Some Reactions of Magnesium Arylporphyrazines: Evidence of Dehydroporphyrazine Formation

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The reactivity of the 2,3-dibromobenzo-annulated 2,3,7,8,12,13-hexakis(*m*-trifluoromethylphenyl)porphyrazine magnesium complex **1** towards butyllithium and *tert*-butylmagnesium chloride in the presence of metallic magnesium was studied. It was found that *n*-butyllithium reacts mainly with the porphyrazine macrocycle to give tetraazachlorins and other reduction products, similarly to porphyrins. On treatment of **1** with *t*BuMgCl and Mg, dehydroporphyrazine **4** (arynoporphyrazine) was generated and trapped with furan, confirming the possibility of the formation of a dehydrophthalocyanine. The structures of the products were verified by UV/Vis and NMR spectroscopy, and also mass spectrometry (MALDI-TOF). Utilization of the tetrapyrrolic macrocycle **1** for this type of reaction may become a new synthetic strategy for unsymmetrical peripheral derivatization of phthalocyanines and related compounds.

Introduction

Peripheral derivatization of phthalocyanines for potential applications as functional materials has received much attention, different strategies for unsymmetrical functionalization of phthalocyanines having recently been developed.[1] Many of the reactions and approaches that turned out to be effective with simple aromatic compounds have also been applied for phthalocyanines and related systems. However, despite all the diversity of synthetic approaches to unsymmetrical phthalocyanines, the development of new strategies in this field is still important.

Diels−Alder reactions between dienes and dehydrobenzenes, widely used in common syntheses, may also be useful for the derivatization of phthalocyanines. Reactions involving the generation of 2,3-dehydrophthalocyanine and its trapping with dienes have, to the best of our knowledge, not yet been described, and so the possibility of the generation of such a species merits investigation.

One long-known convenient approach to the generation of dehydrobenzenes involves thermal decomposition of aromatic *ortho*-diazonium carboxylates, obtained from *ortho*-amino carboxylic acids.[2] This type of peripheral functionalization is not yet known for phthalocyanines, because it is rather difficult to achieve. Another widely utilized route to the generation of benzynes is based on treatment of *ortho*-dihalobenzenes with organolithium compounds to give unstable *ortho*-halogen-substituted lithium aryls, which subsequently lose LiHal.[2] The application of this approach for phthalocyanine-like systems has been validated in this work with the 2,3-dibromobenzo-annulated 2,3,7,8,12,13-hexakis(*m*-trifluoromethylphenyl)porphyrazine magnesium complex **1** as a model compound (see Scheme 1). This compound was chosen because it can be prepared and isolated in a pure state relatively easily, and because, similarly to its non-brominated analogue, it possesses the necessary high solubility for further conversions in solution.[3]

Results and Discussion

Compound **1** was prepared by a template cross-condensation of 4,5-dibromophthalonitrile and bis(*m*-trifluoromethylphenyl)fumaronitrile in the presence of magnesium alkoxides in pentanol/octanol mixtures, analogously to the corresponding non-brominated mono-benzoporphyrazine **7**.[3] Compound **1** was separated from the statistical mixture of products by column chromatography (silica gel, CH_2Cl_2/THF) and was crystallized from hexane rather than methanol[3] to minimize coordination or inclusion of water and alcohol.

Treatment of **1** with *n*-butyllithium (BuLi) in THF in the presence of excessive furan under different conditions did not, however, provide the expected dehydro derivative and

