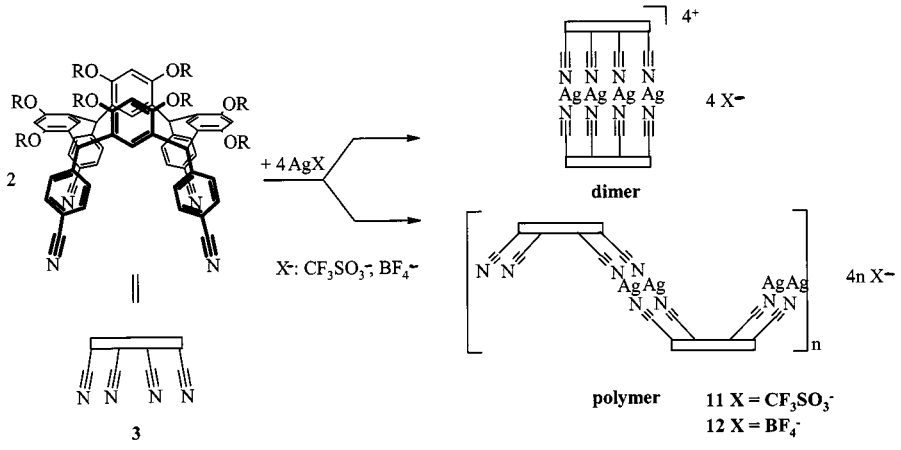


Figure 1. Preliminary X-ray crystal structure of **11** in benzene

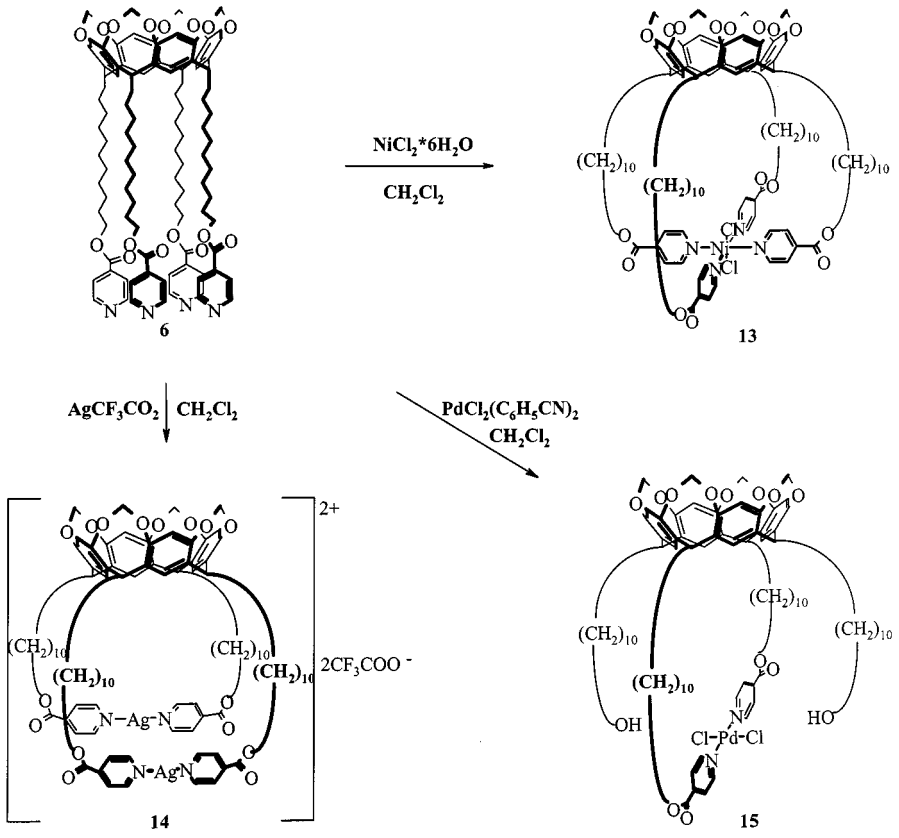
Each of the clefts formed by this polymeric assembly includes a solvent benzene molecule and two $CF_3SO_3^-$ counter ions. The tilting of the aromatic substituents therefore drives the self-assembly toward the formation of polymeric structures.

Since (i) the direct introduction of aromatic groups at the lower rim did not result in the desired dimerization and (ii) CN−M interaction are coordinatively weak, pyridine groups were introduced in place of nitrile groups as ligating groups at the lower rim. Cavitand **6**, with ω-decylisonicotinic tails, was treated with three different metal precursors: (1) $NiCl_2\cdot 6H_2O$, (2) $AgCF_3CO_2$, and (3) $PdCl_2(C_6H_5CN)_2$ (Scheme 6). In the first case, a yellow precipitate was formed on slow addition of $NiCl_2$ to a solution of cavitand **6** in a 1:1 molar ratio.[14] MS experiments indicated the formation of an intramolecular 1:1 complex: In fact, CI-MS showed the $[MH^+]$ peak as the dominant ion, while $[\mathbf{6}\cdot NiCl_2 - Cl^-]^+$ and $[\mathbf{6}\cdot NiCl_2 - 2\,Cl^-]^{2+}$ ions were observed in the ESI-MS spectrum. The product was also characterized by ^1H NMR, but in this case the *o*-Py and *m*-Py peaks were not detectable because of the paramagnetism of the complex, while the remaining part of the spectrum was highly symmetric, showing the equivalence of the four ligand tethers and the C_{4v} symmetry of the cavitand scaffold. The collected data are consistent with the formation of octahedral complex **13**, with the four pyridine rings of **6** coordinated to a single Ni^{II} ion, leaving the two chloride ions in axial positions. Another intramolecular complex was formed by addition of 2 equiv. of $AgCF_3CO_2$ to a solution of cavitand **6**. As in the previous case, ESI-MS showed a prominent peak of a singly charged ion at *m*/*z* 1913, attributable to $[\mathbf{6}\cdot 2AgCF_3CO_2 - CF_3CO_2^-]^+$ ion. Both NMR and MS data are consistent with the formation of the intramolecular dinuclear complex **14**, in which each pair of adjacent pyridines coordinates in a linear fashion to a silver ion. Complexation of $PdCl_2(C_6H_5CN_2)_2$ with **6** resulted in the formation of an intramolecular monomeric complex, possessing peculiar catalytic properties. The ^1H NMR spectrum of this complex exhibits a 0.26 ppm downfield shift of all the *o*-Py peaks and a 50% reduction in the integrals relative to both the *o*-Py and *m*-Py peaks; moreover a new set of signals − indicative of the presence of two CH_2OH groups in AC positions (C_{2v} symmetry) − appeared.

ESI-MS data show a prominent peak of a singly charged ion at *m*/*z* 1512, associated with the formation of an intramolecular Pd^{II} complex and the subsequent hydrolysis of two isonicotinic esters groups. This behaviour can be explained by assuming that the complex formed through *trans* coor-



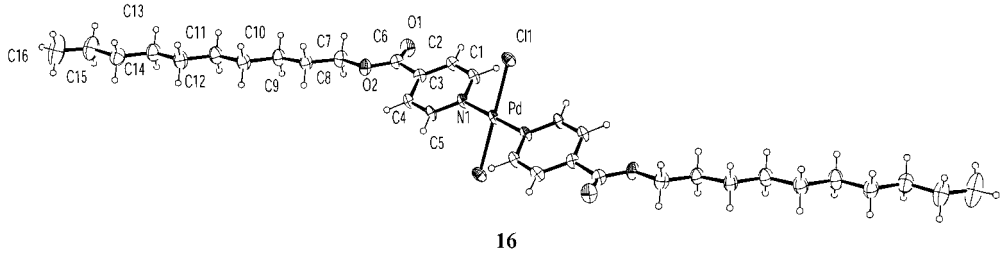
Scheme 5. Dimer versus polymer formation by coordination of nitrile moieties of cavitand **3** to the metal centre



Scheme 6. Coordinative behaviour of cavitand **6** in the presence of different metal precursors: $NiCl_2{\cdot}6H_2O$, $AgCF_3CO_2$, and $PdCl_2(C_6H_5CN)_2$

