carceplex with a single small molecule as template.[12] A current challenge is the exploration of larger containers, for which a large molecule or several small molecules can act as templates. Such a system would add the dimension of guest molecularity to the template question. Moreover, the effect of solvation would be far more complex because excluding solvent by simply using a large molecule would no longer be practical. We have demonstrated here the first step toward such a program, the creation of a large robust container that permanently entraps several molecules, the number, identity, "effective phase," mobility, and orientation of which have been clearly characterized. Efforts are currently underway to optimize the synthesis of **5** · guest complexes so as to analyze the role of templation.

Experimental Section

5 · 3DMF: Trimer **3** (25.4 mg, 0.00823 mmol), K_2CO_3 (70 mg, 0.506 mmol, 61 equiv), KI (85 mg, 0.512, 62 equiv), and 1,3,5-(bromomethyl)mesitylene (20.5 mg, 0.0511 mmol, 6 equiv) were added to DMF (10 mL). The reaction mixture was stirred under N_2 for 24 h at 25 °C. The solvent was removed in vacuo, and HCl (2 M, 30 mL) was added to the crude mixture. The aqueous layer was extracted with $CHCl_3$ (3×10 mL), and the combined $CHCl_3$ extracts were dried with anhydrous $MgSO_4$, filtered, and evaporated to give a brown residue, which was eluted through a pad of silica gel with $CHCl_3$. A purple band indicating the presence of I_2 was coeluted with the desired product. This purple band was collected, solvent was removed and the residue was recrystallized from $CHCl_3$/hexanes to give 10.7 mg of **5** · 3DMF as a white solid (0.00295 mmol, 36%). M.p. > 250 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 7.10-7.30$ (br m, $CH_2CH_2C_6H_5$, $CHCl_3$), 6.99 (s, 6H, p-H_{OAr}), 6.77 (s, 6H, p-H_{acetal}), 5.97 (s, 3H, $(CH_3)_2NCHO$), 5.96 (d, $J = 7.1$ Hz, 12H, H_{out}), 5.85 (s, 6H, H_{acetal}), 5.12 (s, 12H, OCH_2Ar), 4.94 (t, $J = 7.7$ Hz, 12H, $H_{methine}$), 4.47 (d, $J = 7.1$ Hz, 12H, H_{in}), 2.77 (s, 18H, $ArCH_3$), 2.71 (t, 24H, $J = 7.6$ Hz, $CH_2CH_2C_6H_5$), 2.52 (m, 24H, $CH_2CH_2C_6H_5$), 1.04 (s, 9H, $(CH_3)_2NCHO$), -0.11 (s, 9H, $(CH_3)_2NCHO$); IR (KBr): $\tilde{\nu} = 1682$, 1676 cm^{-1} ($\nu_{C=O}$); MS (MALDI): m/z (%): 3640 [M+Na$^+$] (100); calcd for $C_{219}H_{192}O_{36} \cdot 3C_3H_7ON + Na^+$: 3642; elemental analysis calcd for $C_{219}H_{192}O_{36} \cdot 3C_3H_7ON$: C 75.67, H 5.93, N 1.16; found: C 75.27, H 5.95, N 1.00.

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Keywords: carceplexes · cavitands · host–guest chemistry · inclusion compounds · template synthesis

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Porphomethenes and Porphodimethenes Synthesized by the Two- and Four-Electron Oxidation of the *meso*-Octaethylporphyrinogen**

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Rosario Scopelliti, and Carlo Floriani*

Porphomethene **B** and porphodimethene **C** are supposed to pave the way from porphyrinogen **A** to porphyrin (Scheme 1).[1, 2] However, these intermediates have never been synthesized from porphyrinogen but rather from metalloporphyrins by reductive protonation or reductive alkylation.[3] The yield and scale of such synthetic methods are severely limited due to the compulsory use of octaalkylmetalloporphyrins, whose steric bulk is necessary to protect the porphomethene and porphodimethene from the easy oxidation to porphyrins.[3] We report here on the stepwise deal-

