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Arranging Coordination Sites around Cyclotriveratrylene*

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Abstract. This article describes the attachment of coordination sites around a rigid matrix: cyclotriveratrylene (CTV). The synthetic approaches leading to these new ligands possessing pyridines and bipyridines as coordinating sites are discussed and full synthetic details are given. One expanded CTV derivative bearing three 3-pyridyl groups has been characterized by X-ray crystallography and the structure shows that the conformation adopted by the CTV matrix is appropriate for the coordination of transition metals, and inclusion of a range of molecules in the hydrophobic pocket.

Key words: Cyclotriveratrylene, cavities, pyridines, 2,2′-bipyridine.

1. Introduction

For more than twenty-five years, researchers in the constantly expanding field of molecular recognition have been trying to adjust the shape, size, and nature of synthetic receptors in order to bind, extract and activate various substrates [1a–e]. Ultimately, host–guest chemistry and molecular recognition will create simple models for complicated, naturally occurring active sites of enzymes and proteins. Regarding this particular goal, families of compounds possessing hydrophobic cavities such as calixarenes, cyclodextrins [2–9] and cyclophanes [10, 11] are of great interest. These compounds are able to select guests depending on the type of interactions developed with a given substrate, depending on its size and/or its shape. In addition, these motion-restricted cavities offer the tremendous advantage of providing architectural control of the location and directionality of functional groups attached on an edge or in a cleft. Many different binding sites for alkaline and alkaline-earth metals have been preorganized with the help of rigid matrices such as calixarenes [12–14] or cyclotriveratrylene [15], but only a few researchers have taken advantage of rigid cavities to preorganize binding sites for transition metals.

* This paper is dedicated to the commemorative issue on the 50th anniversary of calixarenes.
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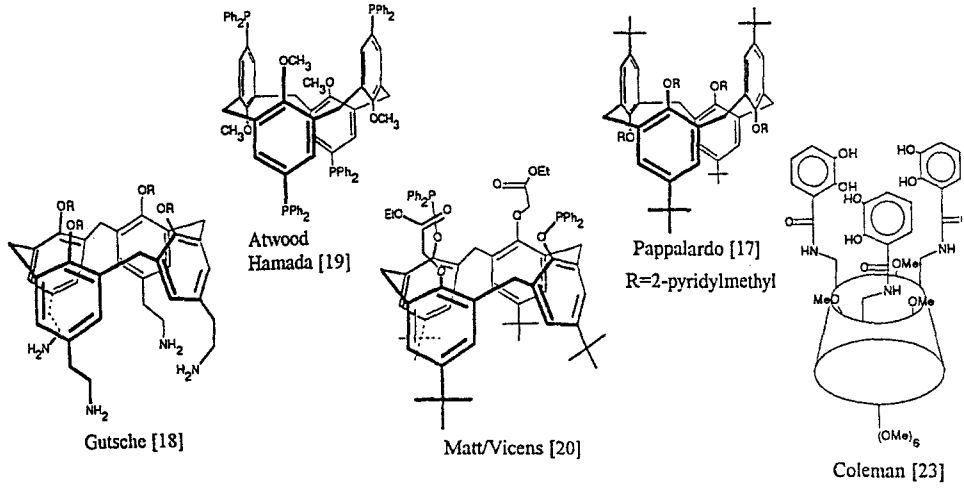
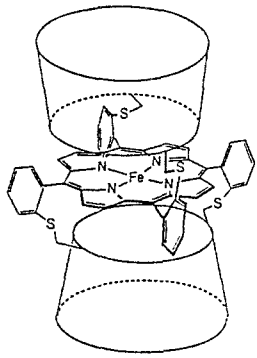


Fig. 1. Arranging binding groups around cavities: selected examples.

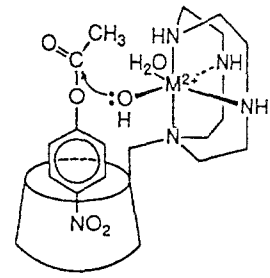
1.1. COMBINATIONS OF CAVITIES AND TRANSITION METALS

The first consequence of organizing phosphorus or nitrogen containing groups around a cavity is the generation of a tridimensional chelate effect, similar to the widely used chelation observed when binding alkaline and alkaline-earth metal cations with functionalized calixarenes. Some examples of cavities preorganizing pyridines, amines and phosphines are represented in Figure 1.

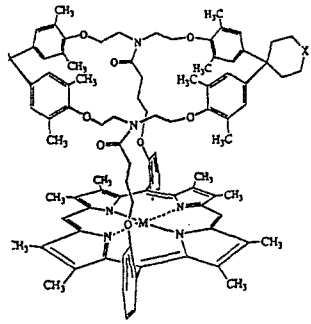
Pappalardo [16] has used the fixed partial cone conformation of a tetra-substituted calix[4]arene to generate chiral ligands bearing two pyridine and two quinoline rings. The synthesis of calix[4]arenes bearing pendant pyridine groups at the lower rim as potential ligands for transition metals has been described in an earlier work [17]. Gutsche [18] has used primary, secondary and tertiary amino groups, arranged in a C_4 symmetry around the upper rim of calix[4]arenes, to coordinate several transition metals in a tetradentate ligand. The possibility of an interaction between an auxiliary ligand and the hydrophobic cavity of the calixarene matrix has been mentioned but no experimental evidence for such a phenomenon has been obtained. The chelate effect with four diphenyl phosphine groups attached on a 1,3 alternate calix[4]arene has been used by Atwood and Hamada [19] for the binding and extraction of alkali and transition metal picrates in organic solvents. More recently and directly oriented towards homogeneous catalysis, calixarenes bearing phosphinites have attracted several groups [20–22]. For example, Matt and Vicens [20] have oriented their synthesis towards sterically hindered phosphine ligands to modify the properties of a metallic center, probably Rh(I) or Ir(I). Finally, Coleman [23] has designed a siderophore analogue built around a cyclodextrin, exhibiting a strong chelate effect in the complexation of iron(III). In their discussion, the authors mentioned the advantage offered by the



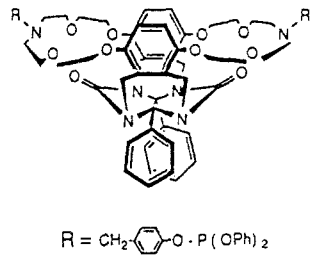
Kuroda [6,24]



Czamick [7]



Diederich [10]



Nolte [25]

Fig. 2. Catalysis with combination of a cavity and binding sites for transitions metals.

cyclodextrin cavity, which is able to carry an organic substrate together with the iron(III) center.

Building ligands by preorganization of binding sites for transition metals around a rigid cavity used as a matrix has a second interest. It provides the opportunity to combine the chemical and physical properties of the hydrophobic cavity with the reactivity of the metallic center. The ability of the cavity to develop specific interactions with substrates can be used to select, bind and properly orient an organic fragment. Thus, the metal complexed within the binding sites at the edge or in a cleft of the cavity can interact with the substrate in the cavity. Two examples emphasizing this useful cooperation, using cyclodextrin derivatives are represented in Figure 2. Besides the classical hydrophobic cavities like cyclodextrins, calix[4]arenes and Högberg bowl derivatives, new functionalized molecular clefts or tweezers will offer chemists a wide range of architectural possibilities as illustrated by the bis-phosphine ligand represented in Figure 2.