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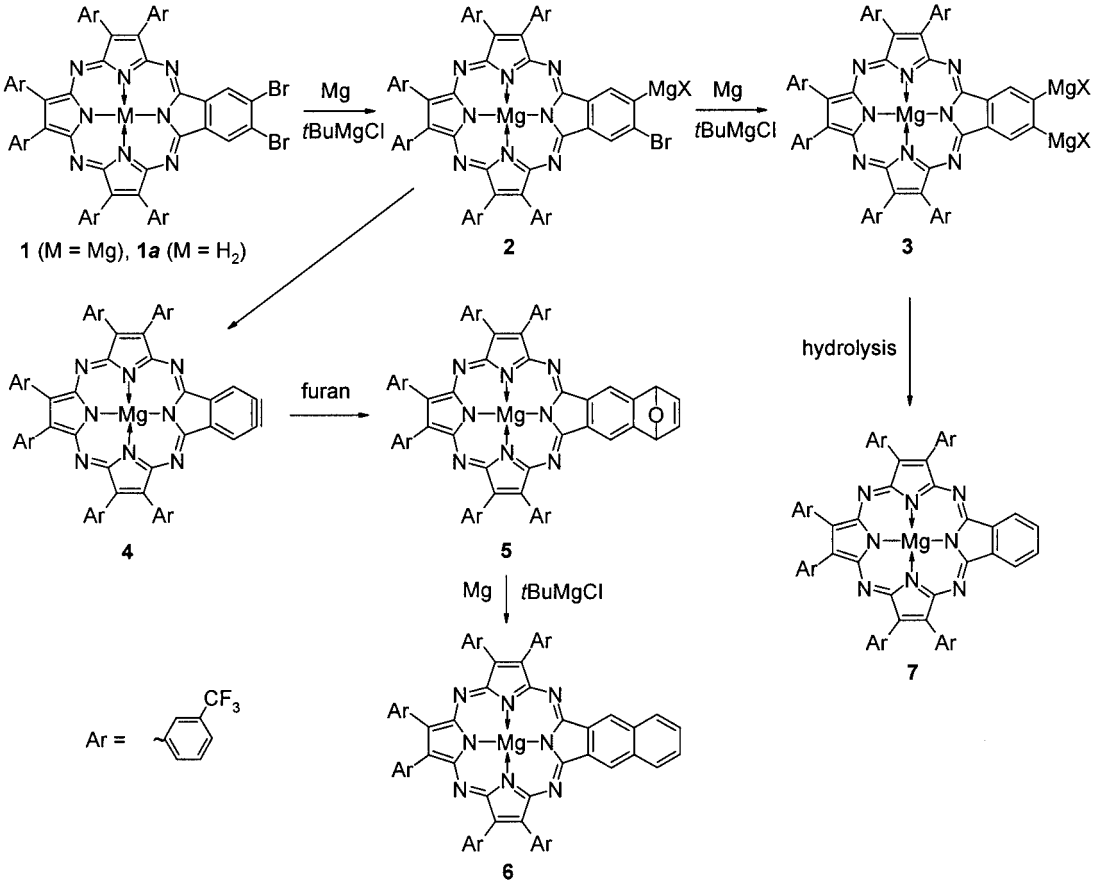


Scheme 1

its Diels–Alder adduct with furan. Use of a fourfold or even higher excess of BuLi at −70 °C or higher temperatures (without quenching) caused complete disappearance of the split Q-band of magnesium porphyrazine **1** at 625 and 629 nm in the reaction mixture, indicating an interruption of the cyclic conjugation. Addition only of equimolar amounts of BuLi at −70 °C resulted in the recovery of starting material **1** and its metal-free derivative **1a**. Analysis of this reaction mixture by the MALDI-TOF technique also revealed traces of compounds with higher molecular masses: namely 1466.4 {**1** + 58 (BuH)} and 1483.4 {**1** + 57 (Bu) + 17 (OH)}. This result clearly shows that no exchange of bromine by lithium occurs under the described conditions, due to faster side reactions between BuLi and the porphyrazine complex. We believe that one of these side reactions is the addition of butyllithium to the pyrrolic C_β=C_β double bond of the macrocycle. In order to shed more light on these processes, we performed similar experiments with octakis(*m*-trifluoromethylphenyl)porphyrazinatomagnesium (**8**), which should possess similar reactivity of the macrocycle towards BuLi but is more readily accessible in larger amounts.