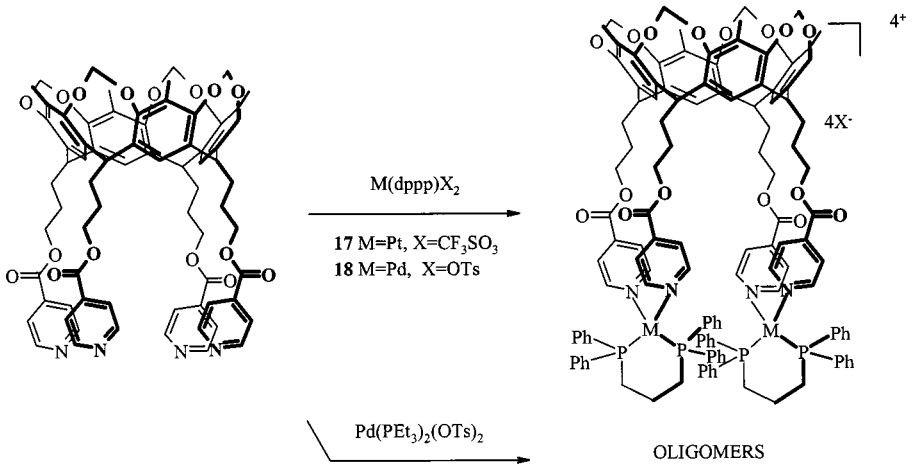
dination of two pyridine rings to $Pd^{II}Cl_2$ catalyses the hydrolysis of the other two, opposite isonicotinic esters in the presence of traces of water, giving complex **15**. A control experiment was carried out to confirm this hypothesis: Decyl isonicotinate was added to a solution of $PdCl_2(C_6H_5CN)_2$ in different ratios (1:1, 1:2, and 1:3) in the presence of a trace of water. In all three cases, ^1H NMR showed a downfield shift of the Py peaks as a consequence of coordination to the metal centre; formation of isonicotinic acid − as evidence of the catalytic activity of the Pd^{II} bis(isonicotinate) complex **16** in the hydrolysis of isonicotinate − was detected only after addition of at least 3 equiv. of the ester. Since the ^1H NMR spectrum of **15** is consistent with an AC-disubstituted isomer and the crystal structure of model complex **16** (Figure 2, ORTEP view[15]) clearly indicates a preference towards *trans* coordination in isonicotinic ligands, the most probable structure for **15** is the *trans*-AC-disubstituted complex shown in Scheme 6.

From all these experiments we deduced that ω-isonicotinoyldecyl tails of cavitand **6** induce intramolecular coordination as a consequence of their conformational freedom; the simplest way to prevent the self-folding of these long alkyl chains and force dimerization was hence to shorten and rigidify such tails. For this reason, cavitand **9**, with short ω-isonicotinoylpropyl chains at the lower rim, was synthesised. As in the previous cases, we examined the coordination properties of this new ligand toward different precursor complexes. It was found that when the precursor complexes had fixed *cis* coordination − $Pt(dppp)(CF_3SO_3)_2$ and $Pd(dppp)(OTs)_2$, for example − they forced the formation of intramolecular dinuclear complexes **17** and **18** instead of dimeric structures (Scheme 7).[16]



16

Figure 2. ORTEP view of complex **16**, formed by addition of 2 equiv. of decyl isonicotinate to $PdCl_2(C_6H_5CN)_2$



Scheme 7. Coordinative behaviour of cavitand **9** in the presence of different metal precursors: $Pt(dppp)(CF_3SO_3)_2$, $Pd(dppp)(OTs)_2$, and $Pd(PEt_3)_2(OTs)_2$

Both products were obtained by adding the metal precursor to a solution of cavitand **9** in a 2:1 molar ratio. ESI-MS data show the $[\mathbf{17} - CF_3SO_3]^+$ and $[\mathbf{18} - OTs]^+$ peaks, respectively; both ions were singly charged: evidence of intramolecular complexation. The formation of complexes **17** and **18** makes the aromatic protons non-equivalent two by two. Moreover, all the methylene protons of the alkyl chains and of the dppp ligands are diastereotopic. As a consequence, some of them [namely the CH_2 α to the resorcinarene CH, the $C(O)OCH_2$ and the PCH_2 protons] exhibited different chemical shifts at 300 K (Figure 3). Variable-temperature NMR found different behaviour patterns for **17** and **18** upon heating. The spectrum of the former compound, as expected, remained unchanged up to 353 K, while the spectrum of **18** underwent coalescence of the resorcinarene aromatic signals and of all the diastereotopic CH_2 signals. This behaviour can only be attributed to fast ligand exchange (on the NMR timescale) of the pyridyl ligands in the Pd complex **18** at high temperature. The absence of this fast exchange in the Pt complex **17** is due to the greater Pt−N bond strength[17] relative to that of Pd−N.

To prevent formation of these intramolecular complexes, *cis*-metal precursors were substituted with *trans*-$Pd(PEt_3)_2(OTs)_2$. ^1H NMR and ESI-MS data show the formation of oligomeric species only. In this case, the corresponding intramolecular complex cannot be formed, since the tethers connecting the pyridine groups to the resorcinarene skeleton are too short. Reducing the conformational freedom of the pyridyl ligands by shortening the alkyl tethers did not avoid the formation of dinuclear intramolecular complexes, nor did it hamper the oligomeric self-assembly. Therefore, a successful strategy to drive the self-assembly toward the formation of dimeric species requires the ruling out of any possible intramolecular pathway. This was achieved by combining the bidentate pyridine cavitand **10** with a metal precursor possessing four labile ligands. By mixing **10** and $Pd(CH_3CN)_4(BF_4)_2$ in a 2:1 ratio, the square-planar complex **19** was obtained in quantitative yields as a white precipitate (Scheme 8).

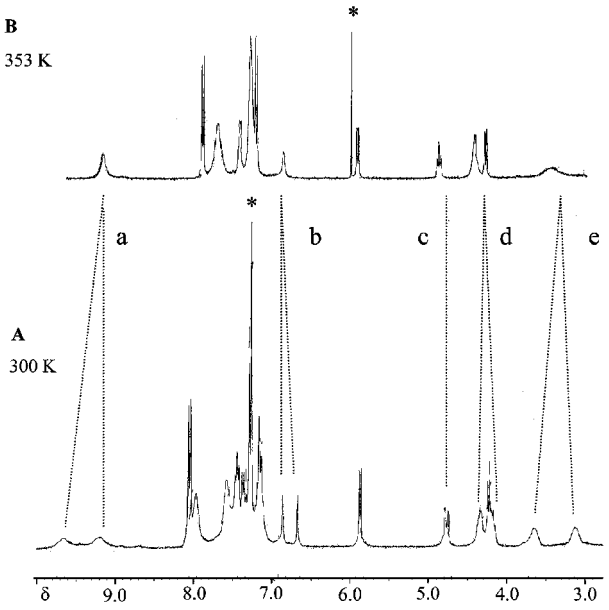
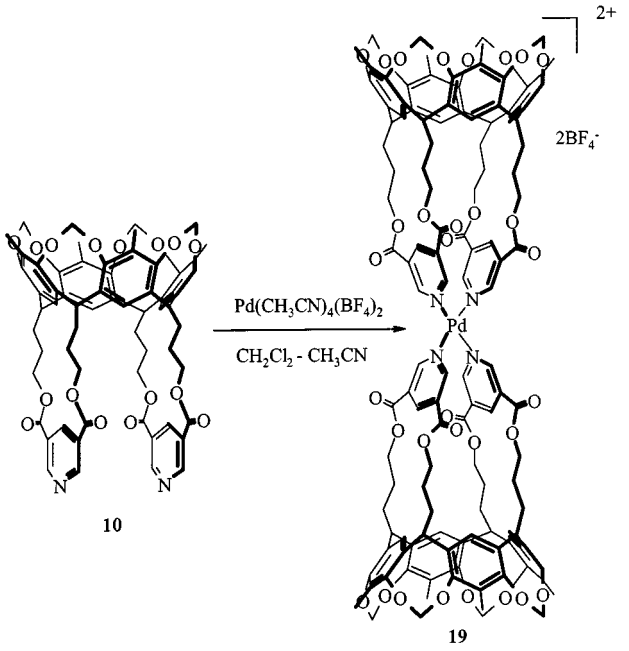


Figure 3. Sections of ^1H NMR spectra of complex **18** as a function of temperature (300 MHz; A: $CDCl_3$, 300 K; B: $C_2D_2Cl_4$, 353 K); a: *o*-Py protons; b: ArH protons in the resorcinarene skeleton; c: ArCHAr protons in the resorcinarene skeleton; d: $C(O)OCH_2$ protons; e: PCH_2 protons of dppp (* solvent resonances)

In the ^1H NMR spectrum of this compound, a 0.5 ppm downfield shift of the *ortho*-pyridyl signals attested to the effective coordination of all the ligands to Pd. Moreover, the splitting of the diastereotopic methylene signals of the alkyl chains is indicative of the rigidification of the system, due to complexation to the metal centre. MALDI MS data confirm the formation of complex **19**, showing the $[\mathbf{19} + K]^+$ ion peak at *m/z* 2491, and rule out the presence of oligomeric species.



