8: To 450 mg (1.22 mmol) of compound **7** was added 2 mL pyridine. The mixture was stirred at room temperature and then 549 mg (2 mmol) of *tert*-butyldiphenylsilyl chloride was added by syringe. The mixture was stirred at room temperature for 1 h. After addition of ethyl acetate (15 mL) the mixture was washed with H₂O, 1 N HCl, and saturated aqueous NaHCO₃, and then dried over Na₂SO₄. The organic solvent was removed under vacuum. The residue was purified by silica gel column chromatography (ethyl acetate/hexane = 1/10 to 1/5) to furnish 683 mg of **8** in 92% yield; $[\alpha]_D^{25} = -54.8$ ($c = 0.61$, MeOH); $R_f = 0.63$ (ethyl acetate/hexane = 1/2); ¹H NMR (500 MHz, CDCl₃): $\delta = 0.96$ (2.9H), 1.25 (s, 3H), 1.29 (s, 3H), 3.09 (ddd, 1H, $J = 10, 10, 10$ Hz), 3.29 (m, 3H), 3.59 (m, 1H), 3.80 (dd, 1H, $J = 10, 10$ Hz), 4.19 (dd, 1H, $J = 2.0, 4.5$ Hz), 4.48 (dd, 1H, $J = 2.0, 2.0$ Hz), 4.95 (s, 1H), 7.38 (m, 20H); ¹³C NMR (125 MHz, CDCl₃): $\delta = 22.3, 25.7, 26.0, 26.8, 61.7, 62.9, 65.6, 71.4, 74.0, 77.5, 79.0, 98.8, 127.1, 127.3, 127.6, 128.1, 128.2, 128.3, 128.6, 129.5, 129.6, 135.3, 135.5, 143.3, 143.4$; HRMS for C₃₈H₄₅O₄NSiCs [$M + Cs^+$]: calcd 740.2172, found 740.2168.

9: To a solution of periodinane [7] (548 mg, 0.9 mmol) in 10 mL CH₂Cl₂ was added 548 mg of **8** in 2 mL CH₂Cl₂. The mixture was stirred at room temperature for 3.5 h. 2 mL of 1 N NaOH was added, and the mixture was stirred for additional 10 min. The organic layer was then washed with 1 N NaOH and dried over MgSO₄, and the solvent was removed under vacuum to give 438 mg of **9** in 80% yield; $[\alpha]_D^{25} = -19.0$ ($c = 1.05$, MeOH); $R_f = 0.41$ (ethyl acetate/hexane = 1/4). ¹H NMR (500 MHz, CDCl₃): $\delta = 1.06$ (s, 9H), 1.33 (s, 6H), 3.39–3.46 (m, 1H), 3.48 (dd, 1H, $J = 6.0, 11$ Hz), 3.50 (dd, 1H, $J = 3.0, 10.5$ Hz), 3.53 (dd, 1H, $J = 8.5, 6.8, 5$ Hz), 3.81 (dd, 1H, $J = 11, 8.5$ Hz), 3.87 (dd, 1H, $J = 10.5, 3.5$ Hz), 4.31 (dd, 1H, $J = 8.5, 1$ Hz), 4.74 (s, 1H), 7.07–7.74 (m, 20H); ¹³C NMR (125 MHz, CDCl₃): $\delta = 25.3, 25.5, 26.8, 54.1, 62.0, 64.0, 67.3, 71.7, 71.8, 127.5, 127.6, 127.7, 128.3, 128.3, 128.7, 129.7, 129.7, 135.8$.

10: To a solution of **9** (400 mg, 0.66 mmol) in 5 mL toluene at -78°C was added diisobutylaluminum hydride (0.5 mL, 1.0 M in hexane) dropwise by syringe. After the addition was complete, the mixture was stirred at -78°C for 0.5 h. The reaction was then quenched with 400 μL methanol followed by addition of 4 mL of 10% aqueous solution of Rochelle's salt (potassium sodium tartrate) and 16 mL ether. The mixture was stirred at room temperature for 1 h, and the organic layer was washed with 1 N HCl and saturated aqueous NaHCO₃, and dried over MgSO₄. The solvent was removed under vacuum and the residue purified by silica gel column chromatography (ethyl acetate/hexane = 1/10 to 1/3) to give 366 mg of **10** in 91% yield; $[\alpha]_D^{25} = -7.2$ ($c = 1.15$, MeOH); $R_f = 0.59$ (ethyl acetate/hexane = 1/2); ¹H NMR (500 MHz, CDCl₃): $\delta = 0.96$ (s, 9H), 1.33 (s, 3H), 1.40 (s, 3H), 3.05–3.08 (m, 1H), 3.30–3.41 (m, 3H), 3.74 (dd, 1H, $J = 10, 5.5$ Hz), 4.27 (t, 1H, $J = 5.5$ Hz), 4.37–4.45 (m, 2H), 4.79 (s, 1H), 7.47 (m, 20H); ¹³C NMR (125 MHz, CDCl₃): $\delta = 21.8, 26.5, 26.7, 59.8, 62.5, 63.3, 66.9, 71.4, 73.8, 73.9, 127.2, 127.3, 127.8, 128.3, 128.4, 128.5, 129.6, 129.7, 135.3, 135.4$; HRMS for C₃₈H₄₅O₄NSiCs [$M + Cs^+$]: calcd 740.2172, found 740.2170.