Treatment of **8** with two equivalents of BuLi at −80 to −50 °C, after quenching with methyl iodide, water or oxygen, gave mixtures of the starting material together with other coloured compounds. Among these, according to the UV/Vis, ^{1}H and ^{13}C NMR and MALDI-TOF spectra and available literature data relating to tetraazachlorins,[4] mixtures of different magnesium tetraazachlorins had been formed. For example, magnesium 2-butyl-3-hydroxyoctakis(*m*-trifluoromethylphenyl)tetraazachlorin (**9**, see Figure 1) was mainly formed by quenching of the reaction mixture with oxygen, and was stable enough to be isolated by preparative TLC. Its MALDI-TOF spectrum, measured with external calibration and accuracy δ = 10 ppm shows only one cluster peak, corresponding to the molecular formula $C_{76}H_{43}N_8F_{24}MgO$ [MH^+] and fitting well with the calculated isotope distribution. The UV/Vis spectrum of **9** is especially indicative of the tetraazachlorin structure, reported recently.[4] Saturation of the C_β=C_β double bonds in tetraazaporphyrins (or porphyrazines) results in a strong splitting of the Q-band with the Q_x-part being bathochromically shifted and the Q_y-part being shifted towards the blue spectral region (see Figure 1).[4b]

Because of the unsymmetrical structure of **9** and, probably, its isomeric composition (*cis* and *trans* arrangements of hydroxy and butyl substituents), the ^{1}H and ^{13}C NMR spectra of **9** are rather complicated. Additionally, the spectral characteristics of **9** in [D_8]THF differ from those in [D_2]dichloromethane because of strong aggregation in the latter solvent. Furthermore, the obtained amount of the isolated compound was too low for well resolved ^{1}H and

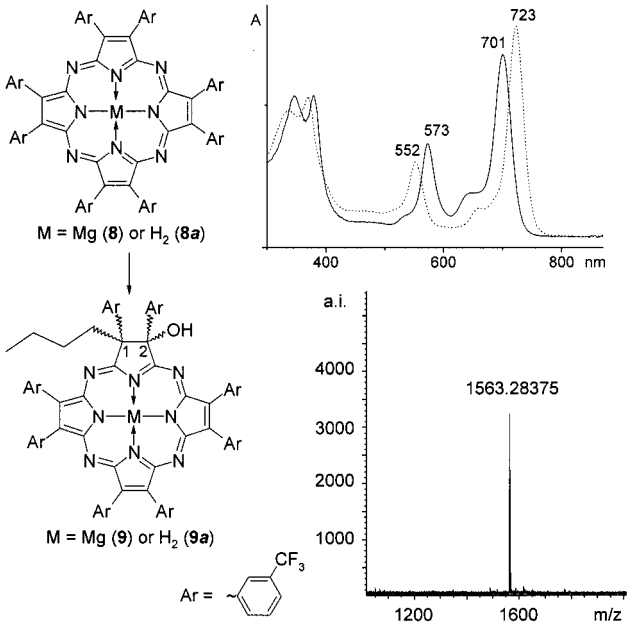


Figure 1. Structures of compounds **8**, **8*a***, **9** and **9*a*** (left); bottom right: MALDI-TOF spectrum of **9**; top right: UV/Vis spectrum of **9** (solid line) and **9*a*** (dotted line) in CH_2Cl_2; the latter was obtained by the treatment of **9** with CF_3COOH and successive partial neutralization with triethylamine directly in the cuvette; for comparison, the absorption maximum (Q-band) of **8** in CH_2Cl_2 is 631 nm[3]

^{13}C NMR spectra to be obtained. Nevertheless, in the ^1H NMR spectrum ([D_8]THF) of **9** we observed a group of signals in the 7.2−8.5 ppm region belonging to eight non-equivalent peripheral aryls, and a triplet ($^3J \approx 7$ Hz) of a CH_3 group of *n*-butyl at $\delta = 0.53$ ppm. In the ^{13}C NMR ([D_2]DCM), additionally to the *n*-butyl signals at 13.1, 22.8, 27.2 and 39.7 (broadened) ppm, two signals at $\delta = 67.1$ and 90.1 ppm could be assigned to carbon atoms 1 and 2, respectively (see Figure 1). Carbon atoms of peripheral aryls in **9** appear as groups of signals in the 122−136 ppm region. The resolution of pyrrolic β- and, especially, α-carbons was not high enough for their unambiguous assignment. Other tetraazachlorins, such as magnesium-2-butyl-octakis(*m*-trifluoromethylphenyl)-3*H*-tetraazachlorin,
which is most probably formed by quenching with water, decompose or convert back to **8** under the aerobic conditions and could not be isolated in a pure state.