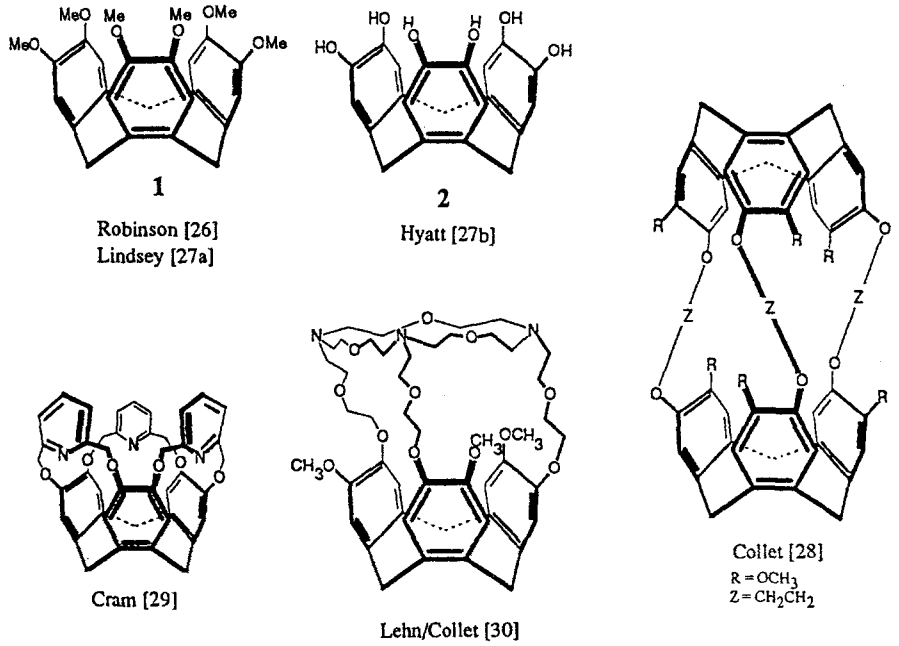


Fig. 3. Cyclotriveratrylene: a hydrophobic cavity for molecular recognition.

When an iron-porphyrin complex was located in a cyclodextrin sandwich, the cyclodextrin cavity could be used for the selection of terminal olefins versus internal olefins [6]. Thus, Kuroda was able to selectively perform the oxidation of olefins with iron-porphyrin complexes, in analogy with cytochrome P-450. When a photosensitive free base porphyrin was sandwiched between two cyclodextrins [24], the cavity was used to select, on a size criterion, an electron acceptor for quenching the excited state of the photosensitive unit. Still using cyclodextrins, Czarnick [7] has described a ligand in which transition metal complexes were attached at the edge of the hydrophobic cavity (see also [9]). These 'cavity-complex' combinations display a significant rate enhancement of the transacylation of both activated and inactivated aromatic esters. The substrate was properly oriented by the cyclodextrin in order to favor the interaction of the ester function with the metallic center. Diederich [10] has described a cytochrome P-450 model in which a cyclophane was used to bind and properly orient some polycyclic aromatics towards a hemic iron(IV)oxo. Finally, the use of hydrophobic cavities to promote interactions between a substrate and a metallic center is not restricted to calixarenes and cyclodextrins derivatives, as demonstrated by Nolte [25] who designed a system combining a cage structure with a phosphine chelate. The corresponding rhodium(I) complex selectively catalyses the hydrogenation of allyl catechol versus allyl veratrole, the former being strongly H-bonded to the receptor and the latter showing no H-bond interaction with the receptor.

As summarized above, it is quite surprising that, among the compounds that qualify as cavitands according to the generic name introduced by Cram at the end of the seventies ([1a] and references therein), only a few of these compounds have been used for organizing coordination sites for transition metal cations. The chemistry of cyclotriveratrylene (CTV) [26, 27] has afforded numerous chiral hosts, the cryptophanes [28], Figure 3, as well as hosts for alkali cations [15]. The chemistry of chiral derivatives of CTV has been reviewed by Collet [28], and detailed data concerning the restricted mobility of this bowl shaped molecule are available in the literature. Although CTV derivatives bearing three phenanthroline units and three pyridine units have been reported by Cram, Figure 3, the heteroatoms were not properly located to allow the formation of complexes, it has never been combined with transition metal complexation. In our approach to CTV functionalization, only achiral derivatives are obtained, thus allowing quick and easy characterization of the target compounds. The attachment of aromatic imines or polyimines to the cyclotriveratrylene and its derivatives are described hereafter.

The first example of a cyclization reaction involving non-adjacent oxygen atoms of the hexademethylated CTV derivative trivially named hexaphenol, Figure 3, was reported by Cram in 1988 [29]. Aromatic spacers have been used to expand the hydrophobic cavity of cyclotriveratrylene by a triple cyclization, under 'pseudo' high dilution conditions, bridging oxygen atoms located on neighbouring catechol subunits. We have extended the macrocycle formation to the synthesis of various functionalized expanded CTVs and, after a brief discussion of the strategies available for attaching binding sites on cyclotriveratrylene, the synthesis of the bridges and the cyclization reaction will be described in detail.

2. Experimental

General

THF was distilled from $LiAlH_4$ under an argon atmosphere. DMSO was purified according to the literature [37]. Dioxane was distilled from $NaBH_4$ under argon. DMF was dried over molecular sieves before use. All other chemicals were reagent grade and used without further purification. When anhydrous conditions were required the glassware was flame-dried under a dry argon stream. ^{1}H-NMR spectra were recorded on Bruker WP-200 (200 MHz) and Bruker AM-400 (400 MHz) spectrometers. Chemical shifts were determined by taking the solvent as a reference: $CHCl_3$ (7.26 ppm), $CHDCl_2$ (5.32 ppm), DMSO-d_5 (2.49 ppm). Melting points were determined on a Kofler Heating Plate type WME and are uncorrected. Elemental analyses were performed by the Service d'Analyse Elementaire de Composés Solides à l'Institut Universitaire de Technologie, Strasbourg Sud and the Service de Microanalyse de l'Institut de Chimie de Strasbourg. Mass spectra were obtained on a FAB: ZAB-HF mass spectrometer. Thin-layer chromatography (TLC) was performed using Macherey-Nagel Polygram Sil G/UV_{254} (0.25 mm) and Polygram Alox N/UV_{254} analytical polyethylene coated plates. E. Merck sil-

ica gel 60 (70–230 mesh) and aluminium oxide 90 (70–230 mesh) were used for column chromatography.

5-BROMOISOPHTHALIC ACID (**3**)

Isophthalic acid (18.3 g, 110 mmol) was dissolved in 250 mL concentrated H_2SO_4. Ag_2SO_4 (20 g, 64 mmol) and bromine (7.5 mL, 140 mmol) were added and the suspension was heated at 110°C for 24 h. Excess bromine was removed by bubbling an argon stream through the solution. The cooled solution was poured into 500 mL of iced water. The resulting white precipitate was isolated and then dissolved in a sodium hydroxide solution. The green AgOH precipitate was removed and the filtrate was acidified with concentrated HCl. The resulting white solid was filtered and dried by azeotrope distillation with ethanol and toluene to afford (24.5 g, 100 mmol, 91%) a white solid. White crystals could be obtained by recrystallization from an acetone/water mixture. This product was characterized by comparison with literature data [31].

