

## Rearrangement

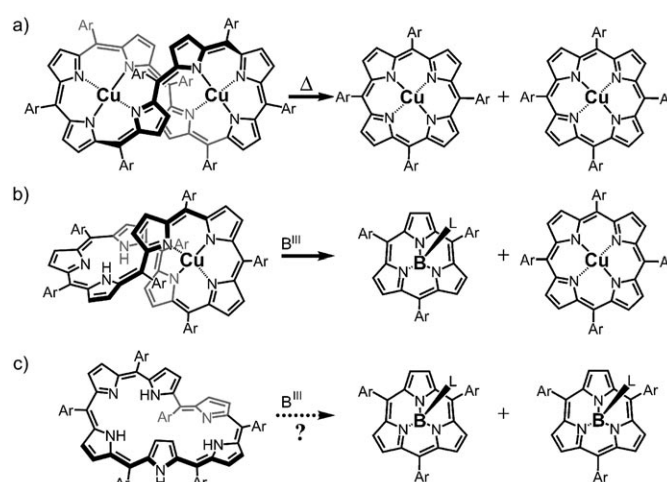
# Boron(III) Induced Skeletal Rearrangement of Hexaphyrin(1.1.1.1.1.1) to Hexaphyrin(2.1.1.0.1.1)\*\*

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In recent years, increasing attention has been focused on expanded porphyrins<sup>[1]</sup> that exhibit attractive properties, such as multi-metal coordination,<sup>[2]</sup> facile redox interconversion,<sup>[3]</sup> anion sensing,<sup>[4]</sup> large nonlinear optical properties,<sup>[5]</sup> and Möbius aromaticity.<sup>[6]</sup> In addition, skeletal rearrangements and the resulting intriguing chemical reactivities, which are often triggered upon metalation have been studied.<sup>[7]</sup> In 2003, Vogel et al. found that metalation of 5,24-dioxo-octaphyrin(1.1.1.0.1.1.1.0) with nickel(II) caused a rearrangement to give a bis-nickel(II) complex of spirodicorrole through the extrusion of two carbon dioxide molecules.<sup>[8]</sup> They also disclosed that the metalation of [34]octaphyrin(1.1.1.0.1.1.1.0) with palladium(II) caused a rearrangement to a bis-spirodi-porphyrin skeleton.<sup>[8]</sup>

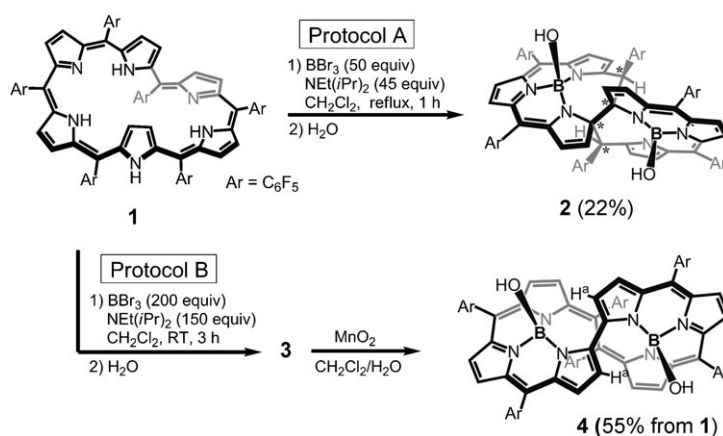
In the last decade, we have focused on the exploration of the chemistry of *meso*-aryl substituted expanded porphyrins.<sup>[9]</sup> In the course of these studies, we found two thermal splitting reactions: 1) from bis-copper(II) [36]octaphyrin(1.1.1.1.1.1.1.1) to two Cu<sup>II</sup> [18]porphyrins (Scheme 1a)<sup>[10]</sup> and 2) from a putative Cu<sup>II</sup>–B<sup>III</sup> complex of [32]heptaphyrin(1.1.1.1.1.1.1) to a Cu<sup>II</sup> [18]porphyrin and a B<sup>III</sup> [14]subporphyrin (Scheme 1b).<sup>[11]</sup> Both reactions are apparently initiated by the transannular  $\pi$ -electron interactions at the hinge positions. These results made us envisage a similar splitting reaction of [28]hexaphyrin(1.1.1.1.1.1) (**1**)<sup>[12]</sup> to produce B<sup>III</sup> [14]subporphyrin molecules as a result of appropriate material balance (Scheme 1c).