Scheme 8. Metal-directed dimerization of cavitand **10**

Conclusions

The results described in this work highlight the difficulties inherent in controlling the outcome of metal-directed self-assembly of lower rim multidentate cavitand ligands. Several coordination complexes were obtained, ranging from mononuclear and dinuclear monomeric complexes with different coordination geometries (octahedral, square-planar, linear) to dimers and oligomers. The reason for such difficulties arises from the loose control over ligand orientation and conformational mobility in lower rim substituted cavitands, which leaves control over the self-assembly to the metal precursor. This is in sharp contrast with derivatization of cavitands at the upper rim, where the preorganization of the cavitand ligands directs the self-assembly.[5a] The most difficult task is not to avoid the formation of oligomeric species, but to block any possible pathway leading to the formation of stable intramolecular complexes. In fact, the desired dimeric structure was finally obtained by restricting the number of pyridyl moieties and at the same time using an appropriate metal precursor capable of complexing the pyridine rings of two ligands. Under these conditions, self-assembly resulted in the exclusive formation of complex **19** even if oligomeric species were possible.

Experimental Section

General: ACS grade reagents were used without further purification. Solvents were dried with 3-Å molecular sieves. − Analytical TLC was performed on Merck silica gel or aluminium oxide 60 F_{254} precoated plates. Preparative TLC employed glass-backed silica gel or aluminium oxide plates (Merck, 60 F_{254}). Column chromatography was performed using silica gel or aluminium oxide (Merck, 70−230 mesh ASTM). − ^{1}H NMR spectra were recorded at 400, 300, and 200 MHz. Chemical shifts are given in part per million ($\delta_{TMS} = 0$) using as internal reference the residual resonances of deuterated solvents ($\delta = 7.25$ for chloroform; $\delta = 6.00$ for 1,1,2,2-tetrachloroethane). − IR spectra were recorded with a FT-IR machine. − Chemical ionisation mass spectra were recorded with a single-stage quadrupole mass spectrometer. Electrospray mass spectra were obtained using an API 100 SCIEX spectrometer with an ionspray interface. MALDI spectra were recorded using a Proflex time-of-flight mass spectrometer (Bruker Daltonics, Billerica, MA, USA). The instrument operates at linear mode using delayed extraction and is equipped with a 1 GHz digitiser, a nitrogen laser and microchannel plate detector. Acceleration voltage was 20 kV, extraction voltage 18 kV, and lens voltage 8 kV. All spectra are sums of 50 or 100 laser shots. 2,5-Dihydroxybenzoic acid (DHB) (20 mg/mL in methanol) or 2-(4-hydroxyphenylazo)benzoic acid (HABA) (10 mg/mL in THF) were used as matrixes. − Melting points were found using an electrothermal melting point apparatus and are uncorrected. − The glassware for the anhydrous reactions were dried by heating under vacuum/argon at the mechanic pump. Yields are given for the isolated product. − Data for the preliminary crystal structure of **11** were recorded with a Nonius Kappa CCD diffractometer using graphite-monochromatised Mo-K_α ($\lambda = 0.71073$ Å) radiation, $T = 173.0(1)$ K.

Tetrakis(4-bromophenyl)resorcin[4]arene Octapentyl Ether 2: A mixture of octol **1** (1.98 g, 1.8 mmol), 1-bromopentane (1.77 mL, 14.3 mmol), and K_2CO_3 (3.95 g, 28.6 mmol) in 50 mL of dry DMF was stirred under argon at 60 °C. Further 1-bromopentane (1.77 mL, 14.3 mmol) was added after 1 and 2 d and the temperature was maintained at 60 °C. After 3 d, the resulting mixture was suspended in water, acidified to pH = 6.5 and extracted with CH_2Cl_2. The collected organic layers were dried (Na_2SO_4), filtered, and concentrated to dryness in vacuo. The residue was purified by column chromatography (SiO_2; hexane/EtOAc, 95:5) to give the resorcin[4]arene **2** in 29% yield (0.86 g) as a white powder, m.p. 289 °C. − ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.18$ (d, 8 H, *o*-BrAr*H*, $J = 8.3$ Hz), 6.63 (d, 8 H, *m*-BrAr*H*, $J = 8.3$ Hz), 6.29 (s, 2 H, Ar*H*), 6.14 (s, 2 H, Ar*H*), 6.07 (s, 2 H, Ar*H*), 5.71 (s, 2 H, Ar*H*), 5.67 (s, 4 H, ArC*H*), 3.78 (m, 8 H, OCH_2), 3.66 (m, 4 H, OCH_2), 3.45 (m, 4 H, OCH_2), 1.45 (m, 16 H, OCH$_2$CH_2), 1.1−1.3 (m, 32 H, CH_2CH_2CH$_3$), 0.84 (t, 12 H, CH_3, $J = 7.2$ Hz), 0.79 (t, 12 H, CH_3, $J = 7.1$ Hz). − CI-MS: *m*/*z* = 1672 [MH$^+$] (100). − $C_{92}H_{116}Br_4O_8$ (1669.5): calcd. C 66.19, H 7.00; found 65.95, H 7.10.

Tetrakis(4-cyanophenyl)resorcin[4]arene Octapentyl Ether 3: CuCN (0.106 g, 1.19 mmol) was added to a solution of resorcin[4]arene **2** (0.248 g, 0.148 mmol) in *N*-methyl-2-pyrrolidinone (NMP) (60 mL). The reaction mixture was heated at 200 °C overnight, after which it was cooled to 90 °C. An acidified aqueous solution of $FeCl_3$ [3.86 g, 23.8 mmol, in H_2O/HCl (37%), 2:1] was slowly added and the mixture was stirred at 90 °C for 1 h; it was then cooled to room temp. and filtered. The solvent was removed under reduced pressure and the residue purified by column chromatography (SiO_2; hexane/EtOAc, 8:2) to give the resorcin[4]arene **3** in 46% yield (0.098 g, 0.067 mmol), m.p. 222 °C. − ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.32$ (d, 8 H, *o*-CNAr*H*, $J = 8.0$ Hz), 6.80 (d, 8 H, *m*-CNAr*H*, $J = 8.0$ Hz), 6.29 (s, 2 H, Ar*H*), 6.18 (s, 2 H, Ar*H*), 5.99 (s, 2 H, Ar*H*), 5.73 (s, 4 H, ArC*H*), 5.39 (s, 2 H, Ar*H*), 3.80 (m, 8 H, OCH_2), 3.64 (m, 4 H, OCH_2), 3.47 (m, 4 H, OCH_2), 1.44 (m, 16 H, OCH$_2$CH_2), 1.0−1.2 (m, 32 H, CH_2CH_2CH$_3$), 0.85 (t, 12 H, CH_3, $J = 7.1$ Hz), 0.77 (t, 12 H, CH_3, $J = 7.3$ Hz). − CI-MS: *m*/*z* = 1456 [MH$^+$] (100). − $C_{96}H_{116}N_4O_8$ (1454.0): calcd. C 79.30, H 8.04, N 3.85; found C 78.95, H 8.02, N 3.55. − FTIR (KBr, cm^{-1}): $\tilde{\nu} = 2227$ (C≡N).