1: To a solution of **10** (296 mg, 0.49 mmol) in 8 mL THF was added 1 mL of 1.0 M tetrabutylammonium fluoride in THF. The mixture was stirred at room temperature for 30 min. The solvent was then removed under reduced pressure, and the residue was dissolved in 15 mL methanol treated with 200 mg of *p*-TsOH·H₂O. The mixture was stirred at room temperature overnight. After 2 mL of saturated aqueous NaHCO₃ was added, the resulting mixture was stirred for another 10 min. The methanol was removed under vacuum and the residue extracted with ethyl acetate and purified by silica gel column chromatography (ethyl acetate) to give 121 mg of **10a** in 75% yield; $[\alpha]_D^{25} \pm 0$ ($c = 1.0$, CH₃OH); $R_f = 0.18$ (ethyl acetate); ¹H NMR (500 MHz, CD₃OD): $\delta = 3.1$ –3.2 (m, 2H), 3.40 (dd, 2H, $J = 3.0, 11.0$ Hz), 3.45 (dd, 2H, $J = 6.0, 11.0$ Hz), 4.05–4.15 (m, 2H), 5.11 (s, 1H), 7.1–7.5 (m, 10H); ¹³C NMR (125 MHz, CD₃OD): $\delta = 61.5, 65.8, 72.8, 73.1, 128.3, 129.2, 130.2, 143.4$; HRMS for C₁₀H₂₃NO₄ [$M + H^+$]: calcd 330.1713, found 330.1711.

1: A solution of **10a** (90 mg, 0.27 mmol) in 10 mL methanol was hydrogenated with 30 mg of Pd(OH)₂ under hydrogen atmosphere at room temperature. After 6 h the catalyst was filtered off and washed with methanol. The combined methanol solutions were concentrated and the oily residue purified by silica gel column chromatography (CHCl₃/CH₃OH/H₂O/NH₄OH = 5/4/1/0.08) to give **1**: ¹H NMR (500 MHz, CD₃OD): $\delta = 3.55$ –3.65 (m, 2H), 3.88 (dd, 2H, $J = 8.0, 12.0$ Hz), 3.92 (dd, 2H, $J = 5.0, 12.0$ Hz), 4.3–4.4 (m, 2H); ¹³C NMR (125 MHz, CD₃OD): $\delta = 59.45, 63.08, 71.69$; HRMS for C₆H₁₃NO₄ [$M + H^+$]: calcd. 164.0923, found 164.0911; correct C,H,N analysis.

Chemoenzymatic synthesis of 1: Ozone was bubbled through a solution of **11** [10] (302 mg, 1.6 mmol) in methanol (10 mL) at -78°C until the reaction solution became pale blue. After nitrogen was passed through the solution to remove excess ozone, the ozonide was treated with dimethylsulfide (1 mL) and water (1 mL) for 12 h at room temperature. Methanol was removed under vacuum, and the residue was then purified by chromatography on Amberlite XAD-II (3.0 $\times$ 10 cm, H₂O) to yield **12**, which was added to an aqueous solution of dihydroxyacetone phosphate (DHAP, 11 mL, 0.3 mmol). The pH of the solution was adjusted to 7.5 with 0.5 N NaOH. Fuculose-1-phosphate aldolase (2.0 mL, 70 U) was added to this solution and the mixture stirred slowly for 1 d at room temperature. After an enzymatic assay indicated that DHAP was completely consumed, the mixture was adjusted to pH 4.7 with 1 N HCl, acid phosphatase (from sweet potato, type XA, 0.8 mL, 200 U) was added, and the mixture was then stirred slowly at room temperature for 1 d. The mixture was adjusted to pH 7.0 with 0.5 N NaOH, and water was removed under reduced pressure. The residue was treated with methanol, and the soluble portion

