

# Substituted $\alpha,\beta,\gamma$ -triazatetrazabenzcorrole: an unusual reduction product of a phthalocyanine

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**4,5-Dipentyl-diiminoisoindoline 1 reacts with hexachloro-disilane ( $\text{Si}_2\text{Cl}_6$ ) to give the ring-contracted hydroxysilicon- $\alpha,\beta,\gamma$ -triazatetrazabenzcorrole 4 which in solution photolyses giving the ring cleavage compounds 5 and 6; the stability of triazatetrazabenzcorroles 4 and 7 with silicon and germanium as central elements is studied by UV-VIS spectroscopy.**

Many of the properties of metallophthalocyanines (PcM) such as semiconductivity, photoconductivity and catalytic properties rely upon the redox properties of the PcM species.<sup>1,2</sup> As a result, the redox chemistry of PcM has been investigated in detail, both by chemical and electrochemical methods with phthalocyanines containing redox inactive as well as redox active metals centres.<sup>3-5</sup> Accordingly, negative ions of Pc or PcM with low valent state metals such as  $\text{PcCo}^{\text{I}}$  and  $\text{PcSn}^{\text{II}}$  have been found,<sup>6-8</sup> however, the basic structure of the resulting reduced macrocycle remained the same.

In 1986, Fujiki *et al.*<sup>9</sup> ascertained for the first time that the earlier reported  $\text{PcGe}^{\text{II}}$ ,<sup>10</sup> produced by reducing  $\text{PcGeCl}_2$  with  $\text{NaBH}_4$ , did not retain the phthalocyanine moiety but was a phthalocyanine-like tetrapyrrole macrocycle, namely hydroxygermanium(IV)- $\alpha,\beta,\gamma$ -triazatetrazabenzcorrole (TBCGeOH) 2. However, probably due to the report<sup>9</sup> that the stability of TBC complexes with different central elements follows the sequence TBCGeOH 2  $\gg$  TBCSiOH 3 > TBCAl > TBCGa, and also that the authors<sup>9</sup> succeeded in obtaining only the pure TBCGeOH 2, no further reports on TBC macrocycles could be found to date.

As part of our ongoing studies to synthesize precursors for polymers containing Pc units,<sup>1,2,11,12</sup> 4,5-dipentyl-diiminoisoindoline 1 was treated with  $\text{Si}_2\text{Cl}_6$  to examine the potential of producing phthalocyanine dimers with an Si-Si bond. Unexpectedly, during purification of the reaction mixture by flash chromatography (silica gel,  $\text{CHCl}_3$ ), besides obtaining  $(\text{C}_5\text{H}_{11})_8\text{PcSi}(\text{OH})_2$ , a deep green solid was also isolated which displayed a very sharp absorption at 448 nm (Soret band) with an intensity nearly twice that of the Q band in its electronic spectrum (Fig. 1), which was later found to be the typical UV-VIS spectrum of TBC macrocycles.<sup>9</sup> The mass spectral,  $^1\text{H}$  NMR, IR and elemental analysis further proved that the compound obtained in this reaction is hydroxysilicon 4,5,11,12,18,19,25,26-octapentyl- $\alpha,\beta,\gamma$ -triazatetrazabenzcorrole (PTBCSiOH) 4.<sup>†</sup> Further studies carried out by treating  $\text{Si}_2\text{Cl}_6$  with 1 in different ratios indicated that if the ratio reached *ca.* 1 : 1, only PTBCSiOH 4 was obtained in 35% yield (Scheme 1). It seems that the excess of  $\text{Si}_2\text{Cl}_6$  reacted with an intermediate phthalocyanine to form the TBC derivative 4 (*vide infra*).