Tetrakis(ω-decenyl)methylene-Bridged Cavitand 4: A mixture of tetrakis(ω-decenyl)octol (1.5 g, 1.44 mmol), Cs_2CO_3 (4.53 g, 13.9 mmol), and CH_2BrCl (4.33 mL, 66.7 mmol) in dry DMSO was stirred in a sealed tube at 88 °C for 3 h. After cooling, the mixture was poured into 2% HCl, and extracted with CH_2Cl_2. The collected organic layers were dried ($MgSO_4$), filtered, and concentrated to dryness in vacuo to give the product as an oil in 95% yield. − ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.05 (s, 4 H, Ar*H*), 6.47 (s, 4 H, Ar*H*), 5.70−5.90 (m, 4 H, *RCH*=CH_2), 5.72 (d, 4 H, OCH_{out}O, *J* = 7.1 Hz), 4.90−5.00 (m, 8 H, *RC*H=CH_2), 4.70 (t, 4 H, ArC*H*, *J* = 8.0 Hz), 4.40 (d, 4 H, OCH_{in}O, *J* = 7.1 Hz), 2.25 (m, 8 H, RCH_2CHAr$_2$), 2.03 (m, 8 H, RCH_2CH=CH_2), 1.50−1.25 (m, 48 H, -CH_2-). − CI-MS: *m*/*z* = 1090 [MH$^+$] (100).

Tetrakis(ω-hydroxydecyl)methylene-Bridged Cavitand 5: BH_3·THF (1 M, 2.68 mL, 2.68 mmol) was added to a solution of cavitand **4** (0.520 g, 0.48 mmol) in dry THF (30 mL), and the reaction mixture was stirred at room temperature for 5 d. The excess of BH_3 was quenched with water, and 1 N NaOH (1 mL) and 30% H_2O_2 (3 mL) were added. After stirring at room temperature for 1 h and at 50 °C for 4 h, the mixture was poured into water and extracted twice with CH_2Cl_2. The organic layer was dried with $MgSO_4$ and concentrated to give **5** as a white solid in 94% yield, m.p. 233 °C. − ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.09 (s, 4 H, Ar*H*), 6.46 (s, 4 H, Ar*H*), 5.71 (d, 4 H, OCH_{out}O, *J* = 7.1 Hz), 4.70 (t, 4 H, ArC*H*, *J* = 8.0 Hz), 4.40 (d, 4 H, OCH_{in}O, *J* = 7.1 Hz), 3.60 (t, 8 H, CH_2OH, *J* = 6.5 Hz), 2.21 (m, 8 H, RCH_2CHAr$_2$), 1.53 (m, 8 H, RCH_2CH$_2$OH), 1.28 (m, 56 H, CH_2). − CI-MS: *m*/*z* = 1161 [M$^+$] (100). − $C_{72}H_{104}O_{12}$ (1161.6): calcd. C 74.45, H 9.02; found C 74.90, H 8.94.

Tetrakis(ω-isonicotinoyldecyl)methylene-Bridged Cavitand 6: Isonicotinoyl chloride hydrochloride (0.184 g, 1.03 mmol) and NEt_3 (0.5 mL, 3.44 mmol) were added to a solution of cavitand **5** (0.200 g, 0.172 mmol) in dry DMF (50 mL). The reaction mixture was stirred at room temp. for 2 d, and then heated at 70 °C for 8 h. It was subsequently cooled to room temp., poured into water, and extracted with CH_2Cl_2. The organic layer was washed with water until neutrality, dried with $MgSO_4$, and concentrated to give product **6** as an oil in 95% yield. − ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.74 (m, 8 H, *o*-Py, XX′ part of an AA′XX′ system), 7.80 (m, 8 H, *m*-Py, AA′ part of an AA′XX′ system), 7.08 (s, 4 H, Ar*H*), 6.45 (s, 4 H, Ar*H*), 5.70 (d, 4 H, OCH_{out}O, *J* = 7.2 Hz), 4.69 (t, 4 H, ArC*H*, *J* = 7.5 Hz), 4.40 (d, 4 H, OCH_{in}O, *J* = 7.2 Hz), 4.31 (t, 8 H, *CH*$_2$OOCPy, *J* = 3 Hz), 2.20 (m, 8 H, RCH_2CHAr$_2$), 1.73 (m, 8 H, RCH_2CH$_2$OOCPy), 1.50−1.13 (m, 56 H, CH_2). − CI-MS: *m*/*z* = 1582 [MH$^+$] (100). − FTIR (KBr, cm^{-1}): ṽ = 1722 (CO).

Dodecol 7: 2-Methylresorcinol (7.77 g, 62.59 mmol) was dissolved under N_2 in 4:1 methanol/37% HCl (65 mL). 2,3-Dihydrofuran (4.73 mL, 62.59 mmol) was then added over 4 h, using a syringe pump. After an additional 4 h of stirring at room temp., the mixture was heated to 50 °C. After 7 d, a considerable amount of precipitate had formed and the reaction mixture was allowed to cool to room temp. The solid was filtered off, taken up in 300 mL of distilled water, and sonicated. The solid was again filtered off and concentrated to dryness in vacuo to give 8.34 g (10.79 mmol) of the desired C_{4v} isomer as a pale yellow solid; yield 69%, m.p. (dec.) 300 °C. − ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 8.64 (br. s, 8 H, ArO*H*), 7.29 (br. s, 4 H, *ArH*), 4.32 (t, 4 H, CH$_2$O*H*, *J* = 4.9 Hz), 4.20 (t, 4 H, ArC*H*, *J* = 7.4 Hz), 3.45 (m, 8 H, CH$_2$CH_2OH), 2.26 (m, 8 H, ArCHCH_2), 1.95 (s, 12 H, ArCH_3), 1.36 (m, 8 H, CH$_2$CH_2CH$_2$). − CI-MS: *m*/*z* = 773 [M$^-$] (65).

Tetrakis(ω-hydroxybutyl)methylene-Bridged Cavitand 8: A mixture of dodecol **7** (1.50 g, 1.94 mmol), K_2CO_3 (2.67 g, 19.33 mmol), and CH_2BrCl (0.75 mL, 11.59 mmol) in dry DMF (30 mL) was stirred in a sealed tube at 88 °C for 4 h. After cooling, the mixture was poured into 2% HCl (200 mL), and the solid formed was filtered and dried. The crude product was purified by column chromatography (SiO_2; CH_2Cl_2/EtOH, 96.5:3.5 and 90:10) to give cavitand **8** in 86% yield (1.37 g, 1.66 mmol), m.p. (dec.) 220 °C. − ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 7.43 (s, 4 H, *ArH*), 5.87 (d, 4 H, OCH_{out}O, *J* = 7.5 Hz), 4.60 (t, 4 H, ArC*H*, *J* = 8.1 Hz), 4.41 (t, 4 H, CH$_2$O*H*, *J* = 5.0 Hz), 4.20 (d, 4 H, OCH_{in}O, *J* = 7.5 Hz), 3.49 (m, 8 H, CH$_2$CH_2OH), 2.36 (m, 8 H, ArCHCH_2), 1.89 (s, 12 H, ArCH_3), 1.43 (m, 8 H, CH$_2$CH_2CH$_2$). − CI-MS: *m*/*z* = 825 (100) [M$^+$]. − $C_{48}H_{56}O_{12}$·2CH_3CH_2OH (917.1): calcd. C 68.10, H 7.47; found C 68.14, H 7.30.

Tetrakis(ω-isonicotinoylpropyl)methylene-Bridged Cavitand 9: Isonicotinoyl chloride hydrochloride (1.56 g, 8.76 mmol) was dissolved in pyridine (15 mL) and heated at 100 °C for 30 min. Cavitand **8** (0.6 g, 0.73 mmol) was then added. After stirring at 100 °C for 3 h, the reaction mixture was cooled to room temp., poured into water and filtered. The precipitate was subsequently washed with methanol and dried in vacuo to give 0.60 g (0.48 mmol) of cavitand **9** in 66% yield, m.p. 139 °C. − ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.74 (d, 8 H, *o*-Py, XX′ part of an AA′XX′ system), 7.81 (m, 8 H, *m*-Py, AA′ part of an AA′XX′ system), 6.97 (s, 4 H, *ArH*), 5.88 (d, 4 H, OCH_{out}O, *J* = 7.0 Hz), 4.90 (t, 4 H, ArC*H*, *J* = 8.1 Hz), 4.45 [t, 8 H, CH$_2$CH_2OC(O)Py, *J* = 6.7 Hz], 4.25 (d, 4 H, OCH_{in}O, *J* = 7.0 Hz), 2.36 (m, 8 H, ArCHCH_2), 1.95 (s, 12 H, ArCH_3), 1.87 (m, 8 H, CH$_2$CH_2CH$_2$). − CI-MS: *m*/*z* = 1244 (100) [M$^+$]. − $C_{72}H_{68}N_4O_{16}$ (1245.4): calcd. C 69.44, H 5.50, N 4.50; found C 69.66, H 5.85, N 4.10. − FTIR (KBr, cm^{-1}): ṽ = 1734 (CO).