To test this idea, we examined the reaction of [28]hexaphyrin **1** with boron(III) reagents. Compound **1** was treated with 50 equivalents of BBr<sub>3</sub> in the presence of NEt(*i*Pr)<sub>2</sub> and the resulting mixture was heated under reflux for 1 h (Scheme 2, Protocol A), which yielded a complicated mixture, from which blue complex **2** was isolated in 22 % yield as the major product. The structure of **2** was determined by X-ray diffraction analysis to be a transannularly  $\alpha$ , $\alpha$ -bridged hexaphyrin bis-boron(III) complex.



**Scheme 1.** Splitting reactions of *meso*-aryl expanded porphyrins:

a) [36]octaphyrin to two [18]porphyrins, b) [32]heptaphyrin to [14]subporphyrin and [18]porphyrin, and c) [28]hexaphyrin to two [14]subporphyrins.



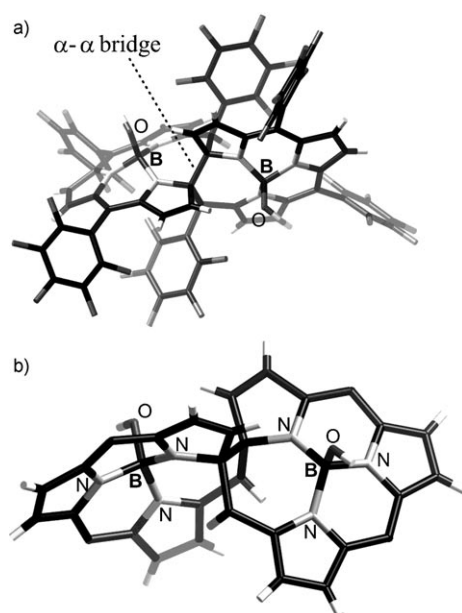
**Scheme 2.** B<sup>III</sup> insertion and resulting rearrangement of **1**. \* = sp<sup>3</sup>-hybridized carbon atom.

(Figure 1).<sup>[13]</sup> The two bridged  $\alpha$ -carbon atoms and neighboring two *meso*-carbon atoms are sp<sup>3</sup>-hybridized as evinced by the <sup>13</sup>C NMR spectrum that displays corresponding signals at  $\delta$  = 41.29 and 83.06 ppm. In accord with the structure, the <sup>1</sup>H NMR spectrum of **2** supports a C<sub>2</sub> symmetrical molecular structure and the absence of a macrocyclic ring current. The <sup>11</sup>B NMR chemical shift is  $\delta$  = –1.91 ppm. The UV/Vis absorption spectrum of **2** shows broad bands at 371, 414, and 645 nm probably arising from the tripyrromethene moieties (Supporting Information). The structure of **2** sug-

