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Synthesis of terpyridine-substituted calix[*n*]arenes

Junmin Liu [a], Markus Tonigold [a], Björn Bredenkötter [a], Tobias Schröder [b], Jochen Mattay [b,*], Dirk Volkmer [a,*]

[a] Ulm University, Institute of Inorganic Chemistry II, Materials and Catalysis, Albert-Einstein-Allee 11, D-89081 Ulm, Germany
[b] Bielefeld University, Department of Chemistry, Universitätsstrasse 25, D-33615 Bielefeld, Germany

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ABSTRACT

Calix[*n*]arenes ($n = 4,5$) comprising 4-(2,2′:6′,2″-terpyridyl)-phenyl substituents at the upper rim were synthesized for the first time, employing Suzuki-type coupling reactions. All calix[*n*]arene derivatives were prepared as cone conformers. The single crystal X-ray structure of *cone*-5,11,17,23-tetra{4-(2,2′:6′,2″-terpyridyl)-phenyl}-25,26,27,28-tetrabutoxycalix[4]arene **4** is analyzed in terms of structural rigidity and potential use of these ligands as novel synthons of cage-type metallosupramolecular assemblies.

1. Introduction

The design and preparation of discrete functional supramolecular compounds is a field of science that has received considerable attention in recent years.[1] Calix[*n*]arenes are a versatile class of macrocyclic compounds that have been studied extensively, both as host materials and as building blocks for the construction of larger molecules or supramolecular assemblies.[2] The most elegant approach, the self-assembly of complementary[3] or self-complementary[4] calix[*n*]arene derivatives, has led to well-defined molecular containers or capsules which are able to include small guest molecules. On the other hand, the 2,2′:6′,2″-terpyridine (terpy) unit represents a highly versatile tridentate ligand in transition metal coordination chemistry,[5] and recently terpy-based metallosupramolecular coordination compounds have been developed as anticancer and antimicrobial agents in the field of biomimetics and medicine.[6] Combining the multiple functions of bis-terpy metal complexes with the structure-directing properties of calix[*n*]arenes thus seems highly rewarding, however, there has been as yet no report on the incorporation of multiple terpy functions into the upper rim of conformationally pre-organized calix[*n*]arenes acting as rigid scaffolds.

We have recently reported on self-assembling metallosupramolecular cages based on cavitand-terpyridine subunits.[7] In contrast to the conformationally rigid resorc[4]arene units described there, the calix[*n*]arene ligands described here are much more flexible, and they can be prepared at various ring sizes and with diverse functional groups attached to the lower rim of the calix[*n*]arene, which could lead to metallosupramolecular cages of topologies and functions largely different from the octahedral ones reported previously.

In this Letter we describe the synthesis of calix[*n*]arene-terpyridines ($n = 4$, 5) by Suzuki cross-coupling reaction of *p*-bromocalix[*n*]arenes with 4′-{4-(Neopentyl glycolatoboron)phenyl}-2,2′:6′,2″-terpyridine **3**. Structural properties of these novel ligands are exemplified by the X-ray crystal structure analysis of *cone*-5,11,17,23-tetra{4-(2,2′:6′,2″-terpyridyl)-phenyl}-25,26,27,28-tetrabutoxycalix[4]arene **4**.

2. Synthesis

Direct synthesis of *p*-*tert*-butylcalix[*n*]arenes and *p*-phenylcalix[*n*]arenes via a 'one-pot' method was reported previously by several groups.[8] For example, Raston and co-workers described an environmentally benign preparation procedure of *para*-substituted calix[*n*]arenes, which involves a rapid and solventless synthesis with low waste formation.[8e] Thus, our initial attempts to synthesize calix[*n*]arene-terpy ligands were based on a similar approach, anticipating that *p*-terpyridyl-phenol condensation with formaldehyde under basic or acidic catalytic conditions might generate a mixture of calix[*n*]arene-terpy derivatives of different ring sizes, which might then be separated chromatographically. However, in our hands all attempts in this direction have failed so far (the major problem being that the condensation reaction proceeds at a very slow rate).