Additionally, the demetallated starting material **8a** and tetraazachlorins such as **9a** were detected by TLC and UV/Vis analysis of the reaction mixtures. Other products of these reactions could not be identified. Similar processes also take place in the reactions between *n*-butyllithium and tetraphenylporphyrins, resulting in the addition of BuLi to the $C_\beta{=}C_\beta$ double bond.[5]

Benzynes can also be generated from *ortho*-halo aryl-Grignard reagents, which can in turn be prepared from dihalobenzenes and metallic magnesium, by splitting off magnesium halide.[2,6] In our case, **1** did not react with pure metallic magnesium to give the Grignard compound **2** even at reflux in THF. Therefore, in order to obtain the intermediate **2**, we investigated a metal-exchange reaction[7] of *tert*-butylmagnesium chloride with **1** (Scheme 1). *t*BuMgCl in a mixture with metallic magnesium was indeed found to be suitable for the generation of **2** from **1** and, as a consequence, for the production of dehydroporphyrazine (arynoporphyrazine) **4**. Stirring of the mixture of **1**, *t*BuMgCl, Mg and furan in THF at room temperature gave the 2,3-naphtho-annulated 2,3,7,8,12,13-hexakis(*m*-trifluoromethylphenyl)porphyrazine magnesium complex **6** in 24% yield, most probably by the route shown in Scheme 1. The reaction requires an excess of the Grignard reagent *t*BuMgCl, but it proceeds fairly rapidly after initiation. In situ aromatisation of the intermediate 1,4-epoxy derivative **5**, which is formed through cycloaddition between furan and the dehydroporphyrazine **4**, occurs under these conditions. Aromatisation in the presence of Grignard reagents has also been reported recently for 1,4-dihydroepoxynaphthalene.[8] Non-brominated magnesium mono-benzo-porphyrazine **7** was formed as a minor by-product, probably by the process shown in Scheme 1. It is not yet clear whether **7** is formed by hydrolysis of the corresponding bis-Grignard compound **3** after workup of the reaction mixture, or through another mechanism. The formation of **3** in the presence of the excessive *t*BuMgCl and Mg becomes possible only if the decomposition of the corresponding mono-Grignard compound **2** to form arynoporphyrazine **4** is slow.

Other by-products of this reaction, according to UV/Vis and MALDI-TOF analysis, are probably different tetraazachlorins and other reduction products[9] formed through addition of *t*BuMgCl to the porphyrazine macrocycle. They remained on the chromatography column and required high concentrations of THF to be eluted (as a mixture), while **6** and **7** were eluted with CH_2Cl_2 or CH_2Cl_2 +0.2% THF. Addition of *t*BuMgCl to the dehydroporphyrazine's triple bond could also be possible, but did not occur, since no corresponding *tert*-butyl-substituted product was observed.

We also tried to generate the dehydroporphyrazine **4** under similar conditions and to trap it with anthracene. However, only **7** was obtained instead of the expected triptyceno derivative. This was clearly for the same reason as the formation of traces of **7** in the experiments with furan: bis-Grignard compound **3** was formed from **2** more rapidly than the generation of dehydroporphyrazine **4** (see Scheme 1). It is known that the yields and rates of metal-exchange reactions of Grignard reagents with halogenated compounds, as well as the stability of Grignard compounds, depend strongly on the solvents.[7] The experiments in which anthracene was used were performed in pure THF, whereas the others were carried out in the THF/furan binary solvent. It is very probable that the solvation and, as a consequence, the stabilization of **2** in pure THF is higher than in THF/furan, resulting mainly in the formation of **3**. Additionally, pure THF could promote a metal-exchange reaction, resulting in the faster formation of bis-Grignard compound **3** from mono-Grignard species **2**.

