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[10] Although oxidation to the [(salen)Co^{III}(acetate)] complexes using HOAc/O$_2$ is the method of choice for the preparation of the monomeric catalysts (see ref. [7d]), this proved impractical with the PAMAM-Co complexes because of the basic amine sites in the dendrimer. The [(salen)Co^{III}(iodide)] complexes obtained by oxidation with I$_2$ have been found to display similar reactivity to the corresponding acetate complexes.[8c]

[11] **4**-Co-PAMAM: IR (KBr): $\tilde{\nu}_{max} = 3339$, 2948, 2864, 1663 (br.), 1609, 1526, 1435, 1253, 1170, 1031, 783; ^{1}H NMR (400 MHz, [D$_6$]DMSO): $\delta = 8.1$ (br., 8H), 7.83 (s, 4H), 7.79 (s, 4H), 7.47 (s, 4H), 7.43 (s, 4H), 7.33 (s, 4H), 7.29 (s, 4H), 3.62 (br. s, 16H), 3.38 (br. s, 12H), 3.10 (br. s, 16H), 2.6 – 2.2 (br., 16H), 1.98 (br., 4H), 1.89 (br., 4H), 1.76 (s, 36H), 1.72 (s, 36H), 1.60 (br. m, 8H), 1.28 (s, 36H); ^{13}C NMR (100 MHz, [D$_6$]DMSO): $\delta = 170.7$, 164.4, 163.7, 162.5, 161.6, 141.9, 141.4, 135.6, 133.0, 132.2, 129.0, 128.5, 121.2, 118.4, 118.2, 69.2, 69.1, 41.2, 38.2, 35.7, 35.5, 33.5, 31.4, 30.3, 30.2, 29.5, 29.4, 24.2.

[12] **1b**: IR (KBr): $\tilde{\nu}_{max} = 3365$, 2950, 2864, 1630, 1611, 1526, 1436, 1254, 1170, 783; ^{1}H NMR (400 MHz, [D$_6$]DMSO): $\delta = 8.00$ (t, $J = 5.6$ Hz, 1H), 7.85 (s, 1H), 7.80 (s, 1H), 7.50 (d, $J = 2.4$ Hz, 1H), 7.43 (d, $J = 2.4$ Hz, 1H), 7.33 (s, 1H), 7.30 (s, 1H), 3.62 (br. s, 2H), 3.35 (s, 2H), 3.10 (br. s, 2H), 3.05 (m, $J = 6.8$ Hz, 2H), 2.00 (br., 2H), 1.91 (br., 2H), 1.76 (s, 9H), 1.60 (br. m, 2H), 1.40 (m, $J = 7.2$ Hz, 2H), 1.32 (s, 9H), 1.28 (m, $J = 7.2$ Hz, 2H), 0.85 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, [D$_6$]DMSO): $\delta = 170.7$, 164.6, 164.0, 162.8, 162.0, 142.2, 141.8, 135.9, 133.2, 132.3, 129.2, 128.7, 122.0, 118.8, 118.6, 69.3, 69.2, 41.4, 38.1, 35.7, 35.5, 33.5, 31.5, 31.2, 30.4, 30.3, 29.6, 29.4, 24.2, 19.5, 13.7. **2**: IR (KBr): $\tilde{\nu}_{max} = 3307$, 2949, 2862, 1658, 1620, 1526, 1435, 1253, 1170, 1030, 783; ^{1}H NMR (400 MHz, [D$_6$]DMSO): $\delta = 8.1$ (br., 4H), 7.82 (s, 2H), 7.78 (s, 2H), 7.47 (s, 2H), 7.43 (s, 2H), 7.31 (s, 2H), 7.27 (s, 2H), 3.62 (br. s, 8H), 3.35 (br. s, 7H), 3.10 (br. s, 8H), 2.6 – 2.2 (br., 8H), 1.98 (br., 4H), 1.89 (br., 4H), 1.76 (s, 18H), 1.72 (s, 18H), 1.60 (br. m, 4H), 1.28 (s, 18H); ^{13}C NMR (100 MHz, [D$_6$]DMSO): $\delta = 171.7$, 165.3, 164.7, 163.5, 162.6, 142.8, 142.4, 136.6, 133.9, 129.9, 129.5, 122.3, 119.4, 119.2, 70.1, 70.0, 42.0, 39.2, 36.6, 36.4, 34.3, 32.3, 31.2, 31.1, 30.4, 30.3, 25.1; MS (FAB) of the corresponding Co^{II} complex: 1456 $[M+Na]^+$ (calcd exact mass: 1433.76).