Bis(ω-dinicotinoylpropyl)methylene-Bridged Cavitand 10: 3,5-Bis(chlorocarbonyl)pyridine(dinicotinoylchloride) was prepared immediately before use by treatment of 3,5-pyridinedicarboxylic acid (0.400 g, 2.4 mmol), suspended in benzene (12.5 mL), with $SOCl_2$ (8.5 mL) at 50 °C. Five drops of DMF were added to catalyse the reaction. The solvent and excess $SOCl_2$ were removed, benzene was added again and the solution was refluxed for 10 min. The solvent was removed and pyridine (20 mL) was added. The solution was heated at 100 °C for 30 min, and cavitand **8** (0.622 g, 0.75 mmol) was added. After stirring at 100 °C for 3 h, the reaction mixture was cooled to room temp., quenched with 10 mL of water and concentrated to dryness. The crude product was purified by column chromatography (SiO_2; CH_2Cl_2/EtOH, 98:2) to give cavitand **10** in 21% yield (0.17 g, 0.16 mmol), m.p. > 320 °C. − ^{1}H NMR ($CDCl_2CDCl_2$, 353 K, 300 MHz): δ = 9.32 (br. s, 4 H, *o*-Py), 8.16 (br. s, 2 H, *p*-Py), 7.26 (s, 2 H, Ar*H*), 7.21 (s, 2 H, Ar*H*), 5.96 (d, 4 H, OCH_{out}O, *J* = 6.9 Hz), 4.92 (t, 4 H, ArC*H*, J = 7.3 Hz), 4.47 [m, 8 H, CH$_2$CH_2OC(O)Py], 4.27 (d, 4 H, OCH_{in}O, *J* = 6.9 Hz), 2.61−2.44 (m, 8 H, ArCHCH_2), 2.05 (s, 6 H, ArCH_3), 2.04 (s, 6 H, ArCH_3), 1.88 (m, 8 H, CH$_2$CH_2CH$_2$). − CI-MS: *m*/*z* = 1087 [M$^+$] (100).

{Tetrakis(4-cyanophenyl)resorcin[4]arene Octapentyl Ether}−AgO_3SCF_3 Complex 11: CF_3SO_3Ag (3.0 mg, 0.012 mmol) was added to a solution of resorcin[4]arene **3** (7.0 mg, 0.005 mmol) in toluene (6 mL). The reaction mixture was stirred at room temperature for 24 h. The solvent was removed under reduced pressure to give complex **11** as the only product. − ^{1}H NMR ($CDCl_3$, 300 K, 300 MHz): δ = 7.54 (d, 8 H, *o*-CNAr*H*, *J* = 8.0 Hz), 6.86 (br. s, 8 H, *m*-CNAr*H*), 6.30 (s, 2 H, Ar*H*), 6.21 (s, 2 H, Ar*H*), 5.94 (s, 2 H, Ar*H*), 5.78 (s, 4 H, ArC*H*), 5.25 (s, 2 H, Ar*H*), 3.82 (m, 8 H, OCH_2), 3.62 (m, 4 H, OCH_2), 3.49 (m, 4 H, OCH_2), 1.45 (m, 16 H, OCH$_2$CH_2), 1.2−1.0 (m, 32 H, CH_2CH_2CH$_3$), 0.84 (t, 12 H, CH_3, *J* = 7.1 Hz), 0.76 (t, 12 H, CH_3, *J* = 7.3 Hz). − ^{1}H NMR

($CDCl_3$, 330 K, 300 MHz): δ = 7.55 (d, 8 H, *o*-CNAr*H*, *J* = 8.3 Hz), 6.88 (d, 8 H, *m*-CNAr*H*, *J* = 8.3 Hz), 6.33 (s, 2 H, Ar*H*), 6.21 (s, 2 H, Ar*H*), 6.01 (s, 2 H, Ar*H*), 5.81 (s, 4 H, ArC*H*), 5.30 (s, 2 H, Ar*H*), 3.80 (m, 8 H, OCH_2), 3.63 (m, 4 H, OCH_2), 3.47 (m, 4 H, OCH_2), 1.45 (m, 16 H, OCH$_2$CH_2), 1.2−1.0 (m, 32 H, CH_2CH_2CH$_3$), 0.82 (t, 12 H, CH_3, *J* = 7.1 Hz), 0.73 (t, 12 H, CH_3, *J* = 7.3 Hz). − ESI-MS: *m*/*z* = 1818.7 [**3**·Ag]$^+$ and 1561.7 [**3**·2AgCF_3SO_3 − CF_3SO_3]$^+$. − FTIR (KBr, cm^{-1}): ṽ = 2231 (C≡N).

{Tetrakis(4-cyanophenyl)resorcin[4]arene Octapentyl Ether}−$AgBF_4$ Complex 12: $AgBF_4$ (6.0 mg, 0.031 mmol) was added to a solution of resorcin[4]arene **3** (18.0 mg, 0.012 mmol) in toluene (6 mL). The reaction mixture was stirred at room temperature for 24 h. The solvent was removed under reduced pressure to give the complex **5** as the only product. − ^{1}H NMR ($CDCl_3$, 300 K, 300 MHz): δ = 7.64 (br. s, 8 H, *o*-CNAr*H*), 6.96 (br. s, 8 H, *m*-CNAr*H*), 6.28 (s, 2 H, Ar*H*), 6.19 (s, 2 H, Ar*H*), 6.09 (s, 2 H, Ar*H*), 5.79 (s, 4 H, ArC*H*), 5.42 (s, 2 H, Ar*H*), 3.83 (m, 8 H, OCH_2), 3.66 (m, 4 H, OCH_2), 3.42 (m, 4 H, OCH_2), 1.51 (m, 16 H, OCH$_2$CH_2), 1.2−1.0 (m, 32 H, CH_2CH_2CH$_3$), 0.86 (t, 12 H, CH_3, *J* = 7.1 Hz), 0.78 (t, 12 H, CH_3, *J* = 7.3 Hz). − ^{1}H NMR ($CDCl_3$, 330 K, 300 MHz): δ = 7.70 (br. d, 8 H, *o*-CNAr*H*), 6.95 (br. d, 8 H, *m*-CNAr*H*), 6.32 (br. s, 2 H, Ar*H*), 6.24 (s, 2 H, Ar*H*), 6.09 (s, 2 H, Ar*H*), 5.82 (s, 4 H, ArC*H*), 5.42 (s, 2 H, Ar*H*), 3.83 (m, 8 H, OCH_2), 3.66 (m, 4 H, OCH_2), 3.42 (m, 4 H, OCH_2), 1.54 (m, 16 H, OCH$_2$CH_2), 1.3−1.1 (m, 32 H, CH_2CH_2CH$_3$), 0.86 (t, 12 H, CH_3, *J* = 7.1 Hz), 0.78 (t, 12 H, CH_3, *J* = 7.3 Hz). − ESI-MS: *m*/*z* = 1756.6 [**3**·Ag]$^+$ and 1561.8 [**3**·2AgBF_4 − BF_4]$^+$. − FTIR (KBr, cm^{-1}): ṽ = 2228 (C≡N).

[Tetrakis(ω-isonicotinoyldecyl)methylene-Bridged Cavitand]−$NiCl_2$ Complex 13: A solution of $NiCl_2$·6H_2O (10 mg, 0.041 mmol) in ethanol 99% (5 mL) was added drop by drop to a solution of cavitand **6** (64 mg, 0.041 mmol) in CH_2Cl_2 (10 mL); the solution changed colour from green to yellow. After 3 h of stirring at room temp., a yellow precipitate had formed in quantitative yield. − ^{1}H NMR ([D$_6$]DMSO, 323 K, 300 MHz): δ = *o*-Py and *m*-Py peaks absent, due to the paramagnetism of the complex, 7.51 (s, 4 H, Ar*H*), 6.47 (s, 4 H, Ar*H*), 5.67 (d, 4 H, OCH_{out}O, *J* = 7.7 Hz), 4.56 (t, 4 H, ArC*H*, J = 7.9 Hz), 4.37 (d, 4 H, OCH_{in}O, *J* = 7.7 Hz), 4.28 (t, 8 H, *CH*$_2$OOCPy, *J* = 3.0 Hz), 2.20 (m, 8 H, RCH_2CHAr$_2$), 1.73 (m, 8 H, RCH_2CH$_2$OOCPy), 1.40−1.15 (m, 56 H, CH_2). − ESI-MS: *m*/*z* = 1676 [M − Cl]$^+$, 819 [M − 2 Cl]$^{2+}$ where M = **6**·$NiCl_2$. − CI-MS: *m*/*z* = 1713 [MH$^+$] (100). − FTIR (KBr, cm^{-1}): ṽ = 1732 (CO).