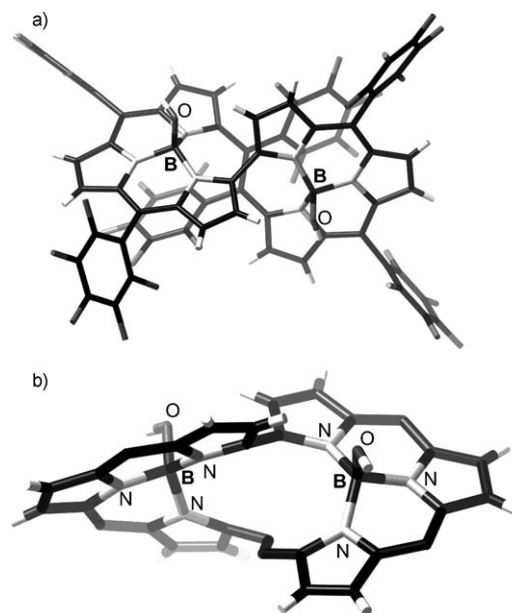
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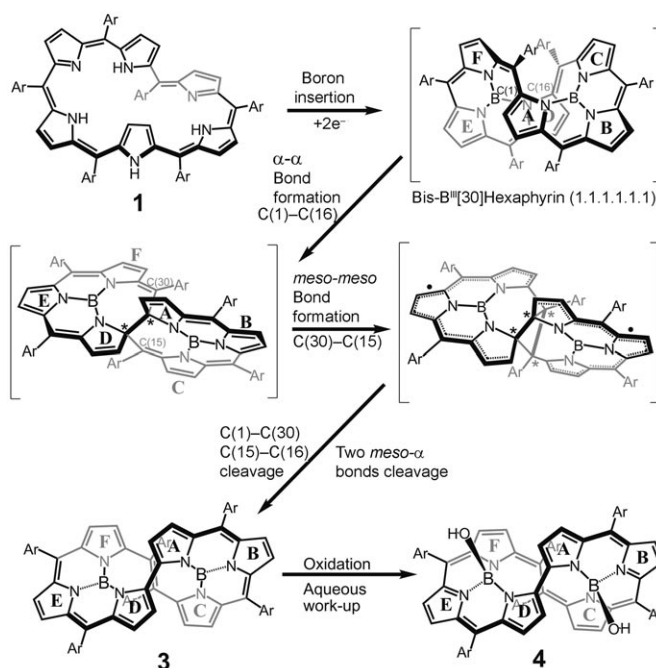
**Figure 1.** X-ray crystal structure of **2**: a) top view and b) side view; *meso*-C<sub>6</sub>F<sub>5</sub> substituents in the side view are omitted for clarity.



**Figure 2.** X-ray crystal structure of **4**: a) top view and b) side view; *meso*-C<sub>6</sub>F<sub>5</sub> substituents in the side view are omitted for clarity.

gests that the transannular interactions are mandatory during the complexation of B<sup>III</sup> by **1** but do not drive the molecule to make the double *meso*, $\alpha$ -linkage that is required for the targeted splitting reaction.<sup>[10b]</sup>

We found that the treatment of **1** with 200 equivalents of BBr<sub>3</sub> in the presence of NEt(*i*Pr)<sub>2</sub> and subsequent aqueous work-up (Scheme 2, Protocol B) gave the reddish brown **3** as the main product (see below), which slowly changed under ambient conditions to purple bis-boron(III) complex **4**. The synthetic procedure was optimized by a final oxidation with 3 equivalents of MnO<sub>2</sub> to produce **4** immediately (in 55% yield from **1**). Employing Protocol B, complex **2** was not detected, while following Protocol A a trace amount of **4** was obtained (Supporting Information). Quite unexpectedly, the structure of **4** was revealed by single-crystal X-ray diffraction analysis to be a bis-B<sup>III</sup> complex of [28]hexaphyrin(2.1.1.0.1.1) that has a figure-of-eight conformation containing a directly connected bipyrrole unit and a *s-trans* 1,3-butadienyl linkage at the opposite position (Figure 2).<sup>[13]</sup> Distinct bond-length alternation along the 28 $\pi$  electron circuit is also apparent. Bond lengths of the directly connected  $\alpha$ - $\alpha$  carbon bond and the central bond in the *s-trans* 1,3-butadienyl linkage are 1.46 and 1.45 Å, respectively, which are similar to that of the central C–C bond of 1,3-butadiene (1.48 Å). The formation of **4** requires a drastic and unprecedented skeletal rearrangement, namely the transposition of an aryl-substituted *meso*-position over pyrrole units. The mechanism of this rearrangement is still not settled, but is considered to involve the formation of  $\alpha$ - $\alpha$  and *meso*-*meso* bonds and the subsequent cleavage of two *meso*- $\alpha$  bonds (Scheme 3 and Supporting Information). This route is different from the mechanism of the anticipated splitting reaction to produce two subporphyrins, which requires the formation of two *meso*- $\alpha$  bonds and the subsequent cleavage of two *meso*- $\alpha$  bonds.<sup>[10b]</sup>