It is also important to mention that the experiments at elevated temperatures mainly gave rise to side-reactions between *t*BuMgCl and the porphyrazine macrocycle, whereas at room temperature the described products **6** or **7** were

formed with good reproducibility. In contrast, 4,5-dibromo-*o*-xylene could not be induced to react with Mg, *t*BuMgCl and furan or anthracene under similar conditions; only the starting material was recovered. This observation indicates a higher reactivity of the bromines in the periphery of **1** as compared with 4,5-dibromo-*o*-xylene.

The structures of **1**, **6** and **7** were determined by different techniques. MALDI-TOF spectra of each compound gave cluster peaks of the molecular ions consistent with the suggested molecular formulas (see Exp. Sect.). The UV/Vis spectra of **1**, **6** and **7** are shown in Figure 2 and demonstrate the changes in electronic structure of magnesium porphyrazines caused by annulation of the additional benzene ring (from **1** to **6**) or by the loss of two bromine atoms (from **1** to **7**). A red shift of the Q_x-band found for **6** in relation to **1** or **7** is consistent with what would be expected.[10] The UV/Vis spectrum of **7** is identical with the spectrum of 2,3,7,8,12,13-hexakis(*m*-trifluoromethylphenyl)benzo[*q*]-porphyrazinatomagnesium that we had prepared earlier directly by cross-condensation.[3]

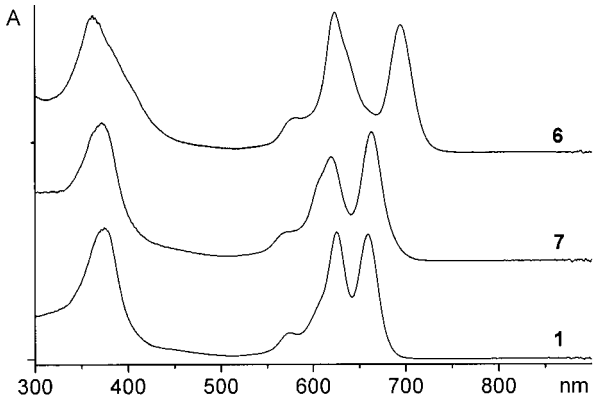


Figure 2. UV/Vis spectra of compounds **1**, **6** and **7** in THF

The ^{1}H and ^{13}C NMR spectra also support the structures of the prepared porphyrazines **1**, **6** and **7**, despite the complicated spectral patterns caused by the low symmetry of these compounds. Six aryls in the periphery of **1**, **6** or **7** are not equivalent, giving rise to several singlets and multiplets in the ^{1}H NMR spectra, which may cover the signals of other aromatic fragments. In the case of **6**, according to the integration, the signals of the 2,5- and 3,4-protons (see Figure 3 and Scheme 2) are masked by two multiplets from the *m*-trifluoromethylphenyl groups at 8.3−8.6 and 7.7−8.0 ppm, respectively. In contrast, the signals of the 1,4- and 2,3-protons in **7** can clearly be seen (albeit only with [D_8]THF as solvent: the ^{1}H NMR spectrum of this compound in [D_6]acetone[3] was slightly different due to the difference in solvation). In the ^{13}C NMR spectra of **1** and **6** all carbons of nonequivalent peripheral aryls give groups of peaks consisting mainly of three signals. The presence of fluorine atoms in **1**, **6** and **7** causes additional quadruplet splitting of some carbon signals, making the spectral pattern more complicated. However, all the groups of signals

