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# Photo electron transfer induced desilylation of N,N-bis(trimethylsilyl)aminodibenzoborole to aminodibenzoborole\*

3 could be synthesized independently.

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The synthesis of 9-amino-9-borafluorene is described using a photoinduced twofold desilylation of the N,N-bis(trimethylsilyl) derivative 2. The mechanistic analysis suggests an initial single electron transfer step from 2 to the halogen containing solvent. 9-Amino-9-borafluorene undergoes a photoinduced cyclooligomerization, most reasonably to the dimer.

The last ten years have experienced significant progress in the chemistry of boroles and dibenzoboroles (9-borafluorenes).<sup>1-6</sup> Ring enlargement reactions<sup>7</sup> vielding 1,2-dihydro-1,2-azaborine derivatives have been observed upon treatment with di(trimethylsilyl)hydroxyl amine8 and organic azides.9-15 In addition, the thermolytic denitrogenation of 9-azido-9-borafluorene results in ring expansion and products of self-trapping of 10,9-BNphenanthryne.<sup>16,17</sup> Aminoboroles featuring the NH<sub>2</sub> group remain unknown in free form for the parent and dibenzo systems, but are interesting compounds for investigation of chemical transformations that are related to the fulvene - benzene isomerization<sup>18-20</sup> by the isoelectronic relationship of the CC and BN units.<sup>21</sup> We thus sought access to unknown 9-amino-9-borafluorene and here report that photoinduced desilylation provides an alternative means for deprotection of N,N-bis(trimethylsilyl)amino-dibenzoborole and more generally can also be used for deprotection of N,N-bis(trimethylsilyl)aniline. The reaction is a useful alternative to conventional deprotection of trimethyl silyl amines if the substrate is not tolerant towards fluoride ions or water, and was not described before to the best of our knowledge.

Initial experiments aimed at transforming 9-chloro-9-borafluorene (1) to 9-amino-9-borafluorene (4) by treatment with sodium amide were unsuccessful in our hands. On the other hand,

CH2CI2 C2H4CI2 CCI + HN(SiMe<sub>3</sub>)<sub>2</sub> - SiMe<sub>3</sub>Cl Scheme 1 Synthesis of 2 and its photolysis in different solvents. Compound

9-bis(trimethylsilyl)amino-9-borafluorene (2) is readily available from 1 and potassium bis(trimethylsilyl)amide (Scheme 1) by analogy to the synthesis of bis(trimethylsilyl)amino-2,3,4,5tetraphenylborole.<sup>3</sup> After sublimation of the dried residue, 2 could be isolated as a slightly yellow solid in 69% yield and fully characterized including single crystal X-ray crystallography (see ESI,† Fig. S22).

Desilylation of 2 by treatment with fluoride is not successful in our hands, presumably due to the high fluoride affinity of the boron center. Motivated by the photo induced desilylation of trimethylsilyl enol ethers,<sup>22</sup> we investigated the photoreactivity of 2. The photochemistry of boroles has been investigated recently, but not for bis(trimethylsilyl)amino derivatives.<sup>23-27</sup> As an absorption maximum of 2 is at  $\lambda = 254$  nm (see ESI,† Fig. S21), light of this wavelength was chosen for photochemical experiments.

Irradiation of 2 in dichloromethane solution led to three new signals in the <sup>11</sup>B NMR at 44, 41, and 1 ppm (see Fig. 1). In the beginning, the signal at 44 ppm grew fastest, but started to decrease as soon as the starting material was consumed completely. Once the signal at 44 ppm was not observable anymore, the intensity of the signal at 41 ppm started to decrease, finally leading to the signal at 1 ppm. Irradiation was terminated





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and this state was defined as endpoint of the photoreaction. If the sample was irradiated even longer, a mixture of signals with lower intensities arose. Among these, the signal at 64 ppm might be associated with formation of **1**, the educt in the synthesis of compound **2**.