* Corresponding authors. Tel.: +49 521 106 2072; fax: +49 521 106 6920 (J. Mattay); tel.: +49 731 50 23921; fax: +49 731 50 23039 (D. Volkmer).
E-mail addresses: oc1jm@uni-bielefeld.de (J. Mattay), dirk.volkmer@uni-ulm.de (D. Volkmer).

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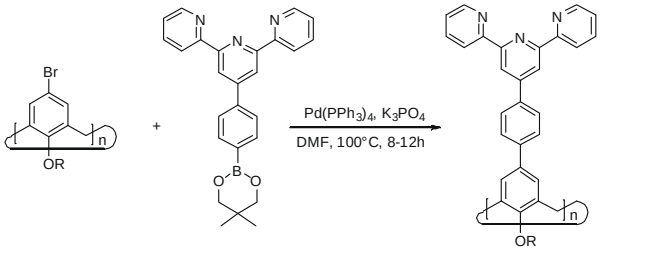

1 n = 4, R = n-butyl
2 n = 4, R = CH_2COOEt
6 n = 5, R = CH_2COO^tBu

3

4 n = 4, R = n-butyl (50%)
5 n = 4, R = CH_2COOEt (60%)
7 n = 5, R = CH_2COO^tBu (60%)

Scheme 1. Synthesis of terpyridine-substituted calix[*n*]arenes **4**, **5**, and **7** by *n*-fold Suzuki-coupling.

As an alternative strategy we resorted to prepare calix[*n*]arenes via a 'classical' Suzuki cross-coupling reaction, starting from *p*-*tert*-butylcalix[*n*]arenes. The following procedure is representative for a successful aryl-aryl cross-coupling reaction. A *p*-bromocalix[*n*]arene is cross-coupled with 4′-{4-(Neopentyl glycolatoboron)phenyl}-2,2′:6′,2″-terpyridine **3** (*n*-times 1.7 equiv) in DMF at 100 °C in the presence of *n*-times 0.03 equiv of $Pd(PPh_3)_4$ and *n*-times 1.7 equiv of K_3PO_4. The reaction is monitored by TLC, and shortly after the bromide calix[*n*]arene has been used up, the reaction mixture is allowed to cool down to room temperature. The product is extracted with $CHCl_3$, washed with water, dried over Na_2SO_4, and finally purified by column chromatography on basic Al_2O_3 using a mixture of CH_2Cl_2 and acetone as eluent.

The *cone*-tetrabromocalix[4]arenes **1**[9] and **2**[10] react with the terpyridylboronic ester **3**[11] in a palladium-catalyzed fourfold Suzuki-coupling reaction leading to the *cone*-calix[4]arene-terpyridines **4** and **5** in 50% and 60% yields, respectively (Scheme 1). The cone conformation of every compound is clearly shown in the signal pattern of the ^{1}H NMR.

Most interestingly, the *p*-bromocalix[5]arene **6**[3e] reacts with 7.5 equiv of **3** in a fivefold Suzuki-coupling to give compound **7** in 60% yield (Scheme 1). The product is of special interest because the structural and supramolecular chemistry of calix[5]arenes hitherto is less well established if compared to other calix[*n*]arenes (with *n* = 4, 6, or 8, respectively). Calix[5]arenes might be used to construct very large icosahedral cages constructed from twelve identical pentagonal subunits, provided that a suitable structurally pre-organized conformer of the calix[5]arene moiety can be prepared. The ^{1}H NMR spectrum (THF-d_8) of **7** shows only two doublets at 5.11 and 3.72 ppm (J = 14.1 Hz) with the integral of 5 each, which can be assigned to the methylene protons of **7** in cone conformation.

The protons of the five $-OCH_2COO^tBu$ groups at the lower rim of the calix[5]arene give rise to two singlets at 4.81 ppm and 1.55 ppm, respectively. All ^{1}H NMR signals of the aryl-terpyridine protons are also clearly observed in the aromatic region (Supplementary data).