[13] Experimental procedure for the kinetic experiments: 10 mL vials were charged with a stir bar and 12.5 μmol (referring to Co) catalyst **1b**, **2**, **4**-Co-PAMAM, **8**-Co-PAMAM, or **16**-Co-PAMAM. The catalysts were dissolved in THF (4.00 mL), then *(rac)*-1,2-epoxyhexane (3.00 mL, 25 mmol) and bromobenzene (200 μL; as an internal standard) were added to the dark brown solution. After the mixture had been stirred for 1 h at 4 °C, water (250 μL) was added. Reaction conversion was monitored by GC analysis (HP-5 column) of 20 μL aliquots withdrawn periodically from the reaction mixture.

Structural Characterization of a Cyclohexameric *meta*-Phenyleneethynylene Made by Alkyne Metathesis with In Situ Catalysts**

Ping-Hua Ge, Wei Fu, Wolfgang A. Herrmann,
Eberhardt Herdtweck, Charles Campana,
Richard D. Adams,* and Uwe H. F. Bunz*

Cyclophenyleneethynylenes (CPEs) have recently made a spectacular appearance as a novel class of carbon-rich supramolecular materials.[1, 2] Moore and co-workers have established *meta*-cyclophenyleneethynylenes (*m*-CPEs)[1–3] as tubular discotic liquid crystals[3d] and as porous, hydrogen-bonded, channel-forming organic solids.[4] Channels in *m*-CPEs are formed through a combination of hydrogen bonds and the internal cavities of the hexagonally packed *m*-CPE. However only a low-quality single-crystal X-ray structure of this exciting CPE was obtained[4] and to our surprise, no high-quality X-ray structures of *m*-CPE-derivatives are known.[2b, 5]

In the past CPEs have been made by the Pd/Cu-catalyzed coupling of the Heck – Sonogashira type. Substrates were either a preformed linear oligomer,[3] a half-cycle,[5] or 1-ethynyl-3-halo-substituted benzenes.[6] The latter compounds gave only very low yields of CPEs. Weiss et al.,[7] Fürstner et al.,[8] and our group[9] have reported that alkyne metathesis either with defined carbyne complexes[7, 8] or with in situ catalysts, which are obtained from [Mo(CO)$_6$] and 4-chlorophenol in off-the-shelf 1,2-dichlorobenzene,[10, 11] is an excellent method for preparing saturated and unsaturated ring systems. Herein, we report the synthesis of the new hexameric *meta*-cyclophenyleneethynylenes **2a, b, d** from dipropynylated benzenes **1** by alkyne metathesis as well as the isolation of the corresponding polymers **3a – d** (Scheme 1).[12] The isolated *m*-CPE **2a** and its triosmiumdecacarbonyl complex **4a** have been characterized structurally by single-crystal X-ray diffraction analyses.

The monomers **1** were prepared from the corresponding diiodides[12] by Pd-catalyzed propynylations.[10] Heating **1a**, [Mo(CO)$_6$], and either 4-chlorophenol or 4-trifluoromethylphenol in off-the-shelf 1,2-dichlorobenzene under a slow stream of nitrogen furnishes a mixture of oligomers and