The mechanism for the formation of the TBC macrocycles by reaction of a reducing agent such as  $\text{NaBH}_4$  with, for example,  $\text{PcGeCl}_2$  has not been proven experimentally, although in the original work<sup>9</sup> a mechanism for the Pc ring contraction was proposed.  $\text{Si}_2\text{Cl}_6$  is a known deoxygenating reagent, for example, it has been used to produce phosphine from phosphine oxide<sup>13</sup> and phosphine sulfides.<sup>14</sup> On the other hand,  $\text{Si}_2\text{Cl}_6$  is very sensitive to water, affording products in which the Si-Si bond is broken or an oxygen is inserted into the Si-Si bond. As a result, during the reaction of 1 with  $\text{Si}_2\text{Cl}_6$  the dihydroxy-

silicon phthalocyanine  $(\text{C}_5\text{H}_{11})_8\text{PcSi}(\text{OH})_2$  and/or  $\mu$ -oxo dimers  $[(\text{C}_5\text{H}_{11})_8\text{PcSi}(\text{OH})_2\text{O}]_2$  will be produced first, and then reduced by an excess of  $\text{Si}_2\text{Cl}_6$  to form PTBCSiOH 4. Indeed, in the reaction of  $\text{Si}_2\text{Cl}_6$  with the isoindoline 1 in a ratio of 1 : 2,  $(\text{C}_5\text{H}_{11})_8\text{PcSi}(\text{OH})_2$  was isolated by flash chromatography. The assumption that  $(\text{C}_5\text{H}_{11})_8\text{PcSi}(\text{OH})_2$  was formed first and then reduced by  $\text{Si}_2\text{Cl}_6$  was confirmed by reacting  $(\text{C}_5\text{H}_{11})_8\text{PcSi}(\text{OH})_2$  with  $\text{Si}_2\text{Cl}_6$  in quinoline and isolating PTBCSiOH 4 from the reaction mixture.

PTBCSiOH 4 is stable in the solid state under ambient conditions. However, air saturated solutions of 4 are found to be light sensitive. Of particular interest is that the green solution of 4 in, for example,  $\text{CHCl}_3$  changed from green to red under light after some time. The resulting 'photolysis' products were separated on silica gel with a mixture of  $\text{CHCl}_3$  and  $\text{CH}_2\text{Cl}_2$  (v:v, 3:2) as eluent to give a purple and a red compound. Based on mass spectroscopy, IR, UV-VIS and  $^1\text{H}$  NMR data, the purple 5 $\ddagger$  and the red 6 $\ddagger$  compounds were characterized as cleavage products of the 1,2-double bond of compound 4. As a result, the central coordinated element is lost. The overall reaction is shown in Scheme 1.

The UV-VIS spectra of PTBCSiOH 4 (Fig. 1) and PTBCGeOH 7 [produced by reducing  $(\text{C}_5\text{H}_{11})_8\text{PcGeCl}_2$  with  $\text{NaBH}_4$  according to a literature method<sup>9</sup>] (Fig. 2) in  $\text{CHCl}_3$  under air with irradiation at different times were determined in order to investigate the influence of the central element on the stability of TBC complexes under these conditions. In contrast to the earlier report,<sup>9</sup> it is evident both from the decrease in intensity of the Soret and the Q bands that PTBCSiOH 4 is more stable than the germanium complex 7 under the same conditions. As a ring contracted entity of Pc, the TBC ring will prefer the central element with a smaller radius than that of Pc. Obviously Si, with a smaller radius than Ge, forms a more stable complex with the TBC macrocycle than Ge, though the accurate radius of the internal hole of the TBC ring is not known. Fujiki *et al.*<sup>9</sup> did not succeed in producing pure unsubstituted