2.1. X-ray structure of *cone*-5,11,17,23-tetra{4-(2,2′:6′,2″-terpyridyl)phenyl}-25,26,27,28-tetrabutoxycalix[4]arene (4)

Single crystals of $C_{128}H_{108}N_{12}O_4{\cdot}4CH_3OH{\cdot}2CHCl_3{\cdot}4H_2O$ were obtained by slow diffusion of methanol into a chloroform solution of **4**. X-ray crystallographic analysis reveals that **4** crystallizes in the triclinic space group $P\bar{1}$. The occluded chloroform molecules are rapidly lost upon removal of the crystals from the mother liquor, which leads to rapid aging of crystals.

In the crystal lattice, the calix[4]arene moieties are fixed in the 'flattened cone' (or 'pinched cone') conformation, with two distal benzene rings almost parallel to each other and the other ones almost perpendicular (Fig. 1).

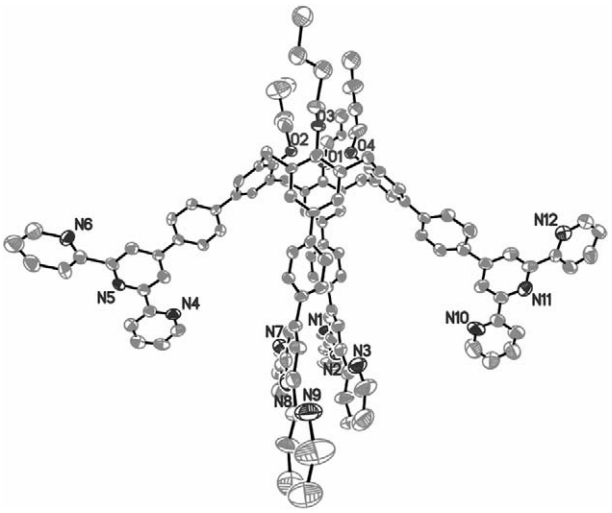

Figure 1. ORTEP plot of the asymmetric unit in **4** (40% probability), hydrogen atoms and occluded solvent molecules are omitted for clarity.

This C_{2v} symmetrical cone conformation is thermodynamically more stable for symmetrically substituted calix[4]arenes than a C_{4v} cone conformation[12] and is usually observed in the solid state.[13] In the unit cell, the cone-shaped molecules of **4** are close packed, building one dimensional chains along the *a*-axis. In each chain, the terpyridine units of **4** point alternately in opposing directions. These one dimensional chains are interconnected via π–π stacking of the peripheral terpyridine units (Fig. 2), forming a two dimensional sheet structure. Adjacent terpyridine units of **4** have close distances between 3.3 and 3.6 Å (Fig. 2), which are the same as for other terpyridines in the solid state (3.0–3.9 Å).[14] Also the torsion angles between the aromatic groups present in **4** are in the normal range for calix[4]arenes and terpyridines.[13,14] The geometry of the 'flattened cone' therefore seems to be unaffected by the π–π stacking of the terpyridine units.

Preliminary investigations on the metal coordination behavior employing ^{1}H NMR titration experiments and electrospray ionization mass spectrometry reveal that calix[4]arene-terpyridine **4** forms a variety of structurally different zinc complexes in polar organic solvents such as acetonitrile, DMF, or DMSO. Among these, octahedral metallosupramolecular cages were identified, but the yield depends on various experimental conditions such as relative concentrations of metal ions and ligands, the type of counter anions being used, and the solvents. In-depth investigations on complex stabilities and guest inclusion properties of the supramolecular complexes formed between the calix[*n*]arene ligands shown here and metal cations are currently underway.