was collected and purified by silica gel chromatography (CHCl₃/MeOH/H₂O = 8/2/0.1) to yield compound **13** (50.4 mg, 82%). $[\alpha]_D^{25} = -13.5$ ($c = 0.60$, MeOH); ¹H NMR (400 MHz, D₂O): $\delta = 3.50$ (1H, d of AB type, $J = 11.8$ Hz), 3.60 (1H, t, $J = 10.8$ Hz), 3.71 (1H, d of AB type, $J = 11.80$ Hz), 3.75 (1H, ddd, $J = 10.80, 9.92, 5.60$ Hz), 3.84 (1H, dd, $J = 10.80, 5.60$ Hz), 3.88 (1H, d, $J = 3.24$ Hz), 3.92 (1H, dd, $J = 9.92, 3.24$ Hz); ¹³C NMR (100 MHz, D₂O): $\delta = 58.70, 60.85, 64.25, 69.68, 70.37, 98.65$; HRMS for C₆H₁₁N₃O₂Na [$M^+ + Na$]: calcd 228.0596, found 228.0590.

A solution of **13** (28.4 mg, 0.14 mmol) in ethanol (10 mL) was hydrogenated with 10% Pd-C (10 mg) under 50 psi of hydrogen for 12 h. The catalyst was removed by filtration, and the solvent was evaporated under vacuum. The residue was purified by silica gel chromatography (CHCl₃/MeOH/H₂O/NH₄OH = 6/4/1/0.1) to yield compound **1** (14 mg, 61%). The NMR data (¹H and ¹³C) are the same as those for **1** prepared chemically.

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Synthesis and Structure of the First Organometallic Galloxane Hydroxide Mes₆Ga₆O₄(OH)₄**

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Dedicated to Professor Hubert Schmidbaur on the occasion of his 60th birthday

Recently structural investigations by Barron et al. revealed that the controlled hydrolysis of alkylaluminum compounds can afford both hydroxides and oxides.^[1] The formation of a mixed

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hydroxide oxide was not observed. The commercially used, partially hydrolyzed alkylaluminum compounds^[2] and the corresponding gallium compounds^[3] are important cocatalysts for metallocenes of group 4 of the periodic table. In considering polymerization reactions with metallocenes containing fluorine and methylaluminoxane as cocatalyst^[4] we were chiefly interested in the function and structure of the cocatalyst systems.

In order to obtain crystalline products, we carried out hydrolysis with Mes_2GaCl (**1**) and Mes_3Ga (**2**) (Mes = mesityl). Compound **1** reacts with hydrated KOH in THF leading to the formation of KCl and probably Mes_2GaOH [Eq. (a)], which condenses to give $\text{Mes}_6\text{Ga}_6\text{O}_4(\text{OH})_4$ (**3**) [Eq. (b)]. The resulting KCl could be separated by filtration and MesH could be detected by ^1H NMR spectroscopy. In order to confirm this reaction pathway, we treated **2** with water in toluene [Eq. (c)], since the hydrolysis of organogallium compounds affords the corresponding gallium hydroxides.^[5] The reaction led to the formation of **3** and MesH. The condensation of the homologous aluminum compounds^[6] has so far not been explained unambiguously.

The IR spectrum of $[\text{3}(\text{thf})_4]$ shows the characteristic OH vibrations: a sharp band at 3671 for free and a broad band at 3521 cm^{-1} for bridging OH groups, which can be explained by partial release of the coordinating THF molecules. The EI mass spectrum shows the peak for the molecular ion at $m/z = 1264$ and that of the hydroxide-free hexameric galloxane at $m/z = 1228$ (100% rel. intensity, $M^+ - 2\text{H}_2\text{O}$). In the ^1H NMR spectrum, two signals each are observed for the ring protons ($\delta = 6.73\text{--}6.71$) as well as for the *ortho* ($\delta = 2.57\text{--}2.53$) and the *para* ($\delta = 2.18$) methyl protons of the mesityl group. Thus, the mesityl groups are arranged differently. This is confirmed by the distorted octahedral structure in the solid state. The OH protons occur at $\delta = 6.37$.