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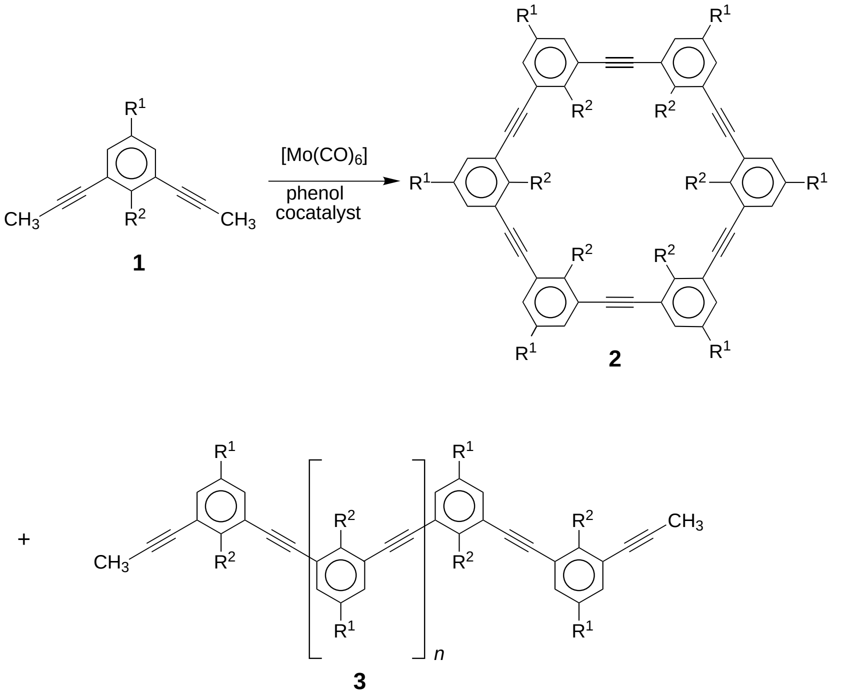

Scheme 1. Synthesis of **2** and **3**. Substituent pattern: **a**: R^1 = *tert*-butyl, R^2 = H; **b**: R^1 = hexyl, R^2 = H; **c**: R^1 = dodecyl, R^2 = H; **d**: R^1 = *tert*-butyl, R^2 = methyl.

polymers. Mass spectrometry of the reaction mixtures showed the occurrence of at least one significant peak, which could be assigned to the respective cyclohexamer (**2a**–**d**). A second molecular ion of considerably decreased intensity was assigned to the corresponding cycloheptamers. While it was easy to establish the *presence* of *m*-CPEs in the reaction mixture,[7c] their separation was tedious, and the rings **2a** and **2b** could only be isolated after repeated thin-layer chromatography on silica gel by using hexane–dichloromethane mixtures. With this protocol **2a** (6%), **2b** (1.2%), and **2d** (0.5%) were obtained from the polymerization mixtures of **1a**, **1b**, and **1d**, respectively. The cycles **2** were unambiguously characterized by mass spectrometry, ^{1}H NMR and ^{13}C NMR spectroscopy, and in the case of **2a** by an X-ray single-crystal diffraction analysis. A suitable specimen of **2a** was grown from dichloromethane–hexane mixtures at room temperature.[13] In the solid state the molecule **2a** contains a center of symmetry and is nearly planar (Figure 1a). The three independent C–C triple bond distances are 1.199(3), 1.203(3), and 1.205(3) Å. They are not significantly different from each other or the C–C triple bond length found in tolane.[14] The crystal contains two equivalents of disordered hexane (not shown in Figure 1) per molecule, as supported by elemental analysis results. One of the hexane molecules passes through the center of each ring and a second one is located between stacks of rings. The rings in **2a** are aligned and stacked in columns[15] to form channels (5 Å × 8 Å; see Figure 1b). At the same time the molecules in these columns are tilted by approximately 60° with respect to the column axis (see Figure 1b). The stacks themselves are oriented to form a herringbone-type pattern, not unusual for large aromatic systems.[16] Interspersed in these stacks and parallel to the *a* axis is the second molecule of hexane solvent, which separates the stacks. Thus despite the fact that we have formally extended channels in this structure (see Figure 1b), the material is not porous in a materials sense, and the hexane is retained in the crystal at ambient temperature. In this regard cycle **2a** resembles decaphenylanthracene prepared by Pascal, Jr., et al.[17]