[Tetrakis(ω-isonicotinoyldecyl)methylene-Bridged Cavitand]−$AgOOCCF_3$ Complex 14: CF_3COOAg (14 mg, 0.063 mmol) was added to a solution of cavitand **6** (50 mg, 0.031 mmol) in dry CH_2Cl_2 (5 mL). The mixture was stirred for 5 h and the solvent was removed under reduced pressure, giving the complex in quantitative yield as a white powder. − ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.67 (br. s, 8 H, *o*-Py), 7.92 (br. s, 8 H, *m*-Py), 7.10 (s, 4 H, Ar*H*), 6.48 (s, 4 H, Ar*H*), 5.73 (d, 4 H, OCH_{out}O, *J* = 7.2 Hz), 4.70 (t, 4 H, ArC*H*, *J* = 8.0 Hz), 4.42 (d, 4 H, OCH_{in}O, *J* = 7.2 Hz), 4.36 (t, 8 H, *CH*$_2$OOCPy, *J* = 6.7 Hz), 2.20 (m, 8 H, RCH_2CHAr$_2$), 1.77 (m, 8 H, RCH_2CH$_2$OOCPy), 1.25 (br. s, 56 H, CH_2). − ESI-MS: *m*/*z* = 1913 [M − CF_3COO^-]$^+$ where M = **6**·2AgCF_3CO_2.

[Bis(ω-isonicotinoyldecyl)bis(ω-hydroxydecyl)methylene-Bridged Cavitand]−$PdCl_2$ Complex 15: $PdCl_2(C_6H_5CN)_2$ (25 mg, 0.064 mmol) was added to a solution of cavitand **6** (50 mg, 0.032 mmol) in toluene (5 mL). The mixture was stirred for 5 h and the solvent was removed under reduced pressure, giving the complex in quantitative yield as a yellow powder. − ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 9.00 (d, 4 H, *o*-Py, *J* = 5.8 Hz), 7.88 (d, 4 H, *m*-Py, *J* = 5.8 Hz), 7.10 (s, 4 H, Ar*H*), 6.47 (s, 4 H, Ar*H*), 5.73 (d, 4 H, OCH_{out}O, *J* = 7.2 Hz), 4.72 (t, 4 H, ArC*H*, J = 8.0 Hz), 4.42 (d, 4 H, OCH_{in}O, *J* = 7.2 Hz), 4.36 (t, 4 H, *CH*$_2$OOCPy, *J* = 6.5 Hz), 3.63 (m, 4 H, RCH_2OH, *J* = 6.5 Hz), 2.20 (m, 8 H, RCH_2CHAr$_2$), 1.77 (m, 4 H, RCH_2CH$_2$OOCPy), 1.64 (m, 4 H, RCH_2CH$_2$OH), 1.50−1.25 (m, 56 H, CH_2). − CI-MS: *m*/*z* = 1512 [**15** − Cl$^-$]$^+$ (100).

[Tetrakis(ω-isonicotinoylpropyl)methylene-Bridged Cavitand]−(dppp)Pt$(O_3SCF_3)_2$ Complex 17: A solution of Pt(dppp)$(SO_3CF_3)_2$ (57 mg, 0.06 mmol) in $CHCl_3$ (8 mL) was added slowly to a solution of cavitand **9** (39 mg, 0.03 mmol) in $CHCl_3$ (6 mL). The mixture was stirred for 8 h at room temp., after which a white precipitate had formed. This was filtered, giving **17** in quantitative yields. − ^{1}H NMR ($CDCl_2CDCl_2$, 353 K, 300 MHz): δ = 9.13 (br. d, 8 H, *o*-Py), 7.88 (m, 16 H, C_6H_5-dppp), 7.63−7.53 (m, 16 H, C_6H_5-dppp and *m*-Py), 7.38 (m, 16 H, C_6H_5-dppp), 7.00 (s, 2 H, Ar*H*), 6.82 (s, 2 H, Ar*H*), 5.92 (d, 4 H, OCH_{out}O, *J* = 6.9 Hz), 4.80−4.77 (2 d, 4 H, ArC*H*), 4.42 [m, 4 H, CH$_2$CH_2OC(O)Py], 4.28 [m, 4 H, CH$_2$CH_2OC(O)Py], 4.20 (d, 4 H, OCH_{in}O, *J* = 6.9 Hz), 3.53 (m, 4 H, Ph$_2$PCH_2CH$_2$CH_2PPh$_2$), 3.27 (m, 4 H, Ph$_2$PCH_2CH$_2$CH_2PPh$_2$), 2.45 (m, 4 H, ArCHCH_2), 2.17 (m, 4 H, Ph$_2$PCH$_2$CH_2CH$_2$PPh$_2$), 2.00 (s, 12 H, ArCH_3), 1.95 (m, 4 H, ArCHCH_2), 1.72 (m, 8 H, CH$_2$CH_2CH$_2$). − ^{1}H NMR ($CDCl_2CDCl_2$, 300 K, 300 MHz): δ = 9.30 (br. s, 4 H, *o*-Py), 8.87 (br. s, 4 H, *o*-Py), 7.85 (br. s, 16 H, C_6H_5-dppp), 7.75−7.35 (m, 16 H, *m*-Py and C_6H_5-dppp), 7.31 (m, 16 H, C_6H_5-dppp), 6.91 (s, 2 H, Ar*H*), 6.72 (s, 2 H, Ar*H*), 5.89 (d, 4 H, OCH_{out}O, *J* = 6.7 Hz), 4.72−4.67 (br. d, 4 H, ArC*H*), 4.41 [m, 4 H, CH$_2$CH_2OC(O)Py], 4.18 [m, 4 H, CH$_2$CH_2OC(O)Py], 4.16 (d, 4 H, OCH_{in}O, *J* = 6.7 Hz), 3.47 (m, 4 H, Ph$_2$PCH_2CH$_2$CH_2PPh$_2$), 3.17 (m, 4 H, Ph$_2$PCH_2CH$_2$CH_2PPh$_2$), 2.40 (m, 4 H, ArCHCH_2), 2.16 (m, 4 H, Ph$_2$PCH$_2$CH_2CH$_2$PPh$_2$) 1.96 (s, 6 H, ArCH_3), 1.95 (s, 6 H, ArCH_3), 1.87 (m, 4 H, ArCHCH_2), 1.64 (m, 8 H, CH$_2$CH_2CH$_2$). − ^{31}P NMR ($C_2D_2Cl_4$, 81 MHz): δ = 13.75, *J*(Pt-P) = 3080 Hz. − ^{19}F NMR (188.3 MHz, $C_2D_2Cl_4$): δ = −77.3. −ESI-MS: *m*/*z* = 2906.7 [M − CF_3SO_3]$^+$, 1379.6 [M − 2 CF_3SO_3]$^{2+}$ where M = **9**·2Pt(dppp)$(CF_3SO_3)_2$. − FTIR (KBr, cm^{-1}): ṽ = 1734 (CO).