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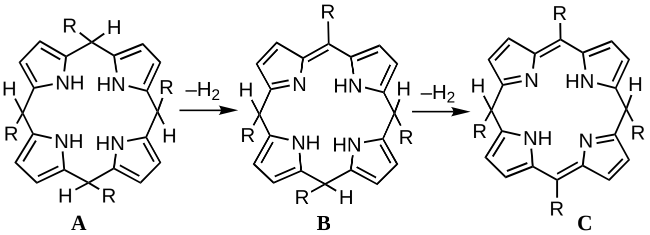
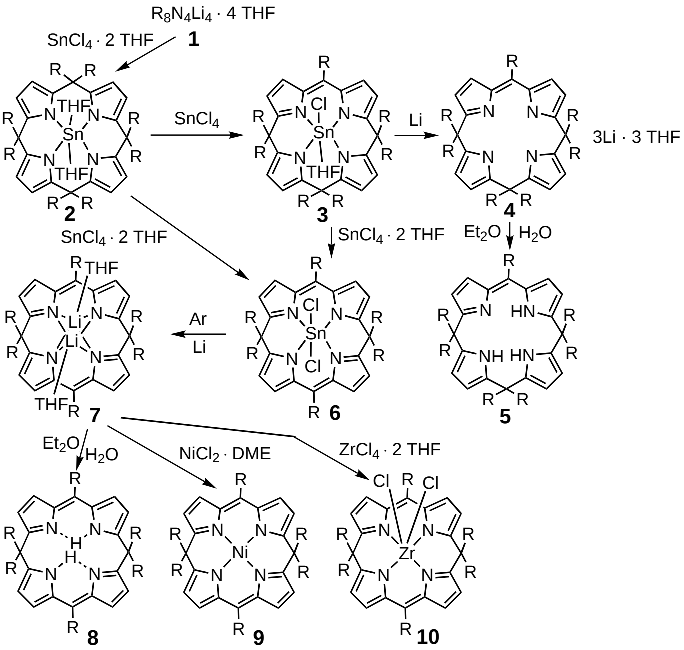


Scheme 1. The two- and four-electron oxidation of porphyrinogen **A** to porphomethene **B** and porphodimethene **C**.

kylation of the *meso*-octaethylporphyrinogen [**A** (R = Et)][4, 5] to porphomethene [5,10,15-triethyl-22-hydroporphyrin, **B** (R = Et)] and porphodimethene [5,15-diethylporphyrin, **C** (R = Et)], which accounts for an overall two- and four-electron oxidation of the porphyrinogen skeleton.[6]

The synthetic sequence, which provides porphomethene and porphodimethene on a large scale in their metalated or metal-free forms, is shown in Scheme 2. The tin(IV) derivative



Scheme 2. The tin-assisted dealkylation of the *meso*-octaethylporphyrinogen to give porphomethene **3** and porphodimethene **6**, and subsequent complexation with other metal ions. R = Et; DME = 1,2-dimethoxyethane.

2, synthesized following a conventional procedure, underwent a dealkylation in the presence of $SnCl_4$ (ca. 2 equiv) to yield the porphomethene(tin chloride) complex **3**, which was converted into the corresponding lithium derivative **4** and subsequently hydrolyzed to afford the free acid form **5**. Such a sequence provides access to large quantities of **4** and **5**, which are very useful for synthetic purposes. A large excess of $SnCl_4 \cdot 2THF$ both with **3** or, better, with **2** led to the dealkylation of both *trans meso* carbon atoms with the formation of the porphodimethene(tin dichloride) complex **6**. The reductive demetalation of **6** with lithium metal was a very clean reaction leading to **7**, which can be hydrolyzed to the free acid form, **8**, or can serve for the complexation of a variety of metals. For example, we prepared porphodimethene complexes with nickel(II), **9**, and zirconium(IV), **10**. In the case of **10**, the conformation of the ligand explains the *cis* arrangement of the chloride ions. Complexes **2**–**10** have all been fully characterized;[7] the structures of all except compound **4** were also determined by X-ray crystallography. Some details are reported here for **7**.[8]