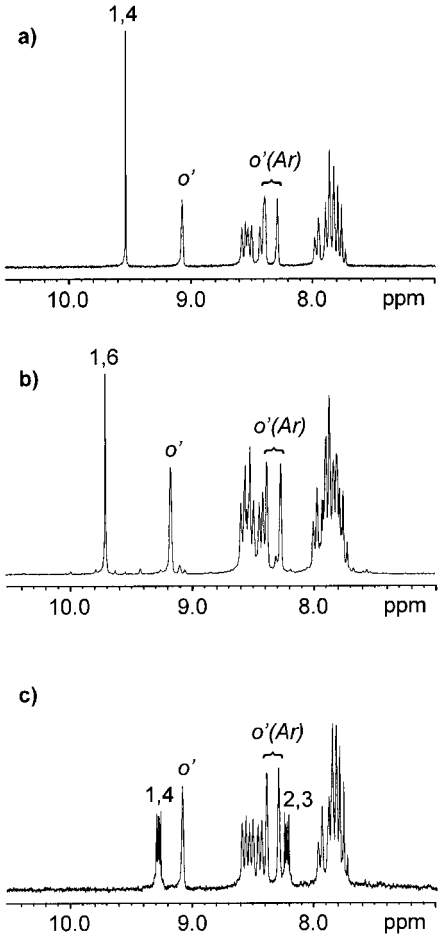
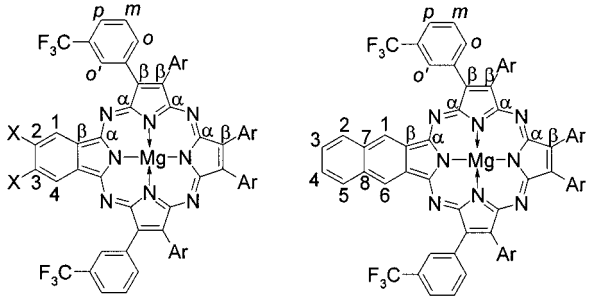


Figure 3. ^{1}H NMR spectra of **1** (a), **6** (b) and **7** (c) in [D_8]THF (see Scheme 2 for designation)



Scheme 2. Designation of the protons and carbon atoms in the ^{1}H and ^{13}C NMR spectra of **1** (left, X = Br), **7** (left, X = H) and **6** (right)

can be assigned reasonably reliably. The chemical shifts of the carbon atoms of the peripheral aryls in the 123−137 ppm range are almost the same for the three different macrocycles **1**, **6** and **7**, and were given for **7** in our previous work.[3] For **1**, the annulated benzo-ring carbon signals appear at 128.9 (1,4-*C*) and 127.8 (2,3-*C*) ppm. In the spectrum of **6**, the carbon atoms of the fused naphthalene fragment appear at 124.4 (1,6-*C*), 131.0 (2,5-*C*), 128.8 (3,4-*C*) and 135.7 (7,8-*C*) ppm.

Additional indication relating to the structural distinction between **6** and the starting material **1** is a drastic difference in the chemical shifts of the α and β carbons, depicted in Figure 4. Because of the unsymmetrical structures of these porphyrazines, the pyrrolic carbons of the macrocycle (α and β, see Scheme 2) give two groups of signals each consisting of four peaks. The positions of these signals are the most sensitive to the distribution of π-electron density in the macrocycles. A strong electronic influence of the additionally fused benzene ring in **6** can be clearly seen from comparison of the spectral patterns of α and β carbon atoms in **1** and **6** (see Figure 4).

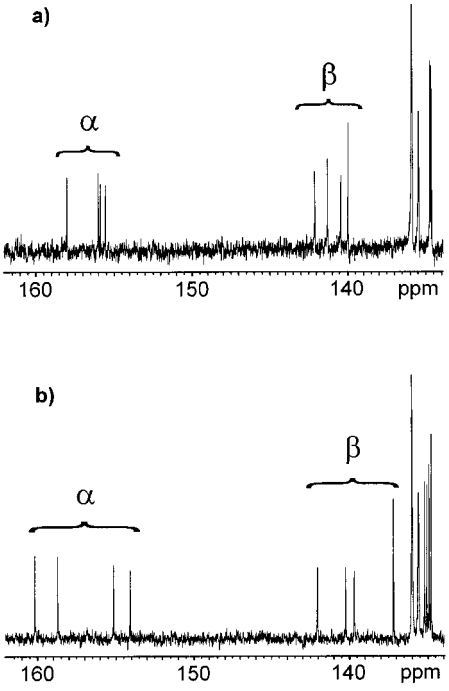


Figure 4. Fragments from ^{13}C NMR spectra of **1** (a) and **6** (b) in [D_8]THF (see Scheme 2 for designation)