[Tetrakis(ω-isonicotinoylpropyl)methylene-Bridged Cavitand]−(dppp)Pd$(OTs)_2$ Complex 18: A solution of Pd(dppp)$(OTs)_2$ (69 mg, 0.08 mmol) in CH_2Cl_2 (8 mL) was added slowly to a solution of cavitand **9** (50 mg, 0.04 mmol) in $CHCl_3$ (6 mL). The mixture was stirred for 8 h and the homogeneous solution was concentrated to dryness, to give **18** in quantitative yield. − ^{1}H NMR ($CDCl_2CDCl_2$, 353 K, 300 MHz): δ = 9.32 (br. s, 8 H, *o*-Py), 7.98 (d, 8 H, $CH_3C_6H_4SO_3$, *J* = 8.0 Hz), 7.78 (br. s, 16 H, C_6H_5-dppp), 7.49 (br. d, 8 H, *m*-Py), 7.35 (m, 24 H, C_6H_5-dppp), 7.27 (d, 8 H, $CH_3C_6H_4SO_3$, *J* = 8.0 Hz), 6.91 (s, 4 H, Ar*H*), 5.92 (d, 4 H, CH_{out}O, *J* = 6.9 Hz), 4.83 (t, 4 H, ArC*H*, J = 8.0 Hz), 4.35 [br. t, 8 H, CH$_2$CH_2OC(O)Py], 4.21 (d, 4 H, OCH_{in}O, *J* = 6.9 Hz), 3.30 (m, 8 H, Ph$_2$PCH_2CH$_2$CH_2PPh$_2$), 2.46 (s, 12 H, C$H_3C_6H_4SO_3$), 2.45−2.10 (m, 12 H, ArCHCH_2, Ph$_2$PCH$_2$CH_2CH$_2$PPh$_2$), 2.00 (s, 12 H, ArCH_3), 1.77 (m, 8 H, CH$_2$CH_2CH$_2$). − ^{1}H NMR ($CDCl_3$, 300 K, 300 MHz): δ = 9.66 (br. s, 4 H, *o*-Py), 9.20 (br. s, 4 H, *o*-Py), 8.04 (d, 8 H, $CH_3C_6H_4SO_3$, *J* = 7.9 Hz), 7.96 (br. s, 8 H, C_6H_5-dppp), 7.60−7.28 (m, 24 H, *m*-Py and C_6H_5-dppp), 7.27 (d, 8 H, $CH_3C_6H_4SO_3$, *J* = 7.9 Hz), 7.14 (m, 16 H, C_6H_5-dppp), 6.86 (s, 2 H, Ar*H*), 6.67 (s, 2 H, Ar*H*), 5.87 (d, 4 H, OCH_{out}O, *J* = 6.9 Hz), 4.78−4.75 (2 d, 4 H, ArC*H*), 4.34 [m, 4 H, CH$_2$CH_2OC(O)Py], 4.23 (d, 4 H, OCH_{in}O, *J* = 6.9 Hz), 4.18 (m, 4 H, CH$_2$CH_2OC(O)Py), 3.64 (m, 4 H, Ph$_2$PCH_2CH$_2$CH_2PPh$_2$), 3.13

(m, 4 H, $Ph_2PCH_2CH_2CH_2PPh_2$), 2.42 (s, 12 H, $CH_3C_6H_4SO_3$), 2.27−2.16 (m, 8 H, $Ph_2PCH_2CH_2CH_2PPh_2$ and ArCHCH_2), 1.95 (s, 6 H, ArCH_3), 1.94 (s, 6 H, ArCH_3), 1.87 (m, 4 H, ArCHCH_2), 1.69 (m, 8 H, $CH_2CH_2CH_2$). − ^{31}P NMR ($CDCl_3$, 81 MHz): δ = 9.8. −ESI-MS: *m*/*z* = 2797.2 [M − OTs]$^+$ where M= **9**·2Pd(dppp)$(OTs)_2$. − FTIR (KBr, cm^{-1}): ṽ = 1734 (CO).

[Bis(ω-dinicotinoylpropyl)methylene-Bridged Cavitand]−Pd$(BF_4)_2$ Complex 19: A solution of $Pd(CH_3CN)_4(BF_4)_2$ (12 mg, 0.026 mmol) in CH_3CN (8 mL) was added slowly to a solution of cavitand **10** (57 mg, 0.052 mmol) in CH_2Cl_2 (50 mL); after a few minutes a white precipitate had formed. Filtration afforded complex **19** in quantitative yield. − ^{1}H NMR ($CDCl_2CDCl_2$, 353 K, 300 MHz): δ = 9.81 (s, 4 H, *o*-Py), 9.11 (s, 2 H, *p*-Py), 7.71 (s, 2 H, Ar*H*), 7.23 (s, 2 H, Ar*H*), 5.90 (d, 4 H, OCH_{out}O, *J* = 6.8 Hz), 4.85−4.80 [m, 8 H, CH_2CH_2OC(O)Py, ArC*H*], 4.20 (d, 4 H, OCH_{in}O, *J* = 6.8 Hz), 4.14 [m, 4 H, CH_2CH_2OC(O)Py], 2.79 (m, 4 H, ArCHCH_2), 2.36 (m, 4 H, ArCHCH_2), 1.99 (s, 12 H, ArCH_3), 1.78 (m, 8 H, $CH_2CH_2CH_2$); ($CDCl_2CDCl_2$, 300 MHz): δ = 9.77 (s, 4 H, *o*-Py), 9.06 (s, 2 H, *p*-Py), 7.64 (s, 2 H, Ar*H*), 7.13 (s, 2 H, Ar*H*), 5.88 (br. d, 4 H, OCH_{out}O, *J* = 6.8 Hz), 4.83 [m, 4 H, CH_2CH_2OC(O)Py], 4.75 (t, 4 H, ArC*H*, J = 7.5 Hz), 4.17 (d, 4 H, OCH_{in}O, *J* = 6.8 Hz), 4.10 [m, 4 H, CH_2CH_2OC(O)Py], 2.72 (m, 4 H, ArCHCH_2), 2.33 (m, 4 H, ArCHCH_2), 1.95 (s, 12 H, ArCH_3), 1.70 (m, 8 H, $CH_2CH_2CH_2$). − MALDI-MS: *m*/*z* = 2491 [M + K]$^+$.

Crystal Structure of Complex 16: Complex **16** was prepared by adding 2 equiv. of decyl isonicotinate to a $CHCl_3$ solution of $PdCl_2(C_6H_5CN)_2$. Crystals of complex **16** were obtained from a $CHCl_3$/hexane (1:1) mixture. The complex is centrosymmetric and lies on a crystallographic centre of symmetry which coincides with the Pd atom. The metal centre shows a planar coordination with an angle Cl1−Pd−N1 of 89.85(14)°. The Pd−C1 bond is inclined by 45.5(1)° with respect to the N1−C1−C2−C3−C4−C5 ring, which is planar within the limit of the standard deviations. No distances and angles in the ester terminal atoms deviate from the theoretical values (Table 1). The intensity data of **16** were collected at room temperature with a Philips PW 1100 single-crystal diffractometer, equipped with a graphite-monochromated Mo-K_α radiation source (λ = 0.71073 Å), using the θ/2θ scan technique. Final unit cell parameters were obtained from a least-squares refinement of 24 reflections found in a random search on the reciprocal lattice. The crystal data and the most relevant experimental parameters used in the X-ray measurements and the crystal structure analyses are reported in Table 2. The phase problem was solved by Direct Methods using SIR92[18] and refined by blocked full-matrix, least-squares procedures (based on F^2) with anisotropic thermal parameters in the last cycles of refinement for all the atoms, using the SHELXL-97 program.[19] The hydrogen atoms were taken in their calculated positions and refined riding on the corresponding parent atoms. The final molecular geometry was analysed with the program PARST97.[20] All calculations were carried out with a DEC Alpha 250 workstation at the "Centro di Studio per la Strutturistica Diffrattometrica", CNR, Parma. The supplementary material for the structure includes the list of atomic coordinates for the non-H atoms, of calculated coordinates for the hydrogen atoms and of anisotropic thermal parameters. The details of the crystal structure investigations have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-154791. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033, E-mail: deposit@ccdc.cam.ac.uk].