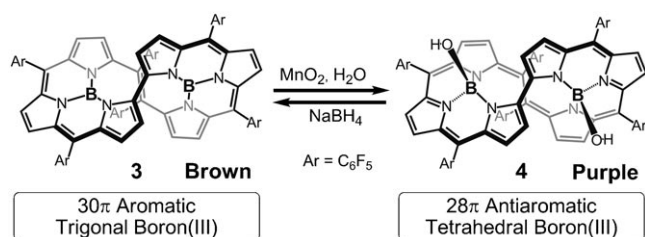


**Scheme 3.** Possible mechanism from **1** to **4**. \* = sp<sup>3</sup>-hybridized carbon atom.

As indicated by the crystal structure, the complex **4** has two tri-*N*-pyrrolyl hydroxy boron(III) hemi-macrocycles, whose axial hydroxy ligands can be exchanged by alkoxy ligands upon treatment with alcohol as found for the subporphyrins (Supporting Information).<sup>[11b]</sup> In line with the C<sub>2</sub> symmetrical structure, the <sup>1</sup>H and <sup>19</sup>F NMR spectra of **4** are simple, exhibiting signals of the peripheral  $\beta$ -protons at  $\delta$  = 8.76, 6.56, 6.23, 5.94, and 5.46 ppm in a integral ratio of

1:1:1:1:2 with a signal at  $\delta = 4.09$  ppm for the axial hydroxy group. The  $^{11}\text{B}$  NMR spectrum showed a signal in a relatively deshielded region at  $\delta = 5.51$  ppm. The  $^1\text{H}$  NMR signal at  $\delta = 8.76$  ppm can be assigned to the  $\text{H}^a$   $\beta$ -protons located above the twisted position of the figure-of-eight conformation (Scheme 2).<sup>[14]</sup> Overall, these NMR data, the calculated molecular orbital diagram, and the NICS<sup>[15]</sup> values ( $\delta = +6.78$  to  $+10.93$  ppm) at the points inside the macrocycle, including the center of the macrocycle and the average positions among two nitrogen atoms and two alpha carbons of neighboring pyrrole units, indicated weak  $28\pi$  Hückel antiaromaticity (Supporting Information). The UV/Vis/NIR absorption spectrum of **4** shows some broad bands, without low-energy bands in near-IR region, which are also consistent with its antiaromatic character (Supporting Information).<sup>[5,16]</sup> Cyclic voltammetry measurement revealed reversible oxidation potentials at 0.24 and 0.54 V (vs.  $\text{Fc}/\text{Fc}^+$ ;  $\text{Fc} = [(\text{C}_5\text{H}_5)_2\text{Fe}]$ ) and reduction potentials at  $-0.67$  and  $-1.07$  V, hence indicating a small electrochemical HOMO–LUMO gap (0.91 V), which is characteristic of antiaromatic species (Supporting Information).<sup>[16]</sup> The weakness of antiaromaticity may be ascribed to the large dihedral angle ( $72^\circ$ ) between directly linked bipyrrrole unit.

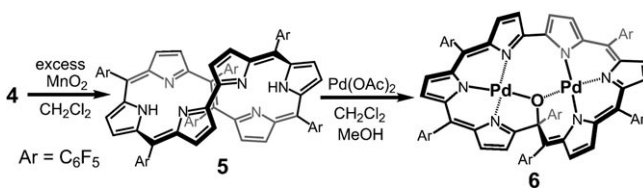
Importantly, the redox interconversion between **3** and **4** was confirmed as shown in Scheme 4. The complex **3**, which was formed as the initial product in Protocol B (Scheme 2),