Conclusions

We have shown in this work, using the dibromobenzo-fused porphyrazine **1** as a model compound, that a dehydrophthalocyanine-like species can be generated from the corresponding dihalo derivatives through treatment with an organometallic compound, by means of a metal-exchange reaction and splitting off of the metal halide. Thus, dehydroporphyrazine (arynoporphyrazine) **4** could be generated from **1** by treatment with a *t*BuMgCl/Mg mixture, and trapped in situ with furan. However, addition of BuLi at the pyrrolic $C_\beta{=}C_\beta$ double bonds of the macrocycle occurred when **1** was treated with butyllithium, no metal-exchange reaction with peripheral bromines being observed in this case. This is caused by a sufficiently high reactivity of the porphyrazine macrocycle towards reagents such as BuLi. Taking a higher chemical stability of phthalocyanines into account, we expect BuLi to be applicable for the generation of dehydrophthalocyanines by the approach described here. This approach opens an alternative possibility for the nonsymmetric peripheral modification of phthalocyanine-type macrocycles and is currently being investigated in our laboratory.

Experimental Section

Instrumentation: UV/Vis: Shimadzu UV-365; ^1H and ^{13}C NMR: Bruker AC 250 (^1H: 250.131 MHz, ^{13}C: 62.902 MHz). MS (MALDI-TOF): Bruker Autoflex, the spectra were measured with α-cyano-*m*-hydroxycinnamic acid as matrix; Elemental analysis: Euro EA 3000; Cryostat: Thermo Haake EK 90.

2,3-Dibromobenzo-Annulated 2,3,7,8,12,13-Hexakis(*m*-trifluoromethylphenyl)porphyrazine Magnesium Complex 1: Preparation according to the route previously described for the synthesis of 2,3,7,8,12,13-hexakis(*m*-trifluoromethylphenyl)benzo[*q*]porphyrazinatomagnesium,[3] by use of bis(*m*-trifluoromethylphenyl)-fumaronitrile (3 g, 8.2 mmol),[11] 4,5-dibromophthalonitrile (0.8 g, 2.8 mmol),[12] magnesium turnings (0.15 g, 6.2 mmol) and 12 mL of solvent. The products were precipitated and washed with hexane and separated by column chromatography similarly to the described procedure.[3] The collected fraction of **1** was diluted with hexane, the solvents were partially removed, and the compound was left to crystallize for several days. The formed dark crystals with violet reflex were filtered off and dried in vacuo, yielding 320 mg (8%) of the solvate (**1** × THF × 0.5 hexane); the inclusion of the solvents was estimated by integration of ^1H NMR spectrum. UV/Vis (THF): λ (rel. int.) = 374 (1.00), 574 (0.20), 625 (0.97), 659 (0.95) nm. MS (MALDI-TOF): *m*/*z* = 1409.3 [MH^+]. $C_{62}H_{26}Br_2F_{18}N_8Mg \times C_4H_8O \times 1/2\,C_6H_{14}$ (1409.04 + 72.11 +43.09): calcd. C 54.37, H 2.71, N 7.35; found C 54.11, H 2.65, N 7.16. For the ^1H and ^{13}C NMR spectra ([D_8]THF) see Results and Discussion.

Octakis(*m*-trifluoromethylphenyl)porphyrazinatomagnesium (8) was separated from the mixture of products described above, similarly to what has been reported before,[3] and crystallised by addition of hexane. It was purified as follows: the compound was dissolved in diethyl ether, dried overnight over anhydrous $MgSO_4$, filtered and diluted with hexane. Diethyl ether was removed under vacuum and the solution was left to crystallise over one day. The formed crystals were filtered off and dried in vacuo, yielding a solvate **8** × $(C_2H_5)_2O$ × 0.25 hexane.