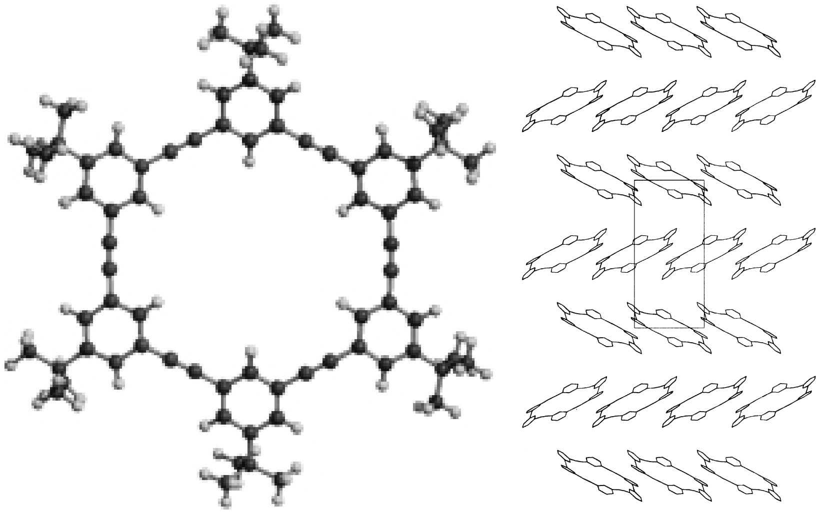

Figure 1. a) Molecular structure of **2a**. b) Packing of **2a** in the crystal; *tert*-butyl substituents and hydrogen atoms are omitted for clarity.

We have found that the alkyne groups in **2a** are active coordination sites for metal atoms. This was demonstrated by the preparation of the triosmiumdecacarbonyl complex **4a**, obtained in 11% yield by treatment of **2a** with $[(MeCN)_2Os_3(CO)_{10}]$. The molecular structure of **4a** shows an $[Os_3(CO)_{10}]$ cluster coordinated, adopting the μ_3-ll (C≡C bond is parallel to an Os–Os bond) coordination mode (Figure 2). Most interestingly, the attachment of the cluster to the CPE leads to a significant disruption of the planarity of the ring. This can be attributed to the induced nonlinearity at the atoms C1-C2-C13 (131(1)°) and C45-C1-C2 (117(1)°), as a consequence of the coordination of the metal atoms and the steric interaction of the CO ligands with the bulky *tert*-butyl groups.

Alkyne metathesis of *meta*-dipropynylated benzenes furnishes macrocycles of the type **2** and the corresponding *meta*-polymers **3**.[12] The high-quality X-ray crystal structure of the hydrocarbon *m*-CPE reveals that **2a** forms a porous solid with infinite elliptical channels. The result demonstrates that nonfunctional but shape-persistent *m*-CPE **2a** does not

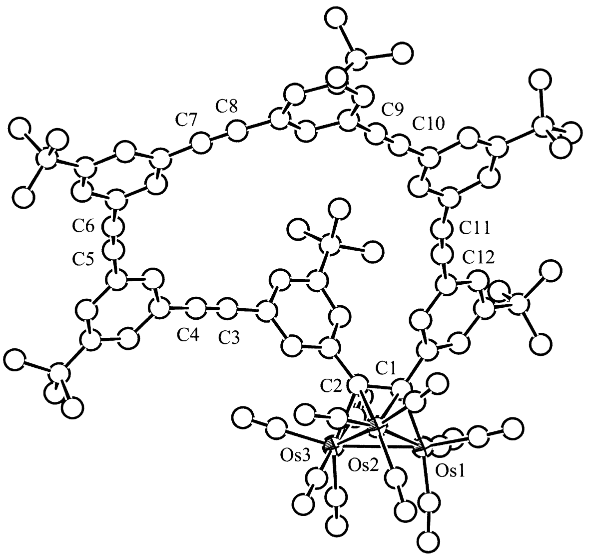

Figure 2. Molecular structure of **4a**.

require hydrogen-bonding or long alkyl chains to arrange into tubular solids with intrastack channels—van der Waals interactions are sufficient to perform this task.