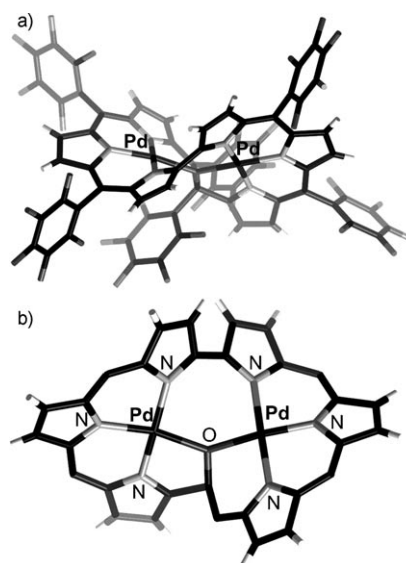
**Scheme 4.** Switching  $\text{B}^{\text{III}}$  coordination mode by the redox interconversion of hexaphyrin(2.1.1.0.1.1).

has been characterized to be [30]hexaphyrin(2.1.1.0.1.1) with  $\text{B}^{\text{III}}$  ions in a trigonal coordination environment. The complex **3** was slowly oxidized to **4** when left standing in the air. High-resolution ESI-TOF mass spectroscopy showed the parent ion peak of **3** at  $m/z$  1480.0861 (calcd for  $\text{C}_{66}\text{H}_{12}\text{B}_2\text{F}_{30}\text{N}_6$   $[M]^+$ : 1480.0856). The  $^1\text{H}$  NMR spectrum shows six doublets at  $\delta = 7.66, 7.62, 7.53, 7.24, 7.21,$  and  $5.44$  ppm without any signal for axial ligands in line with the assigned weakly aromatic  $30\pi$  hexaphyrin structure. The density functional theory (DFT; B3LYP/6-31G(d))<sup>[17]</sup> optimized structure of **3** indicates the figure-of-eight conformation with a *trans* vinylene linkage and the NICS value ( $\delta = -5.72$  to  $-11.70$  ppm) at the corresponding positions inside the macrocycle, whose significant negative values demonstrate macrocyclic diatropic ring current (Supporting Information). The reversible interconversion between **3** and **4** is interesting, in that switching between tetrahedral versus trigonal  $\text{B}^{\text{III}}$  coordination occurs upon the change in the number of  $\pi$  electrons in hexaphyrin(2.1.1.0.1.1).<sup>[18]</sup>

The free-base [26]hexaphyrin(2.1.1.0.1.1) (**5**; Scheme 5) was obtained from **4** in 70% yield upon treatment with a large excess of  $\text{MnO}_2$  (ca. 300–400 equiv) at room temperature. The loss of  $\text{B}^{\text{III}}$  ions is induced by the change in the macrocyclic  $\pi$  network from a  $28\pi$  to  $26\pi$  system and thus from being a tetraanionic to a dianionic ligand. The parent ion peak of **5** was observed at  $m/z$  1461.0933 (calcd for  $\text{C}_{66}\text{H}_{15}\text{F}_{30}\text{N}_6$   $[M+H]^+$ : 1461.0874). The  $^1\text{H}$  NMR spectrum showed a broad signal at  $\delta = 11.41$  ppm arising from NH and six signals for  $\beta$ -protons in the range of  $\delta = 6.93$ – $6.34$  ppm, indicating intramolecular hydrogen bonds between aminic/iminic pyrrole subunits and the non-aromaticity of the twisted  $26\pi$  conjugated system. The DFT optimized structure of **5** indicated a figure-of-eight macrocycle with a *trans*-vinylene linkage. The calculated NICS values ( $\delta = -0.31$  to  $-3.70$  ppm) at the corresponding points inside the macrocycle support its non-aromaticity (Supporting Information). The UV/Vis/NIR absorption spectrum of **5** shows rather broad bands at 345, 548, and 653 nm with relatively small absorption coefficients ( $\epsilon \approx 67\,000\text{ M}^{-1}\text{ cm}^{-1}$ ), which is consistent with the non-aromaticity.<sup>[11]</sup> To our knowledge this is the first synthesis of [26]hexaphyrin(2.1.1.0.1.1).<sup>[19]</sup> The bis-palladium(II) complex **6** was synthesized from **5** in 22% yield upon treatment with  $\text{Pd}(\text{OAc})_2$  (Scheme 5). The crystal structure of **6** shows that the two  $\text{Pd}^{\text{II}}$  ions coordinated in a square-planar manner are bridged by the oxygen atom attached to a  $\text{C}_2$  carbon linkage (Figure 3).<sup>[13]</sup> The oxygenated *meso*-carbon atom is  $\text{sp}^3$ -



**Scheme 5.**  $\text{B}^{\text{III}}$  removal from **4** to give [26]hexaphyrin(2.1.1.0.1.1) **5** and its subsequent  $\text{Pd}^{\text{II}}$  metalation to give **6**.