1-BROMO-3,5-BIS(HYDROXYMETHYL)BENZENE (**4**)

To a degassed solution of 5-bromo-isophthalic acid **3** (12.5 g, 51 mmol) in 190 mL of THF, a 1 M solution of BH_3 in THF (200 mmol, 200 mL) was added via cannula under argon. The clear solution was refluxed for 3.5 h, then allowed to cool to room temperature before carefully quenching with 50 mL of MeOH. The solvents were removed under vacuum and two additional portions of MeOH were added and evaporated. The resulting oil was dissolved in 200 mL of Et_2O and extracted with 200 mL of 5% aqueous Na_2CO_3 and then with H_2O. All aqueous phases were washed with Et_2O. The combined organic layers were dried over $MgSO_4$, filtered, and evaporated to dryness. Filtration over silica gel (CH_2Cl_2), 10% MeOH) yielded a white solid (10.8 g, 51 mmol, 100%). White crystals could be obtained from recrystallization in hot benzene. ^{1}H-NMR (DMSO-d_6) δ ppm: 7.34 (s, 2H, $H_{2,6}$), 7.23 (s, 1H, H_4), 5.31 (t, J = 6 Hz, 2H, OH), 4.66 (d, J = 6 Hz, 4H, H_{Bz}). *Anal. Calcd.* for $C_8H_9BrO_2$ (217.1): C, 44.26; H, 419. *Found*: C, 44.08; H, 4.07. Melting point: 93–95°C.

PROTECTION OF 1-BROMO-3,5-BIS(HYDROXYMETHYL)BENZENE (**5**)

A degassed solution of **4** (9.8 g, 46 mmol), dihydropyran (13 mL, 140 mmol), and pyridinium *p*-toluene sulfonate (PPTS) (514 mg, 2 mmol) in 400 mL of CH_2Cl_2 was stirred under argon for 40 h. The solution was extracted with water. The organic layer yielded, after drying ($MgSO_4$) and removal of solvents under vacuum, a yellow oil (17.6 g, 45 mmol, 98%). If necessary the oil could be purified by filtration over aluminia (CH_2Cl_2). ^{1}H-NMR (CD_2Cl_2) δ ppm: 7.46 (s, 2H, $H_{4,6}$), 7.27 (s, 1H, H_2), 4.77 (d, J = 10 Hz, 2H, H_{Bz}), 4.70 (m, 2H, $H_{1',1''}$), 4.46 (d, J = 10 Hz, 2H, H_{Bz}), 3.90 and 3.60 (two m, $4H_{total}$, $H_{5',5''}$), 1.96–1.43 (m, 12H,

$H_{2',2',4',2'',3'',4''}$). *Anal. Calcd.* for $C_{18}H_{25}BrO_4$ (385.3): C, 56.11; H, 6.54. *Found*: C, 56.09; H, 6.58.

BORONIC ACID (7)

To a degassed solution of **5** (7.6 g, 20 mmol) in 120 mL of THF at 78°C two equivalents of 1.5 M *t*-butyl lithium (27 mL, 40 mmol) were added dropwise under argon, maintaining the temperature below -70°C. At the end of the addition, the red solution was rapidly transferred via cannula to a degassed solution of $B(OMe)_3$ (4.5 mL, 40 mmol) in 120 mL of THF at -78°C. The resulting solution was stirred under argon for 30 min. After warming the solution to room temperature the solvent and excess $B(OMe)_3$ were removed under reduced pressure. The crude product, dissolved in 150 mL of Et_2O was washed with 100 mL of 5% aqueous HCl solution, then with water. The organic phase was dried over $MgSO_4$, filtered, and evaporated to dryness. The resulting yellow oil (6.7 g, 20 mmol, 100%) was used without further purification.

BRIDGE SYNTHESES VIA SUZUKI COUPLING REACTIONS

*Synthesis of Protected 2-Pyridine Bridge (**8**).* To a degassed solution of 2-bromopyridine (2.9 g, 18.4 mmol) and $Pd(PPh_3)_4$ (0.751 g, 0.65 mmol) in 300 mL of toluene, a degassed 2 M aqueous solution of Na_2CO_3 (150 mL), and a degassed solution of **7** (6.7 g, 20 mmol) in 75 mL of methanol was added. The vigorously stirred suspension was refluxed under argon for 12 h. After cooling to room temperature, the reaction mixture was extracted twice with 250 mL of 2 M aqueous Na_2CO_3 containing 50 mL of concentrated NH_4OH. The organic phase was dried over $MgSO_4$, filtered, and the solvent was removed under reduced pressure. Purification by column chromatography over alumina (CH_2Cl_2) afforded **8** as a colorless oil (4.87 g, 12.9 mmol, 70%). ^{1}H-NMR (DMSO-d_6) δ ppm: 8.69 (d, J = 5 Hz, 1H, H_α py), 7.89 (s, 2H, $H_{2,6}$ xyl), 7.74 (t, J_1 = 5 Hz, J_2 = 4 Hz, J_3 = 1 Hz, 2H, $H_{\beta,\delta}$ py), 7.46 (s, 2H, H_4 xyl), 7.24 (m, 1H, H_γ py), 4.87 (d, J = 12 Hz, 2H, H_{Bz}), 4.74 (m, 4H, $H_{1',1''}$), 4.58 (d, J = 12 Hz, 2H, H_{Bz}), 3.91–3.56 (two m, 4H, $H_{5',5''}$), 1.85–1.60 (m, 12H, $H_{2',2'',3',3'',4',4''}$). *Anal. Calcd.* for $C_{23}H_{29}NO_4$ (383.5): C, 72.03; H, 7.62. *Found*: C, 71.82; H, 7.74.

Synthesis of Protected 3-Pyridine Bridge (**9**). The procedure described for the preparation of **8** was followed using the following quantities: 3-bromopyridine (3.6 g, 22.7 mmol) and $Pd(PPh_3)_4$ (0.939 g, 0.81 mmol) in 375 mL of toluene, 2 M aqueous Na_2CO_3 (190 mL, degassed), and **7** (8.5 g, 25 mmol) in 100 mL of degassed methanol. Reflux time: 11 h. Purification by column chromatography over alumina (CH_2Cl_2) afforded **9** (8.4 g, 22 mmol, 89%) as a colorless oil. ^{1}H-NMR (DMSO-d_6) δ ppm: 8.86 (d, J = 2 Hz, 1H, $H_{\alpha'}$ py), 8.57 (dd, J_1 = 4.5 Hz, J_2 = 2 Hz, 1H, H_α py), 8.04 (dd, J_1 = 5 Hz, J_2 = 2 Hz, 1H, H_γ py), 7.57 (s, 2H, $H_{2,6}$ xyl), 7.48 (dd, J_1 = 4.5 Hz, J_2 = 5 Hz, 1H, H_β py), 7.39 (s, 1H, H_4 xyl),

4.74 (d, J = 10 Hz, 2H, H_{Bz}), 4.72 (m, 2H, $H_{1',1''}$), 4.52 (d, J = 10 Hz, 2H, H_{Bz}), 3.87–3.40 (two m, 4H, $H_{5',5''}$), 1.85–1.40 (m, 12H, $H_{2',2'',3',3'',4',4''}$). *Anal. Calcd.* for $C_{23}H_{29}NO_4$ (383.5): C, 72.03; H, 7.62. *Found*: C, 72.23; H, 7.48.