Table 1. Selected bond lengths [Å] and angles [°] in complex **16**

Pd−Cl(1)	2.3020(18)	Cl(1)−Pd−N(1)	89.85(14)
Pd−N(1)	2.029(4)	Pd−N(1)−C(1)	120.9(4)
N(1)−C(5)	1.335(7)	Pd−N(1)−C(5)	121.1(4)
N(1)−C(1)	1.357(7)	C(4)−C(3)−C(6)	121.3(6)
C(3)−C(6)	1.509(8)	C(2)−C(3)−C(6)	119.7(6)
C(6)−O(1)	1.218(8)	C(3)−C(6)−O(1)	123.0(6)
C(6)−O(2)	1.309(8)	C(3)−C(6)−O(2)	111.3(5)
O(2)−C(7)	1.454(7)	C(6)−O(2)−C(7)	117.5(5)
C(7)−C(8)	1.493(9)	O(2)−C(7)−C(8)	107.6(5)

Table 2. Crystallographic data and experimental details for **16**

Crystal data	
Empirical formula	$C_{32}H_{50}Cl_2N_2O_4Pd$
Molecular mass	704.04
Crystal size [mm]	0.27 × 0.22 × 0.28
Crystal system	monoclinic
Space group	$P2_1/a$
a [Å]	9.806(5)
b [Å]	7.624(5)
c [Å]	24.091(5)
α [°]	90.000(5)
β [°]	96.270(5)
γ [°]	90.000(5)
V [Å^3]	1790.3(15)
Z	2
ρ(calcd.) [g/cm^3]	1.306
F(000)	736
Data collection	
T [K]	293(2)
Index ranges	$-10 \le h \le 10$, $0 \le k \le 8$, $0 \le l \le 26$
Reflections collected	2555
Independent reflections	2489 (R_{int} = 0.1248)
Observed reflections	1768 [$F_o \ge 4\sigma(F_o)$]
Structure refinement	
Data/restraints/parameters	2489/0/191
Weighting scheme	$w = [\sigma^2(F_o^2) + (0.0957P)^2]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$
Goodness-of-fit on F^2 [a]	0.968
Final *R* indices (obs. data)	*R*1 = 0.0554, w*R*2 = 0.1306
R indices (all data)	*R*1 = 0.0813, w*R*2 = 0.1437
Largest diff. peak and hole [e/Å^3]	1.531, −1.237

[a] $R1 = \Sigma||F_o| - |F_c||/\ \Sigma|F_o|$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w\ F_o^4]^{1/2}$. Goodness-of-fit = $[\Sigma w(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$, where *n* is the number of reflections and *p* the number of parameters.

Acknowledgments

This work was supported by MURST (Molecular Nanoelectronics Project). We acknowledge the Centro Interfacoltà di Misure G. Casnati at the University of Parma for instrumental facilities. Special thanks to Prof. P. Vainiotalo (University of Joensuu, Finland) for the MALDI-MS measurements and to Dr. P. Manini (University of Parma) for ESI-MS measurements. Financial support from the Finnish Ministry of Education to E. W. is gratefully acknowledged.

[1] S. Leininger, B. Olenyuk, P. J. Stang, *Chem. Rev.* **2000**, *100*, 853−908.

[2] For recent reviews see: [2a] C. Weiser, C. B. Dieleman, D. Matt, *Coord. Chem. Rev.* **1997**, *165*, 93−161. − [2b] C. J. Jones, *Chem. Soc. Rev.* **1998**, *27*, 289−299.

[3] [3a] T. N. Sorrel, F. C. Pigge, P. S. White, *Inorg. Chem.* **1994**, *33*, 632−635. − [3b] S. Pellet-Rostaing, J.-B. Regnouf de Vains, R. Lamartine, *Tetrahedron Lett.* **1995**, *36*, 5745−5748. − [3c] W. Xu, J. P. Rourke, J. J. Vittal, R. J. Puddephatt, *Inorg. Chem.* **1995**, *34*, 323−329. − [3d] E. Solari, W. Lesueur, A. Klose, K. Schenk, C. Floriani, A. Chiesi-Villa, C. Rizzoli, *Chem. Commun.* **1996**, 807−808.- [3e] H. Boerrigter, W. Verboom, D. N. Reinhoudt, *J. Org. Chem.* **1997**, *62*, 7148−7155. − [3f] F. Hamada, S. Ito, M. Narita, N. Nashirozawa, *Tetrahedron Lett.* **1999**, *40*, 1527−1530. − [3g] M. Munakata, L. P. Wu, T. Kuroda-Sowa, M. Maekawa, Y. Suenaga, K. Sugimoto, I. Ino, *J. Chem. Soc., Dalton Trans.* **1999**, 373−378.

[4] [4a] P. D. Beer, E. L. Tite, M. G. B. Drew, A. Ibbotson, *J. Chem. Soc., Dalton Trans.* **1990**, 2543−2550. − [4b] P. D. Beer, E. L. Tite, A. Ibbotson, *J. Chem. Soc., Dalton Trans.* **1991**, 1691−1698.

[5] [5a] P. Jacopozzi, E. Dalcanale, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 613−615. − [5b] O. D. Fox, N. K. Dalley, R. G. Harrison, *J. Am. Chem. Soc.* **1998**, *120*, 7111−7112. − [5c] O. D. Fox, M. G. B. Drew, P. D. Beer, *Angew. Chem. Int. Ed.* **2000**, *39*, 136−140. − [5d] O. D. Fox, M. G. B. Drew, E. J. S. Wilkinson, P. D. Beer, *Chem. Commun.* **2000**, 391−392. − [5e]N. Cuminetti, M. H. K. Ebbing, P. Prados, J. De Mendoza, E. Dalcanale, *Tetrahedron Lett.* **2001**, *42*, 527−530.

[6] [6a] W. Xu, J. J. Vittal, R. J. Puddephatt, *J. Am. Chem. Soc.* **1995**, *117*, 8362−8371. − [6b] H. Boerrigter, L. Grave, J. W. M. Nissink, L. A. J. Chrisstoffels, J. H. van der Maas, W. Verboom, F. de Jong, D. N. Reinhoudt, *J. Org. Chem.* **1998**, *63*, 4174−4180 - [6c] I. Dumazet, P. D. Beer, *Tetrahedron Lett.* **1999**, *40*, 785−788.

[7] C. Kaes, M. W. Hosseini, C. E. F. Rickard, B. W. Skelton, A. H. White, *Angew. Chem. Int. Ed.* **1998**, *37*, 920−922 and references cited therein.

[8] L. M. Tunstad, J. A. Tucker, E. Dalcanale, J. Weiser, J. A. Bryant, J. C. Sherman, R. C. Helgeson, C. B. Knobler, D. J. Cram, *J. Org. Chem.* **1989**, *54*, 1305−1312.

[9] E. U. T. van Velzen, J. F. J. Engbersen, D. N. Reinhoudt, *Synthesis* **1995**, 989−997.

[10] B. C. Gibb, R. C. Chapman, J. C. Sherman, *J. Org. Chem.* **1996**, *61*, 1505−1509.

[11] E. Roman, C. Peinador, S. Mendoza, A. E. Kaifer, *J. Org. Chem.* **1999**, *64*, 2577−2578.

[12] [12a] K. A. Hirsch, S. R. Wilson, J. S. Moore, *J. Am. Chem. Soc.* **1997**, *119*, 10401−10412. − [12b] L. Carlucci, G. Ciani, P. Macchi, D. M. Proserpio, S. Rizzato, *Chem. Eur. J.* **1999**, 237−243. − [12c] C. Kleina, E. Graf, M. W. Hosseini, A. De Cian, J. Fischer, *Chem. Commun.* **2000**, 239−240.

[13] Preliminary X-ray structure data of **11**: a = 15.992(2), b = 27.699(4), c = 107.331(8) Å, β = 25.251(3)°, space group $P2_1/c$, R_1 = 22.97%.

[14] A 2:1 addition of $NiCl_2 \cdot 6H_2O$ to **6** resulted in the formation of a mixture of different complexes and oligomeric structures.

[15] *ORTEP32* in the WINGX suite (version 1.63.02): L. J. Farrugia, *J. Appl. Cryst.* **1999**, *32*, 837−838.

[16] For similar behaviour at the upper rim see: C. W. Lim, J.-I. Hong, *Tetrahedron Lett.* **2000**, *41*, 3113−3117.

[17] M. Fujita, *Acc. Chem. Res.* **1999**, *32*, 53−61.

[18] *SIR92*: A. Altomare, M. C. Burla, G. M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, G. Polidori, *J. App., Crystallogr.* **1994**, *27*, 435.

[19] M. Sheldrick, *SHELX-97, Program for Crystal Structure Refinement*, University of Göttingen, Germany, **1997**; http://shelx.uni-ac.gwdg.de/shelx/index.html

[20] *PARST97*, updated version of PARST95: M. Nardelli, *J. Appl. Crystallogr.* **1995**, *28*, 659.

Received December 18, 2000
[O00647]