Experimental Section

Monomer **1a** (2.00 g, 9.52 mmol), [Mo(CO)$_6$] (126 mg, 0.477 mmol), and 4-chlorophenol (1.23 g, 9.57 mmol) were dissolved in off-the shelf 1,2-dichlorobenzene (50 mL) and heated for 16 h to 150 °C under a light stream of N$_2$. The reaction was worked-up by washing with water, dilute HCl, and dilute NaOH followed by precipitation into methanol to furnish a mixture (1.25 g, 84 %) of polymer **3a** and cycle **2a**. Of the product mixture, 500 mg were subjected to repeated thick-layer chromatography (1:6 CH$_2$Cl$_2$/hexane) leading to the isolation of the cycle **2a** (30 mg, 6 %). M.p. > 250 °C; MS: *m/z*: $C_{72}H_{72}$: calcd: 936; found: 936 [M^+]; ^{1}H NMR (CDCl$_3$): $\delta = 7.58$ (s, 1H), 7.55 (s, 2H), 1.33 (s, 9H); ^{13}C NMR (CDCl$_3$): $\delta = 152.73$, 133.66, 129.64, 124.24, 90.37, 36.11, 32.49; IR (KBr): $\tilde{\nu} = 3060$ (w), 2963, (s), 2904 (s), 2889 (s), 2210 (w), 1593 (s), 1475 (m), 1432 (s), 1364 (s), 1242 (s), 1000 (m), 877 (s), 693 (s) cm^{-1}; UV/Vis: $\lambda_{max} = 248$ (sh), 280 (sh), 310 nm; elemental analysis calcd for **2a** · C_6H_{14} (%): C 91.53, H 8.47; found: C 91.37, H 8.02.

2b: Yield: 4.8 mg, 1 %. MS: *m/z*: $C_{84}H_{96}$: calcd: 1104; found: 1105 [M^++1]; ^{1}H NMR (CDCl$_3$): $\delta = 7.52$ (s, 1H), 7.33 (s, 2H), 2.59 (t, 2H), 1.63 (quint, 2H), 1.31 (bs, 6H), 0.88 (t, 3H); ^{13}C NMR (CDCl$_3$): $\delta = 144.30$, 132.89, 132.64, 124.31, 90.12, 36.78, 32.94, 32.36, 30.16, 23.84, 15.38.

2d, **3d**: Yield: 2.3 mg, 0.5 %, mixture of hexamer and heptamer: MS: *m/z*: $C_{78}H_{84}$: 1021 [M^++1]; $C_{91}H_{98}$: 1191 [M^++1]; ^{1}H NMR (CDCl$_3$): $\delta = 7.53$ (s, 2H), 2.75 (s, 3H), 1.31 (s, 9H).

4a: [Os$_3$(CO)$_{10}$(MeCN)$_2$] (10.1 mg, 0.011 mmol) and **2a** (9.3 mg, 0.010 mmol) were dissolved in CH$_2$Cl$_2$ (10 mL) and heated to reflux for 0.5 h. The product was separated by TLC (silca gel) using a 6:1 hexane/dichloromethane solvent mixture to yield **4a** (2.0 mg; 11 %) as a yellow product. Spectral data for **4a**: IR (hexane): $\tilde{\nu}_{CO} = 2100$ (m), 2067 (s), 2046 (s), 2029 (s), 2010 (s), 2000 (m), 1993 (m), 1979 (w), 1961 (vw) cm^{-1}; ^{1}H NMR (CDCl$_3$): $\delta = 7.62$ (m, 4H), 7.52 (m, 8H), 7.28 (s, 2H), $\delta = 7.06$ (s, 2H), 6.85 (s, 2H), 1.36 (s, 18H), 1.35 (s, 18H), 1.17 (s, 18H); MS (FAB): *m/z*: 1788.2 [M^+]; elemental analysis: calcd: C 55.07, H 4.02; found: C 55.04, H 4.09.