Single crystals suitable for X-ray structure analysis^[7] were obtained from THF. In addition to the four THF molecules coordinated to **3**, six uncoordinated THF molecules are present per formula unit. As a result of the latter the crystals disintegrate very rapidly as soon as the mother liquor is removed. The selection of the crystal and subsequent application was therefore carried out at -50°C .^[8] The hexanuclear mesityl galloxane hydroxide **3** crystallizes in the space group $R3c$. The oxygen atoms O4 and O3 lie on the threefold axis (Fig. 1). To a first approximation the structure can be described as a distorted octahedron of six gallium atoms. Each face of this octahedron per hemisphere is capped alternately by an μ_3 -oxygen atom and a μ_3 -hydroxide group. All gallium atoms are formally in the oxidation state +III and are five-coordinate. This degree of coordination is not unusual for gallium compounds (e.g. in $\text{Me}_2\text{GaO}_2\text{C}_7\text{H}_5$; $\text{O}_2\text{C}_7\text{H}_5 = \alpha\text{-tropolyl}$).^[12] The hydroxidic oxygen atoms form significantly longer Ga–O distances than the oxidic oxygen atoms (221 and 245 pm for O1 and O3, respectively, in contrast to 187 and 189 pm for O2 and O4, respectively). Furthermore, the environment of the hydroxidic oxygen atoms is more pyramidalized than that of the oxidic oxygen atoms (Ga–O–Ga for O1 and O3 88.1 and 78.6°, respectively, in contrast for O2 and O4 110.7 and 108.9°, respectively). This observation is consistent with the one made for $\text{Mes}_6\text{Ga}_6\text{F}_4\text{O}_4$,^[13] namely that the

Fig. 1. Crystal structure of $[\text{3}(\text{thf})_4] \cdot 6\text{THF}$. The six noncoordinated THF molecules are not shown. The bond lengths [pm] and angles [°] labeled with an * are average values, the numbers in square brackets are the range of values, the standard deviations are extreme values: O1–Ga 221(1)* [213(1)–230(1)], O3–Ga 245(1), O2–Ga 187(1)* [185.5(9)–189(1)], O4–Ga 189.3(5), Ga–C 196(1)* [195(1)–197(1)], Ga–O1–Ga 88.1(4)* [87.5(3)–88.6(3)], Ga–O3–Ga 78.6(4), Ga–O2–Ga 110.7(5)* [107.6(4)–113.0(5)], Ga–O4–Ga 108.9(5).

oxidic oxygen atoms form a comparable mean angle of 111.6° ($105.9\text{--}117.7^\circ$) with the two bound gallium atoms. The average Ga–C distance of 196 pm is in the range typical for arylgallium compounds.^[14] THF molecules in the spaces left by the six mesityl ligands coordinate by hydrogen bonds to the four OH functions of the $\text{Ga}_6\text{O}_4(\text{OH})_4$ framework (O1...O5 273 and O3...O6 252 pm). Coordination of this sort has already been described for $[(t\text{Bu}_2\text{AlOH})_3 \cdot 2\text{thf}]$.^[11]

It is thus possible to prevent condensation through reaction of all hydroxide groups by the use of sterically demanding substituents. In addition Neumüller and Gahlmann observed the formation of the hexanuclear organogallium fluoride oxide $\text{Mes}_6\text{Ga}_6\text{F}_4\text{O}_4$, isoelectronic to **3**,^[13] in the partial hydrolysis of Mes_2GaF . It may well be possible that OH–metal interactions play a role not only in the polymerization, but also in the water-accelerated zirconium-catalyzed carbalumination of alkynes.^[15]

Experimental Procedure

3: a) A solution of GaMe_3 (1.4 g, 3.3 mmol) in THF (20 mL) was added dropwise to a solution of GaCl_3 (0.3 g, 1.7 mmol) in THF (20 mL) and stirred for 30 h at room temperature. Subsequently KOH (0.28 g, 5.00 mmol, not dried) was added to this solution and the resulting mixture was stirred for 5 d at room temperature under an inert atmosphere. After the KCl had been filtered off, the filtrate was concentrated under vacuum and the white solid obtained was washed with *n*-hexane (20 mL). Crystallization from THF afforded 0.9 g (66%) $[\text{3}(\text{thf})_4]$. The decomposition temperature of the THF-free compound **3** lay above 350°C . Correct elemental analysis for C, H, Ga.