**Figure 3.** X-ray crystal structure of **6**: a) top view and b) side view; *meso*- $\text{C}_6\text{F}_5$  substituents are omitted in the side view for clarity.



hybridized, hence disrupting the macrocyclic  $\pi$  conjugation. The NMR and absorption spectra of **6** are also consistent with the structure (Supporting Information). These results indicate that the hexaphyrin **5** can serve as a metal-binding ligand despite its distorted figure-of-eight structure.

In summary, the unprecedented rearrangement from hexaphyrin(1.1.1.1.1.1) into hexaphyrin(2.1.1.0.1.1) was found upon  $B^{III}$  complexation. Within a hexaphyrin(2.1.1.0.1.1) skeleton, the reversible interconversion between trigonal versus tetrahedral  $B^{III}$  coordination was demonstrated by the redox reactions between  $30\pi$  versus  $28\pi$  electronic system. The free-base hexaphyrin(2.1.1.0.1.1), obtained by the oxidative removal of the boron centers, was shown to serve as a ligand for two  $Pd^{II}$  centers. Boron(III)-induced skeletal rearrangements of other expanded porphyrins are worthy of further investigation, and are being studied in our laboratory.

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- [1] a) A. Jasat, D. Dolphin, *Chem. Rev.* **1997**, 97, 2267; b) H. Furuta, H. Maeda, A. Osuka, *Chem. Commun.* **2002**, 1795; c) J. L. Sessler, D. Seidel, *Angew. Chem.* **2003**, 115, 5292; *Angew. Chem. Int. Ed.* **2003**, 42, 5134.
- [2] a) S. Shimizu, A. Osuka, *Eur. J. Inorg. Chem.* **2006**, 1319; b) J. L. Sessler, E. Tomat, *Acc. Chem. Res.* **2007**, 40, 371.
- [3] a) T. Köhler, D. Seidel, V. Lynch, F. O. Arp, Z. Ou, K. M. Kadish, J. L. Sessler, *J. Am. Chem. Soc.* **2003**, 125, 6872; b) S. Mori, A. Osuka, *J. Am. Chem. Soc.* **2005**, 127, 8030; c) Y. Kamimura, S. Shimizu, A. Osuka, *Chem. Eur. J.* **2007**, 13, 1620.
- [4] J. L. Sessler, S. Camiolo, P. A. Gale, *Coord. Chem. Rev.* **2003**, 240, 17.
- [5] a) T. K. Ahn, J. H. Kwon, D. Y. Kim, D. W. Cho, D. H. Jeong, S. K. Kim, M. Suzuki, S. Shimizu, A. Osuka, D. Kim, *J. Am. Chem. Soc.* **2005**, 127, 12856; b) J. M. Lim, Z. S. Yoon, J.-Y. Shin, K. S. Kim, M.-C. Yoon, D. Kim, *Chem. Commun.* **2009**, 261.
- [6] a) Z. S. Yoon, A. Osuka, D. Kim, *Nat. Chem.* **2009**, 1, 113; b) Y. Tanaka, S. Saito, S. Mori, N. Aratani, H. Shinokubo, N. Shibata, Y. Higuchi, Z. S. Yoon, K. S. Kim, S. B. Noh, J. K. Park, D. Kim, A. Osuka, *Angew. Chem.* **2008**, 120, 693; *Angew. Chem. Int. Ed.* **2008**, 47, 681.
- [7] L. Latos-Grażyński, *Angew. Chem.* **2004**, 116, 5234; *Angew. Chem. Int. Ed.* **2004**, 43, 5124.
- [8] E. Vogel, M. Michels, L. Zander, J. Lex, N. S. Tuzun, K. N. Houk, *Angew. Chem.* **2003**, 115, 2964; *Angew. Chem. Int. Ed.* **2003**, 42, 2857.