Treatment with Butyllithium. General Procedure (a): Compound **1** (50 mg, 33 μmol), dry THF (0.6 mL), and dry furan (0.1 mL), or compound **8** (150 mg, 95 μmol) and dry THF (1 mL) in a 5 mL flask closed with a septum was placed in an acetone/methanol bath and cooled to the desired temperature by use of a cryostat. Before cooling, the air was partially removed from the flask and argon was added (syringe). Upon cooling, the pressure in the flask was kept equal to atmospheric pressure by use of the syringe with argon. BuLi (2.5 M solution in hexane, Aldrich, 1−4 molar excess) was added by micro-syringe over 20−30 min with stirring. The reaction mixture was kept in the bath for an additional 1−3 h. If no quenching was performed, the reaction mixture was allowed to warm slowly up overnight. Quenching with water, O_2 or methyl iodide was performed at the reaction temperature. Quenching with oxygen was performed by exchange of argon atmosphere for O_2 by syringe.

A preliminary analysis of the reaction mixtures was carried out by TLC and UV/Vis spectroscopy. Separation of the products, when possible, was performed by preparative TLC (silica gel) with commercially available chloroform. The yields of highly soluble magnesium tetraazachlorins (e.g. **9**) were rather low and were not calculated due to problems with their stability and complete purification. Their preparation was not the aim of this work, and so the yields were not optimised.

Treatment of 1 with *tert*-Butylmagnesium Chloride and Magnesium in the Presence of Furan or Anthracene. General Procedure (b): A mixture of **1** (50 mg, 33 μmol), magnesium powder (3 mg, 123 μmol), dry THF (0.6−0.7 mL) and furan (0.2 mL, 2.8 mmol) or anthracene (60 mg, 0.34 mmol), in a 5 mL flask closed with septum was stirred at room temperature for 24 h. *tert*-Butylmagnesium chloride (2.0 M solution in THF, Aldrich) was added dropwise to the reaction mixture in portions of 20−30 μL every 1−2 h until the initiation of the reaction, which can be seen by the change in colour (200−300 μL of *t*BuMgCl could be needed for initiation). The course of reaction (the disappearance of the starting material) was also monitored by UV/Vis spectroscopy.

2,3-Naphtho-Fused 2,3,7,8,12,13-Hexakis(*m*-trifluoromethylphenyl)-porphyrazinatomagnesium (**6**) was obtained by procedure (b) when furan was utilised. The reaction mixture was quenched with a small amount of water, and the organic solvents were evaporated. The residue was dissolved in CH_2Cl_2 and chromatographed on silica gel. Compound **6** was collected as the first green fraction eluted with pure CH_2Cl_2 and, afterwards, CH_2Cl_2 + 0.2% THF. The composition of the fraction was continuously monitored by UV/Vis spectroscopy in order to avoid the admixture of **7**, moving directly after **6** on the column. A better separation of **6** and **7** can be achieved by preparative TLC. After complete removal of the solvent from the collected fraction, 2 mL of hexane was added and the mixture was left for several days to crystallize. The solvent was decanted and the formed half-crystalline dark green precipitate was dried in vacuo to yield 11 mg (24%) of **6** × H_2O × hexane. UV/Vis (THF): λ (rel. int.) = 362 (0.97), 580 (0.25), 624 (1.00), 695 (0.91) nm. MS (MALDI-TOF): *m*/*z* = 1302.4 [MH^+]. For **6** crystallized from methanol $C_{66}H_{30}F_{18}MgN_8$ × CH_3OH (1301.31 + 32.04): calcd. C 60.36, H 2.57, N 8.40; found C 60.58, H 2.57, N 8.25. For the ^1H and ^{13}C NMR spectra ([D_8]THF) see Results and Discussion.

2,3,7,8,12,13-Hexakis(*m*-trifluoromethylphenyl)benzo[*q*]porphyrazinatomagnesium (**7**) was obtained as the main product by procedure **(b)** when anthracene was utilised. Compound **7** was isolated by column chromatography with CH_2Cl_2 + 0.2% THF on silica gel (yield 12 mg, 29%). Analytical data: UV/Vis (THF): λ (rel. int.) = 372 (1.00), 573 sh. (0.22), 619 (0.77), 663 (0.96) nm. MS (MALDI-TOF): *m*/*z* = 1252.4 [MH^+]. $C_{62}H_{28}F_{18}MgN_8$ (1251.25). For the ^1H NMR spectrum ([D_8]THF) see Results and Discussion.

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