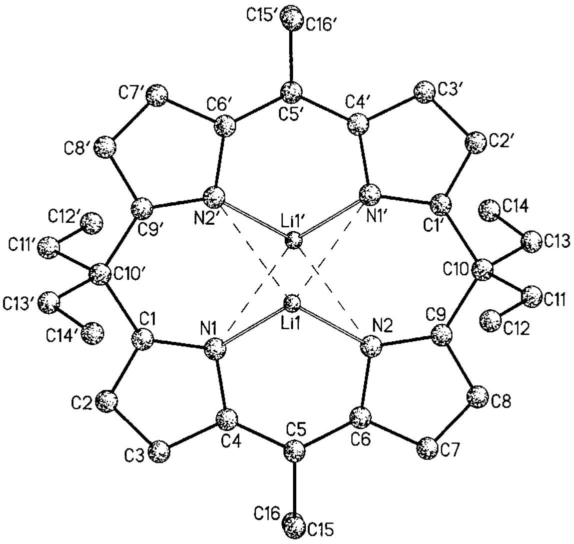


Figure 1. X-ray crystal structure of complex **7** (XP representation). Selected distances [Å]: Li1–N1 2.113(5), Li1–N2 2.156(5), Li1···N1′ 2.523(5), Li1···N2′ 2.465(5), Li1···Li1′ 2.142(8). THF molecules are omitted for clarity. Primed atoms are related to the unprimed by the following symmetry transformation: $-x, -y, -z$.

The structure of **7** is shown in Figure 1 with the most relevant structural parameters. The porphodimethene skeleton is essentially planar with only a slight folding at the two saturated carbon atoms,[3c–f,i,j] as evident from the dihedral angles (N1-C1-C10′)-(N2′-C9′-C10′) = 12.5(4) and (N1-C4-C5)-(C5-C6-N2) = 2.7(4)°. The two lithium cations lie on opposite faces of the N_4 average plane (±1.031(4) Å), and they bind two nitrogen atoms at close distances (Li1–N1 2.113(5), Li–N2 2.156(5) Å), whereas a weak interaction at longer distance occurs with the other two nitrogen atoms (Li1–N1′ 2.523(5), Li1–N2′ 2.465(5) Å). The conformation of the ligand is essentially imposed by the two lithium cations, which complete their coordination sphere with a THF molecule and are quite close together (Li1···Li1′ 2.142(8) Å).[9] The C–C and C–N distances support the proposed bonding scheme.

Some major features of the present report must be emphasized: 1) This synthetic methodology makes available important, but previously poorly accessible molecular skeletons on a large scale and starting from quite simple compounds. 2) The synthetic sequence (Scheme 2) illustrates the controlled two- and four-electron oxidation of porphyrinogen by means of the porphyrinogen → porphyrin transformation (**A** → **B** → **C** in Scheme 1). 3) The porphomethene and porphodimethene derivatives have never been obtained with unsubstituted pyrroles and as oxidatively stable *meso* fully alkylated forms.[3]

Experimental Section

2: In portions, $SnCl_4 \cdot 2THF$ (28.5 g, 70.0 mmol) was added to a solution of **1** (56.0 g, 70.0 mmol) in toluene (700 mL). The reaction mixture was heated at reflux for about 12 h. The undissolved white solid, LiCl, was filtered off, and the resulting red-violet solution was concentrated to dryness. *n*-Hexane (300 mL) was added to the residue to give a pink powder, which was collected and dried in vacuo (yield: 40.0 g, 71 %). Crystals suitable for X-ray structure analysis were grown in a mixture of THF and *n*-hexane. ^1H NMR (200 MHz, C_6D_6, 298 K): $\delta = 6.37$ (s, 8H; C_4H_2N), 3.13 (m, 8H; THF), 1.96 (q, $J(H,H) = 7.4$ Hz, 16H; CH_2), 1.08 (m, 8H; THF), 0.90 (t, $J(H,H) = 7.4$ Hz, 24H; CH_3); elemental analysis calcd for **2** ($C_{44}H_{64}N_4SnO_2$) (%): C 66.08, H 8.07, N 7.01; found: C 66.12, H 8.51, N 7.04.

3: A solution of $SnCl_4$ (1.0 g, 3.8 mmol) in toluene (50 mL) was added dropwise at $-40\,^{\circ}C$ to a solution of **2** (12.2 g, 15.2 mmol) in toluene (200 mL). The reaction mixture was warmed to room temperature and stirred for about 12 h. To complete the reaction, this red solution was heated for 2 h at 80 °C. It was concentrated to dryness, and *n*-hexane (70 mL) was added to give a red powder which was collected and dried in vacuo (yield: 9.3 g, 61 %). Crystals suitable for X-ray structure analysis were grown in toluene. ^1H NMR (200 MHz, C_6D_6, 298 K): $\delta = 7.10$ (d, $J(H,H) = 4.4$ Hz, 2H; C_4H_2N), 6.43 (d, $J(H,H) = 4.0$ Hz, 2H; C_4H_2N), 6.38 (d, $J(H,H) = 4.4$ Hz, 2H; C_4H_2N), 6.31 (d, $J(H,H) = 4.0$ Hz, 2H; C_4H_2N), 2.85 (m, 4H; THF), 2.53 (m, 4H; CH_2), 2.29 (m, 6H; CH_2), 1.89 (m, 4H; CH_2), 1.33 (t, $J(H,H) = 7.3$ Hz, 3H; CH_3), 1.10 (t, $J(H,H) = 7.8$ Hz, 3H; CH_3), 0.91–0.86 (m, 15H; CH_3, overlapping with m, 4H; THF).