- [9] a) J.-Y. Shin, H. Furuta, K. Yoza, S. Igarashi, A. Osuka, *J. Am. Chem. Soc.* **2001**, 123, 7190; b) J.-Y. Shin, H. Furuta, A. Osuka, *Angew. Chem.* **2001**, 113, 639; *Angew. Chem. Int. Ed.* **2001**, 40, 619.
- [10] a) Y. Tanaka, W. Hoshino, S. Shimizu, K. Youfu, N. Aratani, N. Maruyama, S. Fujita, A. Osuka, *J. Am. Chem. Soc.* **2004**, 126, 3046; b) Y. Tanaka, H. Shinokubo, Y. Yoshimura, A. Osuka, *Chem. Eur. J.* **2009**, 15, 5674.
- [11] a) S. Saito, K. S. Kim, Z. S. Yoon, D. Kim, A. Osuka, *Angew. Chem.* **2007**, 119, 5687; *Angew. Chem. Int. Ed.* **2007**, 46, 5591; b) Y. Inokuma, A. Osuka, *Dalton Trans.* **2008**, 2517.
- [12] a) Recently we have shown that *meso*-aryl [28]hexaphyrins are in the equilibrium in solution, where Möbius conformers are dominant rather than a planar Hückel rectangular conformer: J. Sankar, S. Mori, S. Saito, H. Rath, M. Suzuki, Y. Inokuma, H. Shinokubo, K. S. Kim, Z. S. Yoon, J.-Y. Shin, J. M. Lim, Y. Matsuzaki, O. Matsushita, A. Muranaka, N. Kobayashi, D. Kim, A. Osuka, *J. Am. Chem. Soc.* **2008**, 130, 13568; see also: b) M. G. P. M. S. Neves, R. M. Martins, A. C. Tomé, A. J. D. Silvestre, A. M. S. Silva, V. Félix, M. G. B. Drew, J. A. S. Cavaleiro, *Chem. Commun.* **1999**, 385; c) L. Simkhovich, I. Goldberg, Z. Gross, *Org. Lett.* **2003**, 5, 1241.
- [13] See the Supporting Information for crystallographic details. CCDC 765595 (2), 765596 (4), 765597 (6) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).
- [14] S. Saito, J.-Y. Shin, J. M. Lim, K. S. Kim, D. Kim, A. Osuka, *Angew. Chem.* **2008**, 120, 9803; *Angew. Chem. Int. Ed.* **2008**, 47, 9657. The  $H^a$  protons are also located in the range of weak  $C-H^a \cdots O$  hydrogen bonds (Supporting Information).
- [15] P. v. R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao, N. J. R. v. E. Hommes, *J. Am. Chem. Soc.* **1996**, 118, 6317.
- [16] A. Muranaka, O. Matsushita, K. Yoshida, S. Mori, M. Suzuki, T. Furuyama, M. Uchiyama, A. Osuka, N. Kobayashi, *Chem. Eur. J.* **2009**, 15, 3744.
- [17] Gaussian 09 (Revision A.02), M. J. Frisch, et al. Gaussian, Inc., Wallingford CT, **2009**.
- [18] a) A. Flores-Parra, R. Contreras, *Coord. Chem. Rev.* **2000**, 196, 85; b) C. G. Claessens, D. González-Rodríguez, T. Torres, *Chem. Rev.* **2002**, 102, 835; c) N. Kano, J. Yoshino, T. Kawashima, *Org. Lett.* **2005**, 7, 3909; d) A. Weiss, M. C. Hodgson, P. D. W. Boyd, W. Siebert, P. J. Brothers, *Chem. Eur. J.* **2007**, 13, 5982; e) A. Młodzianowska, L. Latos-Grażyński, L. Szterenberga, M. Stępień, *Inorg. Chem.* **2007**, 46, 6950.
- [19] For porphyrin(2.1.0.1) ("Corrphycene"), see the reference: E. Vogel, *J. Heterocycl. Chem.* **1996**, 33, 1461.