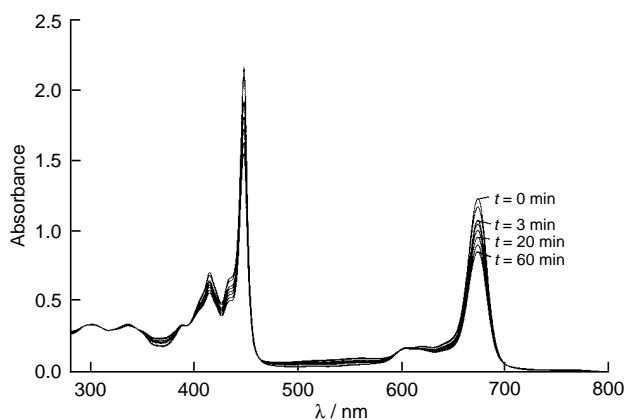
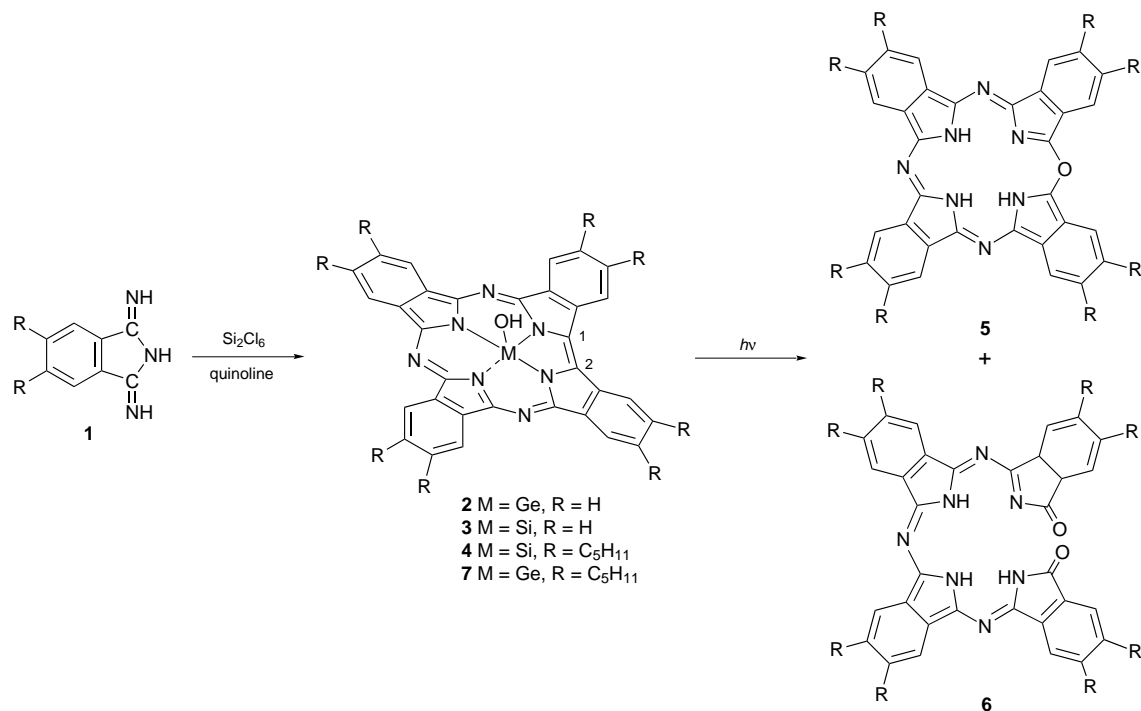
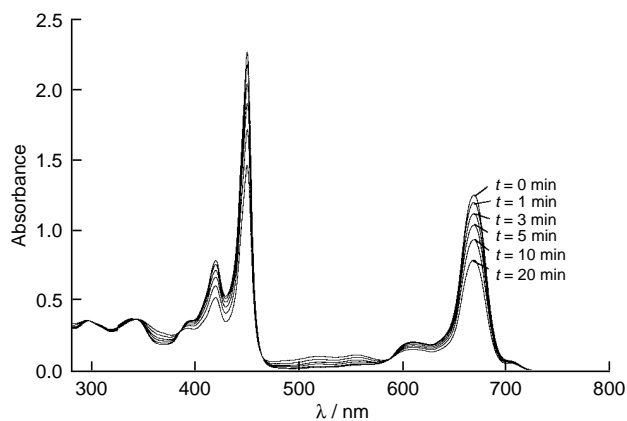


Fig. 1 Changes in the electronic absorption spectra of PTBCSiOH 4 in  $\text{CHCl}_3$  under air upon irradiation with light ( $\lambda = 650\text{--}730$  nm) at room temperature



**Scheme 1** Synthetic scheme for PTBCSiOH and its photolysis products



**Fig. 2** Changes in the electronic absorption spectra PTBCGeOH **7** in CHCl<sub>3</sub> under air upon irradiation with light ( $\lambda = 650\text{--}730$  nm) at room temperature

TBCSiOH **3** by reducing PcSiCl<sub>2</sub> with NaBH<sub>4</sub>, however, pure substituted PTBCSiOH **4** was obtained by using Si<sub>2</sub>Cl<sub>6</sub>, which shows that reducing agents have an influence on the formation of TBC derivatives from the corresponding Pc complexes. The reason for the conflicting results of Fujiki *et al.*<sup>9</sup> and ourselves on the stability of TBC complexes of Si and Ge might be due to the use of an unsubstituted **3** and a substituted **4** respectively in illumination experiments.