2(3',5'-bis(Hydroxymethyl)phenyl)pyridine) Bridge (**10**). The protected 2-pyridine bridge **8** (1.55 g, 4 mmol) was dissolved in 50 mL of absolute ethanol, degassed, and the PPTS catalyst (82 mg, 0.32 mmol) was added. The stirred solution was refluxed under argon for 11.5 h. After cooling to ambient temperature, the solvents were removed *in vacuo*. The yellow oil was taken in 50 mL of CH_2Cl_2 and washed with water and 50 mL of a saturated aqueous NaCl solution. The aqueous phases were repeatedly washed with 50 mL of CH_2Cl_2 as the product was sparingly soluble in dichloromethane. The combined organic layers were dried over $MgSO_4$, filtered, and evaporated to dryness. A colorless oil of **10** (600 mg, 2.8 mmol, 70%) was isolated after filtration over silica gel (CH_2Cl_2, 5% MeOH). The product was used without further purification for the next step. ^{1}H-NMR (DMSO-d_6) δ ppm: 8.65 (dd, J_1 = 1 Hz, J_2 = 3 Hz, 1H, H_α py), 7.88 (m, 4H, $H_{\beta,\delta}$ py, $H_{2,6}$ xyl) 7.35 (m, 2H, H_γ py, H_4 xyl), 5.27 (t, J_1 = 12 Hz, J_2 = 6 Hz, 2H, OH), 4.56 (d, J = 6 Hz, 4H, H_{Bz}).

3-(3',5'-bis(Hydroxymethyl)phenyl)pyridine Bridge (**11**). The procedure described for the preparation of **10** via the deprotection method was followed using the following quantities: **9** (8.4 g, 22 mmol), and PPTS (452 mg, 1.76 mmol) in 250 mL of ethanol. Reflux time: 13 h. Filtration over silica gel (CH_2Cl_2, 5% MeOH) afforded **11** as a yellow oil (3.5 g, 16 mmol, 74%) which was used without further purification for the next step. ^{1}H-NMR (DMSO-d_6) δ ppm: 8.87 (s, 1H, $H_{\alpha'}$ py), 8.57 (d, J = 4 Hz, 1H, H_α py), 8.06 (d, J = 8 Hz, H_γ py), 7.51 (m, 1H, H_β py), 7.51 (s, 2H, $H_{2,6}$ xyl), 7.35 (s, 1H, H_4 xyl), 6.54 (br. s, 2H, OH), 4.57 (s, 4H, H_{Bz}).

BRIDGE SYNTHESIS VIA ORGANOTIN COUPLING REACTIONS

2-(3',5'-bis(Hydroxymethyl)phenyl)pyridine Bridge (**10**). A degassed mixture of 2-trimethylstannylpyridine **14** (630 mg, 2.6 mmol), bromo-3,5-bis(hydroxymethyl)-benzene **4** (500 mg, 2.3 mmol), and $PdCl_2(PPh_3)_2$ (81 mg, 0.12 mmol) in 10 mL of distilled dioxane was refluxed under argon for 25 h. The volume of the crude mixture was reduced to 5 mL, then filtered over a column of alumina (CH_2Cl_2, 0–5% MeOH) to afford **10** (380 mg, 1.77 mmol, 76%) as a colorless oil. This compound was characterized by comparison with data from the product synthesized via the Suzuki cross coupling method described above.

3-(3',5'-bis(Hydroxymethyl)phenyl)pyridine Bridge (**11**). The reaction procedure described for the preparation of **10** was followed using the following quantities: 3-trimethylstannylpyridine **15** (11.82 g, 48.8 mmol), bromo-3,5-bis(hydroxymethyl)-benzene **4** (9.29 g, 43.2 mmol), and $PdCl_2(PPh_3)_2$ (1.52 g, 2.16 mmol) in 85 mL

of distilled dioxane. After 23 h under reflux, 1.52 g (48.8 mmol) of $PdCl_2(PPh_3)_2$ were added to the reaction mixture. After an addition 5 h under reflux, the volume of the black mixture was reduced to 10 mL under reduced pressure. A pale yellow oil of **11** (6.8 g, 31.9 mmol, 74%) was isolated after filtration over a column of alumina (CH_2Cl_2, 2% MeOH). This compound was characterized by comparison with data from the product synthesized via the Suzuki cross coupling method described above.

2(3′,5′-bis(Chloromethyl)phenyl)pyridine (**12**). To a degassed suspension of **10** (40 mg, 0.18 mmol) in 10 mL of CH_2Cl_2, thionyl chloride (0.5 mL, 5.4 mmol) and two drops of DMF were added. After stirring under argon for 3 h, the solvents were removed under reduced pressure. The crude product was taken in 75 mL of CH_2Cl_2 and extracted with 15 mL of H_2O containing several drops of triethylamime (pH 10). The organic layer was dried over $MgSO_4$, filtered, and evaporated to dryness. Filtration over silica gel (CH_2Cl_2/Hexane: 9/1) afforded a white solid (42 mg, 0.16 mmol, 90%). ^{1}H-NMR ($CDCl_3$) δ ppm: 8.70 (s, 1H, H_α py), 7.98 (d, J = 1.6 Hz, 2H, $H_{2,6}$ xyl), 7.78 (m, 2H, $H_{\beta,\delta}$ py), 7.49 (s, 1H, H_4 xyl), 7.28 (m, 1H, H_γ py), 4.67 (s, 4H, CH_2 xyl). Melting point: 65–67°C. *Anal. Calcd.* for $C_{13}H_{11}NCl_2 \cdot 1/3C_6H_{14}$ (280.88): C, 64.14; H, 5.62; N, 4.99. *Found*: C, 64.13; H, 5.45; N, 4.45.

3-(3′,5′-bis(Chloromethyl)phenyl)pyridine (**13**). The reaction procedure described for the preparation of **12** was followed using the following quantities: **11** (400 mg, 1.8 mmol) in 100 mL of CH_2Cl_2, thionyl chloride (2 mL, 21.6 mmol), one drop of DMF. Reaction time: 30 min. The crude crystalline product **13** (445 mg, 1.77 mmol, 98%) was pure by TLC and used without further purification. If necessary, the product could be purified by filtration over silica gel (CH_2Cl_2, 10% MeOH). ^{1}H-NMR ($CDCl_3$) δ ppm: 8.84 (d, J = 2 Hz, 1H, $H_{\alpha'}$ py), 8.63 (d, J = 4 Hz, 1H, H_α py), 7.88 (dd, J_1 = 4.5 Hz, J_2 = 2 Hz, 1H, H_γ py), 7.56 (s, 2H, $H_{2,6}$ xyl) 7.47 (s, 1H, H_4 xyl), 7.37 (dd, J_1 = 4 Hz, J_2 = 4.5 Hz, 1H, H_β py), 4.66 (s, 4H, $ArCH_2Cl$). *Anal. Calcd.* for $C_{13}H_{11}NCl_2$ + 1.5 H_2O (279.15): C, 61.93; H, 4.40; N, 5.55. *Found*: C, 61.48; H, 4.35; N, 5.32. Melting point: 124–126°C.