^1H NMR (250 MHz, $[\text{D}_8]\text{THF}$, TMS_{ext}): $\delta = 6.73\text{--}6.71$ (m, Ar–H), 6.37 (s, OH), 2.57–2.53 (m, 2,6-CH₃), 2.19–2.17 (m, 4-CH₃); IR (nujol): $\tilde{\nu}[\text{cm}^{-1}] = 3671$ s, 3521 s, br., 3015 s, 1719 m, 1601 vs, 1558 s, 1412 m, 1292 m, 1056 vs, 1028 vs, 848 s, 703 s, 589 m, 543 s.

b) Degassed water (106 μL , 5.9 mmol) was added by syringe to a solution of GaMe_3 (2.52 g, 5.9 mmol) in toluene (100 mL) at -78°C and the mixture was stirred and slowly allowed to warm to room temperature. Subsequently it was stirred for 3 d, the volatiles were removed under vacuum, the white residue washed with *n*-hexane (20 mL) and filtered. The residue was dried under vacuum (10^{-4} mbar) for about 15 h. Yield of **3** (0.72 g, 58%). Correct elemental analysis of C and H for $\text{Mes}_6\text{Ga}_6\text{O}_4(\text{OH})_4$. IR and NMR spectra in $[\text{D}_8]\text{THF}$ were consistent with those for the product prepared according to method a).

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Benziporphyrin, a Benzene-Containing, Nonaromatic Porphyrin Analogue

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An interesting approach for modifying the basic porphyrin framework for the most varied applications^[1] is replacing the pyrrole ring by another five-membered ring heteroarene such as furan and thiophene,^[2] or by pyridine^[3, 4] or benzene. When 1,3-disubstituted six-membered rings are incorporated, the macrocycle can achieve 18π aromaticity only at the expense of the 6π aromatic system. The obvious question is which of the two rings wins this competition. Recently we reported on the synthesis of a modified porphyrinogen in which a pyrrole is replaced by a pyridine unit.^[4] However, we could not obtain the 18π aromatic tautomer with maximum unsaturation which corresponds to a porphyrin. The oxidation of the pyriporphyrinogen^[4] leads to the ketone instead.

We report here on the first benzene-containing macrocycle that is a porphyrin analogue, which in contrast to the pyriporphyrins,^[4] was obtained simply by oxidation of the appropriate porphyrinogen **3**. Tripyrranedicarboxylic acid **2b**^[5] was decar-

boxylated in situ and condensed with isophthalaldehyde (**1**) in dichloromethane/THF with 33% HBr in glacial acetic acid as the catalyst. The resulting macrocycle was then oxidized in situ with *p*-chloranil to give **4**. In analogy to pyriporphyrin we propose the name benziporphyrin for the unsubstituted framework and the numbering shown for **4a**.

The spectroscopic data for the compound give no indication of 18π aromaticity and cyclic conjugation in the tautomer. The UV spectrum, for example, does not display the Soret band (420 nm, $\lg \epsilon > 4$) characteristic of porphyrins, and in the ¹H NMR spectrum the pyrrole-NH protons ($\delta = 8.90$) and the inner benzenoid protons ($\delta = 7.88$) do not show the shielding typical for the inner protons of an [18]annulene. Thus the tautomers **4a/b** (**4**: **1** in CDCl₃) have an intact benzenoid arene unit. It is apparent that the aromatic 18π tautomer does not exist even when only one 6π arene would have to be sacrificed. Thus **4**, a prototype of macrocycles in which benzenoid rings successively replace the pyrrole rings of porphyrin, indicates that porphyrin analogues with more than one 6π arene^[6] cannot be [18]annulenes.

The successful preparation of **4** also implies that the surprising behavior of the "pyriporphyrinogens"^[4] towards oxidants results from the side reaction of the reactive α -alkyl group of the pyridine rings and is not a consequence of the unattainable 18π aromaticity.

Experimental Procedure

Diester **2a** (635 mg, 1 mmol) was dissolved in 80 mL of anhydrous THF and treated with 200 mg of Pd/C (10% Pd) and 0.1 mL of triethylamine. After 3 h of hydrogenation at ambient pressure the catalyst was removed by vacuum filtration and the filtrate (**2b**) added dropwise to a solution of isophthalaldehyde (**1**) (134 mg, 1 mmol) in 800 mL of dichloromethane. Argon was then bubbled through the reaction mixture for 15 min, and then 1.8 mL of a solution of HBr in glacial acetic acid (33%) was added. The reaction mixture was stirred for 4 h with exclusion of light. 750 mg of *p*-chloranil was added, and 15 min later the reaction mixture was neutralized with 2.5 mL of triethylamine and left to stand ca. 15 h. The solvent was removed under

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