In summary, we demonstrate the synthesis of novel terpyridine-containing calix[*n*]arene ligands intended as structural building blocks for yet-to-explore large metallosupramolecular compounds. Preliminary investigations on multi-component self-assembly of the calix[*n*]arene-based ligands in the presence of metal ions point

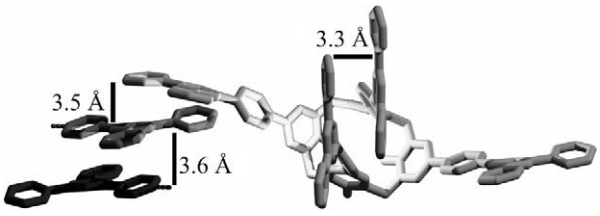

Figure 2. Close distances between adjacent aromatic ring systems.

to a more complex behavior, if compared to the cavitand-based counterparts,[7] which we currently ascribe to their more flexible molecular structures.

3. Experimental

3.1. *cone*-5,11,17,23-Tetra{4-(2,2′:6′,2″-terpyridyl)-phenyl}-25,26,27,28-tetrabutoxycalix[4]arene (4)

A mixture of K_3PO_4 (1.56 g, 0.68 mmol), $Pd(PPh_3)_4$ (139 mg, 12.0 μmol), *cone*-5,11,17,23-tetrabromo-25,26,27,28-tetrabutoxycalix [4]arene **1**[9] (1.02 g, 1.0 mmol), and 4′-{4-(neopentyl glycolatoboron)phenyl-2,2′:6′,2″-terpyridine **3**[11] (2.86 g, 6.79 mmol) in degassed DMF (100 mL) was stirred under argon at 100 °C for 12 h. The reaction mixture was diluted with $CHCl_3$ (800 mL), and the resulting solution was washed with water (2 × 200 mL). The organic layer was dried with Na_2SO_4, the solvent was evaporated, and the residue was purified via dissolution in methanol (100 × 4 mL), leading to precipitation of the crude product as a yellow solid. After column chromatography (basic Al_2O_3; eluent: $CH_2Cl_2 \rightarrow CH_2Cl_2$/acetone 5:1) followed by recrystallization from CH_2Cl_2/methanol 939 mg (0.5 mmol, 50%) analytically pure **4** was obtained as colorless powder. Mp: >300 °C. IR (KBr): $\tilde{\nu}$ 3051.9, 2955.4, 2927.5, 2867.1, 1603.9, 1583.4, 1564.2, 1465.2, 1385.8, 829.9, 790.9, 738.5 cm^{-1}. ^1H NMR (400 MHz, THF-d_8): δ 8.61 (s_{br}, 8H), 8.46 (d, 8H, ^3J = 4.6 Hz), 8.43 (d, 8H, ^3J = 8.1 Hz), 7.70 (dd, 8H, ^3J = 8.1 Hz, ^3J = 7.6 Hz), 7.69 (d, 8H, ^3J = 7.8 Hz), 7.40 (d, 8H, ^3J = 7.8 Hz), 7.21 (s_{br}, 8H), 7.15 (dd, 8H, ^3J = 7.6 Hz, ^3J = 4.6 Hz), 4.70 (d, 4H, ^3J = 13.5 Hz), 4.11 (t, 8H, ^3J = 6.8 Hz), 3.46 (d, 4H, ^3J = 13.5 Hz), 2.12–2.05 (m, 8H), 1.66–1.56 (m, 8H), 1.11 (t, 12H, ^3J = 7.6 Hz). ^{13}C NMR (125 MHz, THF-d_8): δ 156.8, 156.3, 149.8, 149.6, 142.8, 137.0, 136.9, 135.4, 127.9, 127.8, 124.1, 121.3, 118.6, 76.0, 33.4, 32.1, 20.4, 14.6. MS (MALDI-TOF) *m/z*: 1878.1 [M^+]. Anal. Calcd for $C_{128}H_{108}N_{12}O_4$: C, 81.85; H, 5.80; N, 8.95. Found: C, 81.75; H, 5.87; N, 8.91.