2-(3′,5′)-bis(Bromomethyl)phenyl)pyridine (**18**). A solution of **10** in 10 mL of 48% aqueous HBr and 5 mL of acetic acid was heated at 40°C for 20 h. The solution was cooled, neutralized with Na_2CO_3, and washed twice with 20 mL of CH_2Cl_2. The combined organic phases were dried over $MgSO_4$, filtered, and evaporated to dryness. The crude product was further dried by azeotrope distillation with benzene. Filtration over a short column of silica gel (CH_2Cl_2) afforded **18** (25 mg, 0.073 mmol, 31%) as a crystalline solid. ^{1}H-NMR ($CDCl_3$) δ ppm: 8.70 (d, J = 4 Hz, 1H, $H_{\alpha'}$ py), 7.96 (s, 2H, $H_{4,6}$ xyl), 7.76 (m, 2H, $H_{\beta,\delta}$ py), 7.48 (s, 1H, H_2 xyl), 7.28 (m, 1H, H_γ py), 4.55 (s, 4H, $ArCH_2Br$). *Anal. Calcd.* for $C_{13}H_{11}Br_2N$ +

1/6 C_6H_6 (354.06): C, 47.79; H, 3.42; N, 3.96. *Found*: C, 47.28; H, 3.11; N, 3.85. Melting point: 112–114°C.

BRIDGING REACTIONS

Synthesis of **19**. A solution of hexaphenol **2** (0.792 g, 2.16 mmol) and **16** (1.8 g, 7.15 mmol) were dissolved in 100 mL of degassed DMF and added, under argon, over 27 h to a vigorously stirred suspension of Cs_2CO_3 (11.9 g, 36 mmol) in 250 mL of degassed DMF at 70°C. The mixture was stirred for an additional 15 h at 70°C. The solvent was removed by distillation under reduced pressure. The crude product was taken in 400 mL of CH_2Cl_2 and extracted with 400 mL of water. The aqueous layer was washed twice with 300 mL of CH_2Cl_2. The combined organic phases were dried over $MgSO_4$, filtered, and evaporated to dryness. The purified product (column chromatography over silica gel/CH_2Cl_2) was dissolved in 75 mL of THF. The solvent was removed under reduced pressure. This process was repeated twice to afford beige crystalline **19** (500 mg, 0.55 mmol, 28%). This compound was characterized by comparison with literature data [29].

Synthesis of **20**. The reaction procedure for the preparation of **19** was followed using the following quantities: hexaphenol **2** (437 mg, 1.3 mmol) and **18** (1.77 g, 5.2 mmol) in 130 mL of degassed DMF, and Cs_2CO_3 (7.6 g, 23.4 mmol) in 350 mL of degassed DMF at 70°C. Addition time: 18.5 h followed by an additional 15 h of vigorous stirring under argon at 70°C. Purification by column chromatography over alumina (CH_2Cl_2) afforded the yellow crystalline product **20** (184 mg, 0.18 mmol, 14%). ^{1}H-NMR ($CDCl_3$) δ ppm: 8.55 (d, J = 4.7 Hz, 3H, H_α py), 8.01 (s, 6H, $H_{2,6}$ and 1H, DMF), 7.55 (m, 6H, $H_{\beta,\delta}$ py), 7.13 (m, 6H, H_4 xyl, H_γ py), 6.53 (s, 6H, ArH CTV), 5.24 (d, J = 13 Hz, 6H, $ArCH_2$ xyl), 5.05 (d, J = 13 Hz, 6H, $ArCH_2$ xyl), 4.40 (d, J = 13.6 Hz, 3H, $ArCH_2$ CTV), 3.20 (d, J = 13.6 Hz, 3H, $ArCH_2$ CTV), 2.91 (d, J = 14.1 Hz, 6H, CH_3 DMF). *Anal. Calcd.* for $C_{63}H_{52}N_4O_7$ (977.14), i.e, product **20** + DMF: C, 77.45; H, 5.36; N, 5.73. *Found*: C, 77.36; H, 5.35; N, 5.46. Melting point: 207–208°C. Mass spectroscopy: *Calcd.* for $C_{60}H_{45}N_3O_6$: 904.0. *Found*: 904.2 (47%), 180.1 (100%) FAB positive I = 6.9 V.

Synthesis of **21**. The reaction procedure for the preparation of **19** was followed using the following quantities: hexaphenol **2** (0.290 g, 0.8 mmol) and **13** (0.8 g, 3.2 mmol) in 150 mL of degassed DMSO, and Cs_2CO_3 (3.9 g, 11.9 mmol) in 300 mL of degassed DMSO at 80°C. Addition time: 25 h followed by an additional 14 h of vigorous stirring under argon at 80°C. Column chromatography over silica gel (CH_2Cl_2, 1% MeOH) afforded crystalline **21** (289 mg, 0.32 mmol, 40%). ^{1}H-NMR (DMSO-d_6) δ ppm: 8.68 (d, J = 2 Hz, 3H, $H_{\alpha'}$ py), 8.46 (dd, J_1 = 5 Hz, J_2 = 2 Hz, 3H, H_α py), 8.01 (s, 6H, H_4 xyl), 7.78 (d, 3H, J = 8 Hz, H_γ py), 7.56 (s, 3H, $H_{2,6}$ xyl), 7.20 (dd, J_1 = 5 Hz, J_2 = 8 Hz, 3H, H_β py), 6.91 (s, 6H, ArH CTV), 5.75 (s, 12H, $ArCH_2$ xyl), 4.47 (d, J = 14 Hz, 3H, $ArCH_2$ CTV), 3.38 (d, J =

14 Hz, 3H, $ArCH_2$ CTV). Melting point: 265–267°C. Mass spectroscopy: *Calcd.* for $C_{60}H_{45}N_3O_6$: 904.0. *Found*: 904.1 (100%) FAB positive I = 2.4 V.

Synthesis of **23**. A suspension of hexaphenol **2** (79 mg, 0.22 mmol), 6-bromomethyl-2,2′-bipyridine **22** (6.43 mg, 2.58 mmol), and potassium carbonate (547 mg, 6.96 mmol) in 30 mL of DMF was stirred under argon at 60°C for 21 h. After removing the solvent *in vacuo*, the residue was taken in CH_2Cl_2 and washed twice with 100 mL of H_2O. The organic layer was dried over $MgSO_4$, filtered, and evaporated to dryness. Purification by column chromatography over alumina (CH_2Cl_2, 1% MeOH), followed by slow crystallization in CH_2Cl_2 and several drops of methanol afforded white needles of **23** (216 mg, 0.157 mmol, 71%). ^{1}H-NMR 400 MHz ($CHDCl_2$) δ ppm: 8.57 (ddd, $J_{3'-6'}$ = 1.0 Hz, $J_{4'-6'}$ = 1.8 Hz, $J_{5'-6'}$ = 4.7 Hz, 6H, $H_{6'}$), 8.35 (dt, $J_{3'-6}$ = 1.0 Hz, $J_{3'-5'}$ = 1.0 Hz, $J_{3'-4'}$ = 7.8 Hz, 6H, $H_{3'}$), 8.27 (d, J_{3-4} = 7.85 Hz, 6H, H_3), 7.76 (t, J_{3-4} = 7.85 Hz, J_{4-5} = 5.7 Hz, 6H, H_4), 7.62 (td, $J_{4'-t'}$ = 1.8 Hz, $J_{4'-5'}$ = 7.75 Hz, $J_{3'-4'}$ = 7.8 Hz, 6H, $H_{4'}$), 7.53 (d, J_{4-5} = 7.75 Hz, 6H, H_5), 7.21 (ddd, $J_{3'-5'}$ = 1.0 Hz, $J_{5'-6'}$ = 4.7 Hz, $J_{4'-5'}$ = 7.75 hz, 6H, $H_{5'}$), 6.99 (s, 6H, $ArCH_2$ CTV), 5.24 (s, 12H, $ArCH_2$ xyl), 4.71 (d, J = 13.75 Hz, 3H, $ArCH_2$ CTV), 3.49 (d, J = 13.75 Hz, 3H, $ArCH_2$ CTV). *Anal. Calcd.* for $C_{87}H_{66}N_{12}O_6$ (1375.6): C, 75.97; H, 4.84; N, 12.22). *Found*: C, 75.78; H, 4.97; N, 11.99). Melting point: 120–121°C. Mass spectroscopy: *Calcd.* for $C_{87}H_{66}N_{12}O_6$: 1375.6. *Found*: 1375.2 (90%); 1207.2 (32%); 1037.1 (23%); 869.1 (7%); 699.0 (8%); 529.0 (8%); 338.1 (100%) FAB positive$I$ = 4.4 V.