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[13] a) X-ray structure analysis for **2a**: Suitable single crystals for the X-ray diffraction study were grown from *n*-hexane. $C_{72}H_{72}$: (937.30): monoclinic $P2_1/a$; $a = 11.3607(3)$, $b = 23.5383(6)$, $c = 14.1410(3)$ Å, $\beta = 106.661(1)°$. $V = 3622.7(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 0.859$ g cm^{-3}; $\mu = 0.048$ mm^{-1}. A clear colorless plate of **2a** (0.5 mm × 0.4 mm × 0.08 mm) was stored under perfluorinated ether, transferred in a Lindemann capillary, fixed, and sealed. Preliminary examination and data collection were carried out on a Kappa CCD area detector (Nonius; MACH3) equipped with a rotating anode and graphite-monochromated Mo$_{K\alpha}$ radiation (Nonius; FR951, $\lambda = 0.71073$ Å, $2\Theta_{max} = 50°$). The unit cell parameters were obtained by full-matrix least-squares refinements of 11971 reflections. Data collection was performed at 123 K (exposure time: 100 s per frame; 9 sets, θ and ω scans, $\Delta\theta/\Delta\omega$: 1°; dx: 40.0 mm). A total of 12551 reflections were collected. Raw data were corrected for Lorentz and polarization effects, not corrected for absorption and decay effects, and scaled with the program DENZO-SMN. After merging ($R_{int} = 0.0341$), 6366 independent reflections remained and were used for all calculations. All "heavy atoms" of the asymmetric unit were refined anisotropically. All hydrogen atoms were located in the difference Fourier map and refined with individual isotropic temperature parameters. Full-matrix least-squares refinements were carried out by minimizing $\Sigma w(F_o^2 - F_c^2)^2$ by using the SHELXL-97 weighting scheme and stopped at shift/err < 0.001 with *R*1(all data) = 0.0829, R_w2(all data) = 0.1587, and GOF 1.050. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from *International Tables for Crystallograpy.* All calculations were performed on a DEC 3000 AXP workstation and an Intel Pentium II PC, with the STRUX-V system, including the programs PLATON, SHELXS-86, and SHELXL-97. One solvent molecule (C_6H_{14}) is highly disordered in the crystal and could not be located and refined correctly. The problem was solved by using the SQUEZZE strategy (A. L. SPEK, PLATON, 1999); b) X-ray structure analysis for **4a**: A cube of **4a** (0.05 mm × 0.04 mm × 0.05 mm) was grown from dichloromethane. Data were obtained on a Bruker Smart 1000 CCD diffractometer at 298 K. The structure was solved and refined with the programs SHELXS86 and SHELX97 and by using heavy-atom

(Patterson) methods. Hydrogen atoms were localized and refined in the riding mode. The crystal was mounted on a glass fiber. $Os_3O_{30}C_{82}H_{72}$ ($M_r = 1788.00$); $Mo_{K\alpha}$ radiation; $\lambda = 0.71073$ Å, graphite monochromator; $2\Theta_{max} = 22.50°$, monoclinic $C2/c$; $a = 54.641(5)$, $b = 11.7486(10)$, $c = 33.250(3)$ Å, $\beta = 120.447(3)°$, $V = 18401(3)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.291$ g cm^{-3}, $\mu = 41.79$ mm^{-1}, absorption correction: SADABS; 12021 reflections were measured and all reflections with ($I = 2\sigma(I)$) observed, $R = 0.0747$, $R_w = 0.1710$. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-143392 (**2a**) and CCDC-143393 (**4a**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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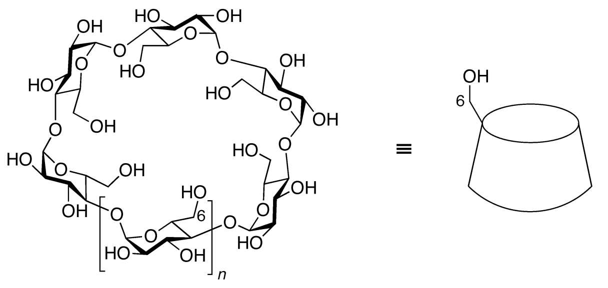
Diisobutylaluminum-Promoted Regioselective De-*O*-benzylation of Perbenzylated Cyclodextrins: A Powerful New Strategy for the Preparation of Selectively Modified Cyclodextrins[**]