Single crystals were obtained by slow diffusion of methanol into a chloroform solution of **4**. *Crystal data* for **4**; $C_{128}H_{108}N_{12}O_4{\cdot}4\text{-}CH_3OH{\cdot}2CHCl_3{\cdot}4H_2O$, M = 2312.84, triclinic system, space group $P\bar{1}$ (no. 2), a = 18.022(4), b = 18.333(4), c = 20.822(4) Å, α = 112.47(3)°, β = 102.09(3), γ = 90.42(3)°, V = 6187(2) Å^3, Z = 2, D_c = 1.244 g cm^{-3}, μ(Mo-Kα) = 0.735 mm^{-1}, λ(Mo-Kα) = 0.71073 Å, T = 190 K, $F(000)$ = 2440, Θ_{max} = 24.15° ($-19 \leqslant h \leqslant 20$, $-20 \leqslant k \leqslant 21$, $-23 \leqslant l \leqslant 23$), 39764 data measured, 18363 unique (R_{int} = 0.148). Final residuals (for 1444 parameters) were R = 0.1113 and R_w = 0.2704 for 3917 reflections with $I \geqslant 2$ (I), and R = 0.3084, R_w = 0.3524, GOF = 0.809 for all 18363 data. Residual electron density was 0.73 and −0.42 e Å^{-3}. Crystallographic data (excluding structure factors) for the structure reported in this Letter have been deposited at the Cambridge Data Centre as supplementary publication no. CCDC 704459 for **4**. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44(1223)336-033, E-mail: deposit@ccdc.cam.ac.uk].

3.2. *cone* -5,11,17,23-Tetra{4-(2,2′:6′,2″-terpyridyl)-phenyl}-25,26,27,28-tetrakis(ethoxycarbonylmethoxy)calix[4]arene (5)

A mixture of $Pd(PPh_3)_4$ (69.5 mg, 6.0 μmol), K_3PO_4 (0.78 g, 0.34 mmol), *cone*-5,11,17,23-tetrabromo-25,26,27,28-tetrakis(ethoxycarbonylmethoxy)calix[4]arene **2**[10] (694 mg, 0.5 mmol) and 4′-{4-(neopentyl glycolatoboron)phenyl-2,2′:6′,2″-terpyridine **3**[11] (1.43 g, 3.39 mmol) in degassed DMF (50 mL) was stirred under argon at 100 °C for 12 h. The reaction mixture was diluted with $CHCl_3$ (400 mL) and the resulting solution was washed with water (2 × 100 mL). The organic layer was dried with Na_2SO_4, the solvent was evaporated and the residue was purified via dissolution in methanol (50 × 4 mL) leading to precipitation of the crude product as a yellow solid. After column chromatography (basic Al_2O_3; eluent: $CH_2Cl_2 \rightarrow CH_2Cl_2$/acetone 4:1) followed by recrystallization from CH_2Cl_2/methanol 832 mg (0.3 mmol, 60%) analytically pure **5** was obtained as colorless powder. Mp: >300 °C; IR (KBr): $\tilde{\nu}$ 3052.3, 2977.7, 2924.5, 1754.3, 1733.9, 1603.7, 1583.6, 1564.6, 1466.9, 1386.2, 1201.5, 1172.5, 1084.0, 830.7, 790.76,738.21 cm^{-1}; ^1H NMR (500 MHz, THF-d_8): δ 8.60 (s, 8H), 8.46 (d, 8H, ^3J = 4.6 Hz), 8.43 (d, 8H, ^3J = 7.9 Hz), 7.68 (dd, 8H, ^3J = 7.9 Hz, ^3J = 7.2 Hz), 7.67 (d, 8H, ^3J = 8.1 Hz), 7.40 (d, 8H, ^3J = 8.1 Hz), 7.21 (s, 8H), 7.13 (dd, 8 H, ^3J = 7.2 Hz, ^3J = 4.6 Hz), 5.19 (d, 4H, ^3J = 13.7 Hz), 4.92 (s, 8H), 4.27 (q, 8H, ^3J = 7.1 Hz), 3.52 (d, 4H, ^3J = 13.7 Hz), 1.35 (t, 12H, ^3J = 7.1 Hz). ^{13}C NMR (125 MHz, THF-d_8): δ 170.6, 157.2, 156.9, 156.4, 149.7, 142.2, 137.2, 136.9, 136.2, 136.1, 128.1, 127.8, 124.1, 121.4, 118.7, 72.4, 61.0, 32.7, 14.7. MS (MALDI-TOF) *m/z*: 2020.0 [M+Na]$^+$, 1998.0 [M^+]. Anal. Calcd for $C_{128}H_{100}N_{12}O_{12}{\cdot}0.7CH_2Cl_2$: C, 75.12; H, 4.97; N, 8.17. Found: C, 75.08; H, 5.18; N, 8.09.