3. Results and Discussion

3.1. Strategies

Two different approaches could be envisioned to attach binding groups to the CTV derivatives. The usually 'low' yield of the triple cyclization reaction may be placed at the end of the synthesis or at the beginning of the synthesis, as represented in Figure 4.

If functionalized bridges are available on a large scale, ending the synthesis with the cyclization should afford the target compound on a larger scale (Strategy A). However, this approach will be limited to the controlled synthesis of symmetrically substituted ligands, as the use of different bridges in the same high dilution reaction would lead to random mixtures of compounds. Strategy B could be used for the synthesis of reactive CTV derivatives (e.g. Z = Br) and the scope of the further functionalization would be broadened as it will allow the introduction of functional groups which are not compatible with the cyclization conditions. The last approach available, not depicted, would be the direct connection of the binding groups to the hexaphenol which will afford six coordinating sites arranged around the cavity of the CTV. Syntheses of ligands, with pyridines as binding groups, involving the first strategy have been used, together with the direct attachment of ligands to the CTV.

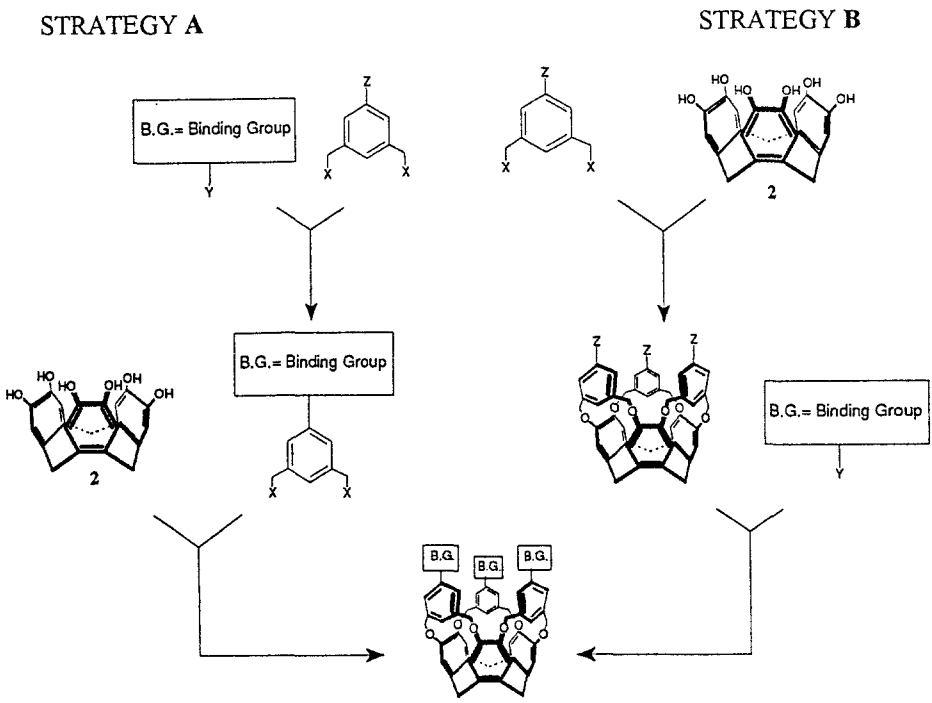


Fig. 4. Two strategies for arranging binding sites around cyclotriveratrylene.

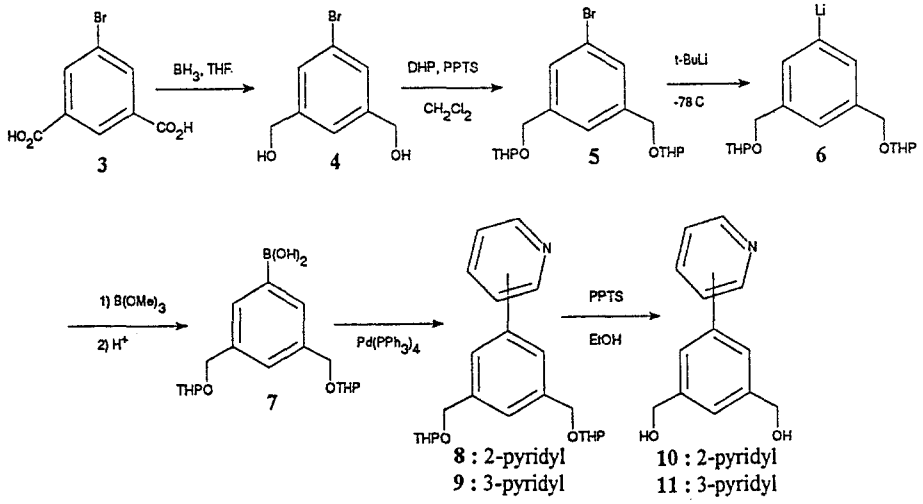


Fig. 5. Synthesis of functionalized bridges for expanded CTVs.

3.2. SYNTHESIS OF THE BRIDGING UNITS

The pyridyl *m*-xylene bridges were synthesized according to the reaction scheme in Figure 5. The 5-bromoisophthalic acid **3** [31] was reduced to the corresponding

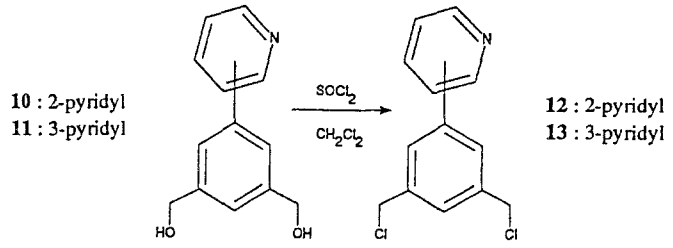


Fig. 6. Synthesis of substituted α, α'-dichloro *m*-xylenes.

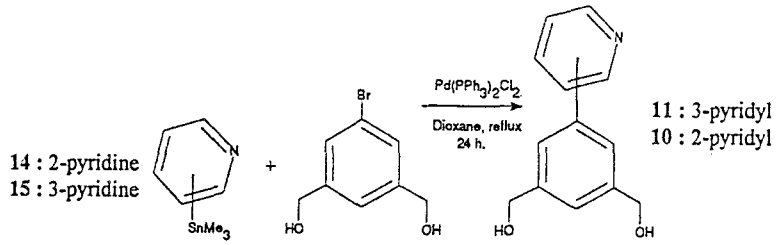


Fig. 7. Alternate route to functionalized bridges via organotin intermediates.

diol **4** by refluxing a solution of **3** in tetrahydrofuran (THF) for 4 h in the presence of an excess of BH_3·THF complex. Before metallation, the diol **4** was protected with dihydropyran in the presence of pyridinium-*p*-toluene sulfonate (PPTS) as catalyst to afford **5** in 98% yield.