Alan J. Pearce and Pierre Sinaÿ[*]

Cyclodextrins (CDs) **1** and their derivatives are of great importance in supramolecular chemistry,[1] analytical chemistry,[2] as artificial enzymes,[3] drug delivery systems,[4] and modifiers of chemical reactions (Scheme 1).[5] The preparation of selectively modified cyclodextrins for these applications remains a crucial challenge in organic synthesis despite considerable effort and several well defined protocols.[6] Traditional methods may be classified[6a] as a) "long", involving lengthy protection and deprotection steps; b) "clever", where the chemistry of cyclodextrin is exploited to get the desired product by the shortest route; and c) "sledgehammer", where indiscriminate reaction leads to complex product mixtures and lengthy separation. A far more elegant alternative approach is the regioselective deprotection of perfunctionalized cyclodextrins,[7] thus combining the advantageous aspects of the first two methods mentioned above.



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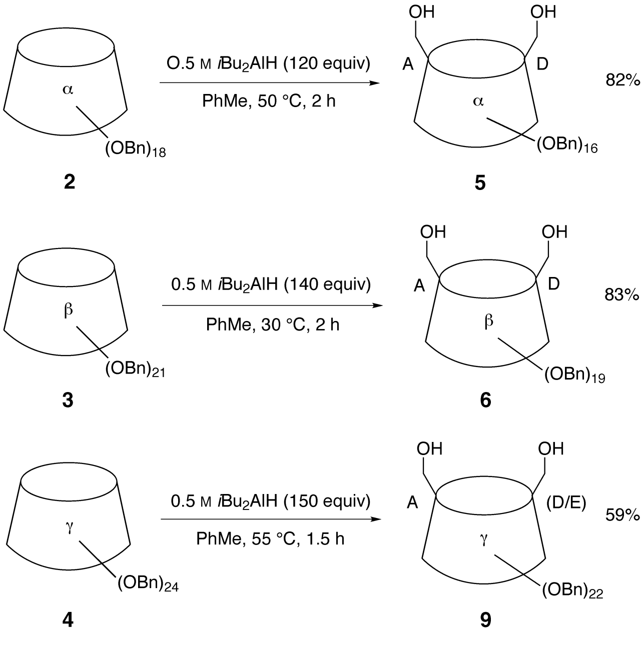
α-CD, *n* = 1
β-CD, *n* = 2
γ-CD, *n* = 3

Scheme 1. Schematic structural representation of CDs.

We recently reported that triisobutylaluminum (TIBAL) led to highly regioselective mono-de-*O*-benzylation of perbenzylated mono- and disaccharide derivatives.[8] Herein, we report the first regioselective de-*O*-benzylation of perbenzylated CDs by application of this methodology.

Perbenzylated CDs **2**–**4** were prepared by direct benzylation of CDs **1** in DMSO with benzyl chloride and NaH, in excellent yield using the method of Sato et al.[9] When α-CD(OBn)$_{18}$ (**2**) was treated with excess diisobutylaluminum (DIBAL)[10] in toluene at 50 °C we observed formation of a single product **5** of di-*O*-debenzylation in 82 % yield (Scheme 2). The structure of **5** was identified as the AD regioisomer by ^{1}H and ^{13}C NMR spectroscopy, which indicated high C_2 symmetry, and was further confirmed by chemical degradation using the "hex-5-enose method" as described below. The regioselectivity of this di-*O*-debenzylation is remarkable. Statistical calculations indicate that for di-*O*-deprotection of α-CD(OBn)$_{18}$ (**2**) 27 regioisomers are possible, of which, we obtain only one in excellent yield.



Scheme 2. Highly regioselective DIBAL-promoted di-*O*-debenzylation affords AD diols in excellent yield.

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