3.3. *cone*-5,11,17,23,29-Penta{4-(2,2′:6′,2″-terpyridyl)-phenyl}-31,32,33,34,35-pentakis(*tert*-butoxycarbonylmethoxy)calix[5] arene (7)

A mixture of K_3PO_4 (978 mg, 4.25 mmol), $Pd(PPh_3)_4$ (86.5 mg, 75 μmol), *cone*-5,11,17,23, 29-pentabromo-31,32,33,34,35-pentakis(*tert*-butoxycarbonylmethoxy)calix[5]arene 6[3e] (745 mg, 0.5 mmol) and 4′-{4-(neopentyl glycolatoboron)phenyl-2,2′:6′,2″-terpyridine 3[11] (1.79 g, 4.25 mmol) in degassed DMF (50 mL) was stirred under argon at 80 °C for 8 h. The reaction mixture was diluted with $CHCl_3$ (400 mL), and the resulting solution was washed with water (100 mL). The organic layer was dried with Na_2SO_4, the solvent was evaporated, and the residue was purified via dissolution in methanol (50 × 4 mL) leading to precipitation of the crude product as a yellow solid. After column chromatography (basic Al_2O_3; eluent: $CH_2Cl_2 \rightarrow CH_2Cl_2$/acetone 2:1) followed by recrystallization from CH_2Cl_2/methanol 791 mg (0.3 mmol, 60%) analytically pure 7 was obtained as colorless powder. Mp: >300 °C. IR (KBr): $\tilde{\nu}$ 3052.9, 2976.6, 2927.9, 1752.4, 1726.3, 1604.3, 1584.1, 1564.6, 1466.5, 1388.5, 1219.7, 1154.0, 1084.1, 831.0, 790.8, 739.2 cm^{-1}; ^1H NMR (400 MHz, THF-d_8): δ 8.41 (d, 10 H, ^3J = 4.1 Hz), 8.29 (s, 10H), 8.24 (d, 10H, ^3J = 7.8 Hz), 7.57 (dd, 10H, ^3J = 7.8 Hz, ^3J = 7.6 Hz), 7.48 (d, 10H, ^3J = 8.1 Hz), 7.40 (s, 10H), 7.36 (d, 10H, ^3J = 8.1 Hz), 7.13 (dd, 10H, ^3J = 7.6 Hz, ^3J = 4.1 Hz), 5.11 (d, 5 H, ^3J = 14.1 Hz), 4.81 (s, 10H), 3.72 (d, 5H, ^3J = 14.1 Hz), 1.55 (s, 45H). ^{13}C NMR (125 MHz, THF-d_8): δ 169.4, 156.9, 156.1, 155.5, 149.6, 149.4, 142.5, 137.1, 136.8, 135.3, 128.5, 128.0, 127.8, 123.9, 118.6, 81.6, 28.5. MS (MALDI-TOF) *m/z* 2676.8 [M+K]$^+$, 2660.8 [M+Na]$^+$, 2638.2 [M^+]. Anal. Calcd for $C_{170}H_{145}N_{15}O_{15}$: C, 77.40; H, 5.54; N, 7.96. Found: C, 77.56; H, 5.61; N 7.79.

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Supplementary data

Supplementary data (synthesis of terpyridine substituted Calix[*n*]arenes) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2009.01.044.

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