As the metallation of **5** using magnesium to form a Grignard reagent was unsuccessful due to lack of reaction of **5** with magnesium, we followed the previously reported [32] efficient preparation of aryl boronic acids via lithio derivatives. A solution of **5** in THF at -78°C was treated with two equivalents of *t*-butyllithium to generate a red solution of **6**. The immediate quenching of **6** with $B(OMe)_3$, afforded the desired boronic acid **7** in 100% yield after hydrolysis and rapid acid and base extraction. It should be noted that **7** was obtained quantitatively only when working with less than 20 mmol of **5**. The Suzuki coupling [33] of bromopyridines with crude **7** in the presence of $Pd(PPh_3)_4$ and 2 M aqueous Na_2CO_3 afforded **8** and **9** in yields of 70 and 89%, respectively.

The protecting groups were removed in refluxing ethanol (PPTS, 40 h). As shown in Figure 6, the corresponding dichlorides **12** and **13** were obtained by treatment of the diols in dichloromethane with an excess of $SOCl_2$ and triethylamine (TEA). For some reason, the dichloride **12** did not react as expected in the cyclization reactions described below, and the corresponding dibromide had to be prepared by treatment of the diol under the usual aqueous HBr conditions to afford the dibromide **18**.

Due to the limitation of the metal/halogen exchange reaction used for the preparation of the lithio derivatives **6** (much lower yields when working with more than 20 mmol), we have developed a quicker, general method for the preparation of the

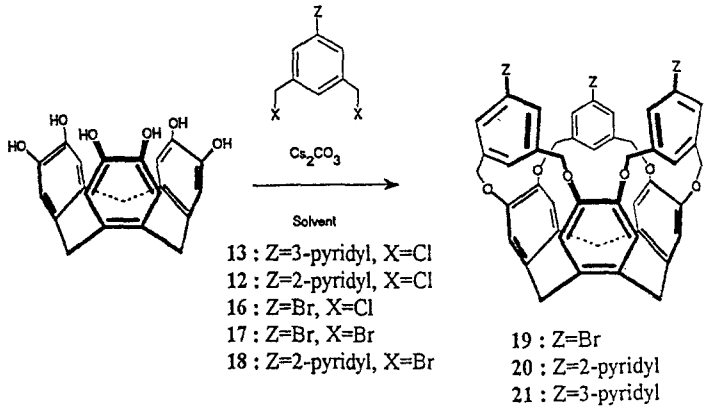


Fig. 8. General synthetic scheme of the formation of expanded CTVs.

pyridyl-substituted xylenes. As depicted in Figure 7, the diols **10** and **11** are easily prepared by direct coupling of the arylbromide **4** and the subsequent trimethyl stannylpyridine derivative **14** or **15** [34], in yields of 74 and 76%, respectively.

Although the yields of the coupling reactions [35] are somewhat lower than those obtained under 'Suzuki' conditions, this method is much shorter than the original method. Furthermore, the overall yields of these syntheses are higher and no problems are encountered when running the reactions on larger scales.

3.3. TRIPLE CYCLIZATION REACTIONS

In order to minimize polymer formation, the bridging reactions, according to the general equation in Figure 8, were carried out in dilute conditions by the slow addition (over 25 h) of **2** and 3.3 equivalents of the subsequent bridge [36] to a suspension of an 18-fold excess of Cs_2CO_3 in DMSO [37] or DMF at 80°C. After purification by column chromatography the tribridged compounds **19–21** were isolated in yields listed in Table I; they strongly depend on the nature of the solvent and the type of leaving group used, Cl or Br.

Surprisingly, when using the bridging reaction with 5-bromo-1,3-bis(halomethyl)benzene as a test reaction, better yields were obtained with chlorine as a leaving group than with bromine. From literature data, the third cyclization seems to require a longer reaction time, probably because of the steric hindrance around the catecholate oxygen after the first two macrocycles have been closed. The dichloride bridge being more stable than the dibromide in the presence of a base like Cs_2CO_3, the stoichiometric bridge/hexaphenol ratio will be less time dependent in the case of the dichloride derivative. Concerning the pyridyl-xylene derivatives, the difference between the reactivity of **12**, **13** and **18** cannot yet be explained; however, in other experiments such as free radical bromination of 5-(3-pyridyl) *m*-xylene and 5-(2-pyridyl) *m*-xylene with *N*-bromosuccinimide, we have observed a similar difference

TABLE I.

Entry	Bridge	Solvent	T (°C)	Product (yield)
1	**16**	DMF	70	**19** (28%)
2	**16**	DMSO	80	**19** (42%)
3	**17**	DMF	70	**19** (22%)
4	**18**	DMF	70	**20** (14%)
5	**12**	DMSO	80	**20** (0%)
6	**13**	DMSO	80	**21** (40%)
7	**13**	DMF	70	**21** (0%)

DMSO (dimethylsulfoxide): purified according to reference [37].
DMF (*N,N*-dimethylformamide): commercial grade dried over 4 Å molecular sieves.

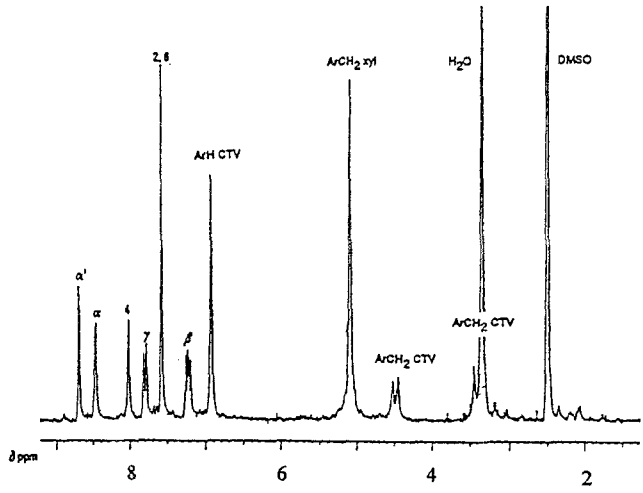


Fig. 9. ^{1}H-NMR (200 MHz) of the tripod **21**.

in reactivity depending on the position of the nitrogen atom within the pyridine ring.

The expanded CTV derivatives obtained have been characterized by the usual techniques, ^{1}H-NMR affording the best evidence for the C_{3v} symmetry of the tripods in solution. For example, in the case of **21**, the AB pattern (J_{AB} = 14 Hz) at 4.49 and 3.28 ppm and the integration ratios for the pyridine and CTV protons observed in the ^{1}H-NMR at 200 MHz, shown in Figure 9, confirms that the isolated product corresponds to a tribridged CTV ligand. The AB pattern indicates that the threefold symmetry axis existing in this type of CTV derivative [29] has been conserved.

The unambiguous structure of **21** has been proved by X-ray crystallographic measurements [38].