6 (one-pot reaction): $SnCl_4 \cdot 2THF$ (72.8 g, 179.0 mmol) was added to a solution of **2** (47.8 g, 60.0 mmol) in toluene (400 mL). The reaction mixture was heated at reflux for about 12 h, and after cooling a red crystalline solid precipitated. This product was collected, washed by extraction with Et_2O (500 mL), and then dried in vacuo (yield: 21.3 g, 53 %). Crystals suitable for X-ray structure analysis were grown in toluene. ^1H NMR (400 MHz, C_5D_5N, 298 K): $\delta = 7.73$ (d, $J(H,H) = 4.4$ Hz, 4H; C_4H_2N), 6.83 (d, $J(H,H) = 4.4$ Hz, 4H; C_4H_2N), 2.98 (q, $J(H,H) = 7.32$ Hz, 8H; CH_2), 2.29 (q, $J(H,H) = 7.32$ Hz, 4H; CH_2), 1.25 (t, $J(H,H) = 7.32$ Hz, 6H; CH_3), 0.93 (t, $J(H,H) = 7.32$ Hz, 12H; CH_3); UV/Vis (THF): λ_{max} (ε) = 240 (34957), 304 (13026), 434 sh (33696), 454 nm (187122); elemental analysis calcd for **6** ($C_{32}H_{38}N_4SnCl_2$) (%): C 57.51, H 5.73, N 8.38; found: C 57.41, H 5.84, N 7.80.

7: Lithium metal (0.37 g, 52.8 mmol) and naphthalene (1.0 g, 7.8 mmol) were added under argon atmosphere to a solution of **6** (8.5 g, 13.2 mmol) in THF (200 mL). The reaction mixture was stirred for about 12 h, and the metallic residue was filtered off. The resulting orange solution was concentrated to dryness, and benzene (200 mL) was added to remove the undissolved LiCl. The solution was concentrated to dryness and the residue washed with *n*-pentane (100 mL). An orange powder was collected and dried in vacuo (yield: 4.2 g, 50 %). Crystals suitable for X-ray structure analysis were grown in a mixture of THF and *n*-hexane. ^1H NMR (200 MHz, C_5D_5N, 298 K): $\delta = 7.41$ (d, $J(H,H) = 3.9$ Hz, 4H; C_4H_2N), 6.67 (d, $J(H,H) = 3.9$ Hz, 4H; C_4H_2N), 3.63 (m, 8H; THF); 3.14 (q, $J(H,H) = 7.32$ Hz, 4H; CH_2), 2.42 (q, $J(H,H) = 7.32$ Hz, 8H; CH_2); 1.59 (m, 8H; THF), 1.44 (t, $J(H,H) = 7.32$ Hz, 6H; CH_3), 1.05 (t, $J(H,H) = 7.32$ Hz, 12H; CH_3); UV/Vis (THF): λ_{max} (ε) = 296 (6147), 426 (43608), 452 (125892), 506 nm (8980); elemental analysis calcd for **7** ($C_{40}H_{54}N_4Li_2O_2$) (%): C 75.45, H 8.55, N 8.76; found: C 74.8, H 8.48, N 8.60.

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[8] Crystal data for **7** ($C_{40}H_{54}Li_2N_4O_2$): $M_r = 636.75$, monoclinic, space group $P2_1/n$, $a = 9.8247(11)$, $b = 10.9196(12)$, $c = 16.940(2)$ Å, $\beta = 90.346(10)^{\circ}$, $V = 1817.3(4)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.164$ g cm^{-3}, $F(000) = 688$, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $\mu(Mo_{K\alpha}) = 0.71$ cm^{-1}; crystal dimensions $0.25 \times 0.20 \times 0.18$. Diffraction data were collected on a KUMA CCD at 143 K. For 2616 observed reflections [$I > 2\sigma(I)$] the conventional R was 0.0658 ($wR2 = 0.1974$ for 3418 independent reflections). Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-116587. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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