#### Footnotes

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† Selected data for **4**: IR  $\nu/\text{cm}^{-1}$  (KBr) 2955, 2928, 1626, 1462, 1416, 1377, 1261, 1111, 1020, 887, 804, 733. UV–VIS (CHCl<sub>3</sub>)  $\lambda_{\text{max}}/\text{nm}$  (relative absorbance) 295(0.27), 342(0.24), 416(0.39), 434(0.35), 448(1.00), 620(0.12), 675(0.56).  $\delta_{\text{H}}$  (250 MHz, [2H<sub>8</sub>]THF) 9.35 (s, 2 H, H<sub>arom.</sub>), 9.25 (s, 2 H, H<sub>arom.</sub>), 8.69 (s, 2 H, H<sub>arom.</sub>), 7.98 (s, 2 H, H<sub>arom.</sub>), 3.38 (m, 8 H, CH<sub>2</sub>), 2.85 (m, 8 H, CH<sub>2</sub>), 2.16–1.64 (m, 48 H, CH<sub>2</sub>), 1.15 (m, 24 H, CH<sub>3</sub>), –1.54 (s, 1 H, OH). MS(FD)  $m/z$ : 1104.1 (M<sup>+</sup>). Anal. calc. for C<sub>72</sub>H<sub>97</sub>N<sub>7</sub>SiO(1103.8): C, 78.28; H, 8.85; N, 8.88. Found: C, 77.38; H, 8.60; N, 8.48%. For **5**: IR  $\nu/\text{cm}^{-1}$  (KBr) 2959, 2928, 2856, 1744, 1730, 1609(s),

1468, 1261, 1221, 1096, 1028, 804, 730. UV–VIS (CHCl<sub>3</sub>)  $\lambda_{\text{max}}/\text{nm}$  (relative absorbance) 366(0.86), 519(0.81), 553(1.00), 597(0.70).  $\delta_{\text{H}}$  (250 MHz, CDCl<sub>3</sub>) 11.68 (s, 3 H, NH), 8.30 (s, 2 H, H<sub>arom.</sub>), 7.95 (s, 2 H, H<sub>arom.</sub>), 7.80 (s, 2 H, H<sub>arom.</sub>), 7.73 (s, 2 H, H<sub>arom.</sub>), 2.79 (m, 16 H, CH<sub>2</sub>), 1.69 (m, 16 H, CH<sub>2</sub>), 1.23 (m, 32 H, CH<sub>2</sub>), 0.93 (m, 24 H, CH<sub>3</sub>). MS(FD and FAB)  $m/z$ : 1078.5 (M<sup>+</sup>). For **6**: IR  $\nu/\text{cm}^{-1}$  (KBr) 2955, 2928, 1744, 1674, 1614, 1564, 1477, 1468, 1209, 1138. UV–VIS (CHCl<sub>3</sub>)  $\lambda_{\text{max}}/\text{nm}$  (relative absorbance) 337(0.59), 515(1.00), 554(0.88).  $\delta_{\text{H}}$  (250 MHz, CDCl<sub>3</sub>) 11.41 (s, 1 H, NH), 11.35 (s, 1 H, NH), 9.35 (s, 1 H, NH), 8.45 (s, 1 H, H<sub>arom.</sub>), 8.33 (s, 1 H, H<sub>arom.</sub>), 8.16 (s, 1 H, H<sub>arom.</sub>), 7.90 (s, 1 H, H<sub>arom.</sub>), 7.87 (s, 1 H, H<sub>arom.</sub>), 7.79 (s, 1 H, H<sub>arom.</sub>), 7.66 (s, 1 H, H<sub>arom.</sub>), 7.57 (s, 1 H, H<sub>arom.</sub>), 2.74 (m, 16 H, CH<sub>2</sub>), 1.67 (m, 16 H, CH<sub>2</sub>), 1.24 (m, 32 H, CH<sub>2</sub>), 0.88 (m, 24 H, CH<sub>3</sub>). MS(FD)  $m/z$ : 1093.3 (M<sup>+</sup>).

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