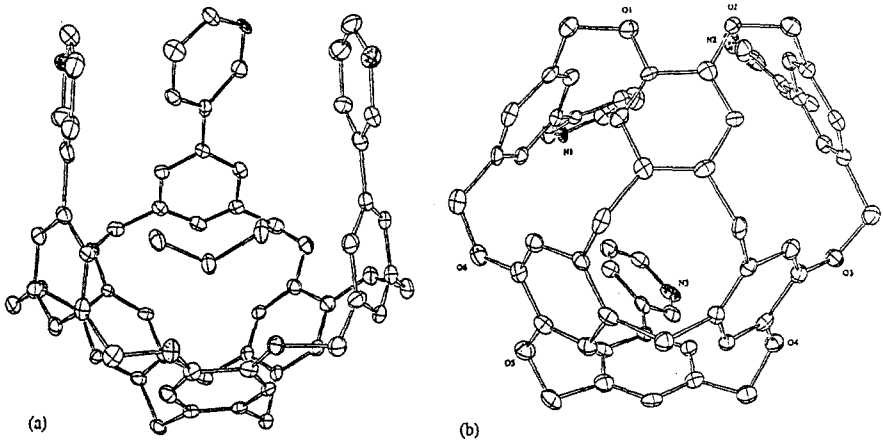


Fig. 10. Ortep drawings of **21**: (a) side view with methylene chloride guest; (b) bottom view of free ligand.

3.4. CRYSTAL STRUCTURE OF TRIPOD **21**

Colorless crystals of the tripod **21**[1] were obtained after several days in the absence of light by vapor diffusion of a hexane/methanol (one drop) layer through a dichloromethane/methanol (two drops) solution of **21**. In contrast to the previously reported [29] crystal structure of a xylene bridged CTV in which only two of the bridges point upward from the cavity whereas the third xylene bridge is bent outside the cavity, the crystal structure of **21** (Figure 10), shows that all three xylene bridges are oriented upward from the CTV cavity. From calculations [29] it appears that the energy difference between different bridge conformations is small (< 1 kcal). The pyridine rings are oriented so as to minimize the global dipole of **21** and the interactions between the three lone pair electrons of the nitrogens. The conformation adopted by ligand **21** should be primarily due to this type of weak interaction. The presence of the dichloromethane guest within the hydrophobic cavity may also favor this conformer in the solid state. A close contact is observed between the chlorine atoms and the uppermost xylene carbon of two of the bridges.

The hydrophobic cavity is quite large, on the order of 9.5 Å in diameter. A close contact between the hydrogen atoms of the CH_2Cl_2 guest and the π cloud of one xylene bridge may exist but the R factor of the structure does not allow for estimation of the H$\cdots\pi$ distance. As has been previously observed for an inclusion complex of methylene chloride in CTV [29], the CH_2Cl_2 guest is disordered in the crystal structure. The three bridges lean slightly towards one another which results in a smaller distance (~6.5 Å) between the pyridines. The tripod **21** is a terpyridine analogue with three electronically independent pyridine rings. Two molecules of this terpyridine analogue are able to coordinate octahedral transition metal cations such as cobalt(II), each subunit occupying opposite faces of the

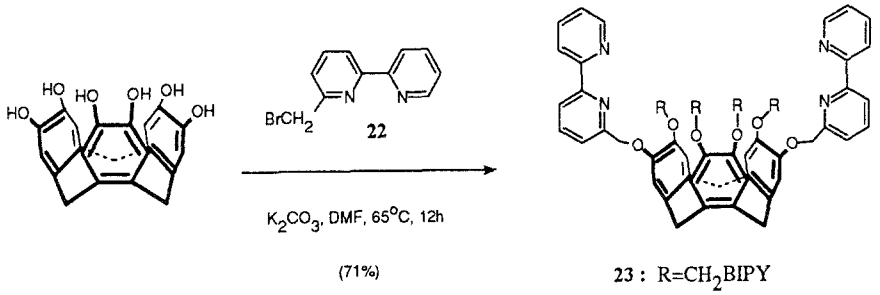


Fig. 11. Direct connection of binding sites to the cyclotriveratrylene matrix.

octahedron [39]. The corresponding tripod ligand with the 2-pyridine bridges is of interest because the nitrogen atoms would be oriented towards the CTV cavity. This orientation would increase the number of lone electron pairs, due to the oxygens around the CTV matrix, within the tripod's hydrophobic cavity. Furthermore, it should facilitate the coordination of metal centers or organic substrates capable of forming hydrogen bonds.

3.5. Direct connection of binding groups to the CTV matrix

As mentioned before, the CTV could also be used as a matrix for the direct preorganization of binding sites, without expansion of the hydrophobic cavity. Starting from the hexaphenol **2**, up to six oxygen atoms can undergo an alkylation with an appropriate functionalized binding group. Due to other research projects in progress in our group, a consequent amount of 6-bromomethyl-2,2′-bipyridine **22** [40] was available to carry out the reaction represented in Figure 11.

Using a stoichiometric amount of **22**, i.e. six equivalents, afforded a mixture of mono- to hexa-alkylated species from which the ligand **23** was isolated by crystallization. The hexa-alkylation process could be enhanced reacting a twofold excess of **22** with the hexaphenol. The ligand CTV(bipy)$_6$ was then isolated in 71% yield. Again, the ^{1}H-NMR provided evidence for the hexasubstitution and the C_{3v} symmetry of the isolated ligand. The compound obtained can accommodate either three square planar (copper(II)) or tetrahedral (copper(I)) transition metals, or, two octahedral transition metals (nickel(II)). The corresponding complexes are of interest in order to study, metal–metal interactions either by electrochemistry, EPR or photochemistry [39].

4. Conclusion

Cyclotriveratrylene, by analogy with calixarenes, cyclodextrins and a few other cyclophane-type compounds, can be used as a matrix to preorganize coordination sites for transition metals, either at the edge of the rigid structure, or around an expanded CTV's cavity. Achiral 2- and 3-pyridine tripod ligands have been synthesized together with a bipyridine multichelate. Studies of these new ligands, both by

UV-visible spectrophotometry and electrochemistry, regarding their coordination to transition metals and the properties of the corresponding complexes are under progress, as well as the extension of the synthetic method described above to the preorganization of other binding groups around the cyclotriveratrylene.

Acknowledgements

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Notes

[1]X-Ray Experimental Data for **21**·$3CH_2Cl_2$·H_2O: Molecular weight: 1352.3; Crystal system: monoclinic; a (Å): 25.735 (9); b (Å): 18.636 (6); c (Å): 12.994 (4); β (deg): 102.68 (2); Volume (Å^3): 6079.9; z: 4; D_{calc} (g cm^{-3}): 1.477; Wavelength (Å): 1.5418; μ (cm^{-1}): 43.892; Space group: $P2_1/n$; Diffractometer: Philips PW 1100/16; Crystal dim. (mm): 0.10 × 0.22 × 0.33; Temperature: -100°C; Radiation: CuK_α graphite monochromated; Mode: $\theta/2\theta$ flying step-scan; Scan speed (deg^{-1}): 0.020; Step width (deg): 0.05; Scan width (deg): $1.20 + 0.14 \times \tan(\theta)$; Octants: $\pm h + k + l$; θ min/max (deg): 3.49; Number of data collected: 6536; Number of data with $I > 3\sigma$ (I): 4213; Abs min/max: 0.70/1.35; R (F): 0.107; R_w (F): 0.156; p: 0.08; GOF: 3.180.

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