The <sup>1</sup>H NMR spectra revealed that the signals of the borafluorene system experienced shifts, but that the backbone stayed intact during irradiation until the defined endpoint (see ESI,† Fig. S19). On the other hand, the <sup>1</sup>H signal of the TMS groups of 2 at 0.34 ppm was decreasing with ongoing irradiation until it had vanished. One new signal at 0.40 ppm was produced, but later decreased until it had completely disappeared before irradiation was terminated. Another signal at 0.43 ppm appeared and constantly increased in intensity. In the <sup>29</sup>Si NMR formation of two new signals at 7.0 ppm and 31.6 ppm was observed. The latter one decreased and eventually vanished with ongoing irradiation. The observed changes in the <sup>1</sup>H and <sup>29</sup>Si NMR indicate that the photoreaction changed the chemical environment of the TMS groups, but the TMS groups themselves stayed intact according to the signal intensities in the <sup>1</sup>H NMR. The signals measured by <sup>1</sup>H, <sup>13</sup>C, and <sup>29</sup>Si NMR spectroscopy at 0.43, 3.3, and 31.6 ppm, respectively, can be assigned to trimethylsilyl chloride based on comparison with an authentic sample.

Separation of the three boron containing photoproducts is difficult, since they show very similar solubility. The compound resonating at 1 ppm in the <sup>11</sup>B NMR decomposed during sublimation, but the other two compounds sublimed without decomposition and could be partially separated. Based on NMR and MS analyses, these are the monosilylated compound 3 and 9-amino-9-borafluorene 4 (Scheme 1). The stability of 4 is remarkable in view of the reactivity of pentaphenylborole as well as 9-phenyl-9-borafluorene towards free amines.<sup>28,29</sup> In contrast, the amino substituent does not lead to a decreased stability as 4 can be stored over weeks without noticeable decomposition.

Compound 3, which could not be isolated in pure state by sublimation, could be synthesized independently by treating 1 with 1 eq. of bistrimethylsilylamine in hexane solution at room temperature (Scheme 1).<sup>30</sup> The spectroscopic data of 3 thus obtained are identical to those obtained in the mixture of 2 and 3, confirming the formation of 3 under photolysis conditions.

Irradiation of independently prepared **3** results in desilylation producing **4**.

The formation of trimethylsilyl chloride shows that the solvent dichloromethane is not inert during photolysis and serves as source of chlorine atoms and, in part, of the hydrogen atoms bound to nitrogen atoms of **3** and **4**. If photolysis experiments were performed in CD<sub>2</sub>Cl<sub>2</sub>, the signal intensity of the nitrogenbound protons decreased in the <sup>1</sup>H NMR and a signal with identical chemical shift could be detected in a <sup>2</sup>H NMR. Since the signal in the <sup>1</sup>H NMR did not completely vanish, deuteration of this position was not complete. Additional hydrogen atom sources could be either the glass wall or TMS groups.

To further analyze reaction mechanisms, additional experiments were conducted. Although DCM does not absorb UV light of 254 nm wavelength, low pressure mercury lamps also emit at 187 nm with low intensity. Irradiation of **2** in dichloromethane solution with a high pressure mercury lamp ( $\lambda = 280$  to 400 nm) resulted in a decelerated reaction rate due to the smaller absorbance of **2** in this wavelength range, but the same reactivity was observed. This shows that the photoexcitation of the DCM solvent is not essential for the outcome of the photoreaction.

Next, different solvents were tested. We found that the photoinduced desilylation only proceeded in halogen-containing solvents (Scheme 1). Without halogen atoms in the solvent (benzene, toluene, cyclohexane, cyclohexene) no photoreaction was observed, even after irradiating the solution ten times longer than regularly. In contrast, halogenated solvents like dichloroethane, carbon tetrachloride, and the monohalogenated benzenes enabled the loss of the trimethylsilyl groups during irradiation. Interestingly, even in carbon tetrachloride, **4** was produced showing that the solvent is, as discussed above, not the only source of hydrogen atoms.

Among the halobenzenes, the reaction proceeded very slowly in fluorobenzene and the reaction rate increased towards iodobenzene enormously. For all halobenzenes, the spectral signature of the corresponding trimethylsilyl halides could be detected by <sup>29</sup>Si NMR and in case of fluorobenzene also by <sup>19</sup>F NMR. This indicates that the mechanism of desilylation is unaltered by change of the halogen atom.

The first step of the photoreaction is assumed to be the excitation of **2**, as some of the solvents, especially DCM, cannot be excited at the applied wavelength. Since the nature of the solvent is essential for photolysis to proceed, it is reasonable to assume that there must be some interaction between **2** in its excited state and the solvent. A possibility is a single electron transfer (SET) from **2** to the solvent formally producing the corresponding radical cation of **2** and a solvent radical anion. This process is only possible if halogen atoms are present that act as electron acceptors and is expected to be faster for solvents with lower reduction potential. Among the halobenzenes the standard reduction potential decreases from fluorobenzene to iodobenzene<sup>31,32</sup> ( $E^0$ : -2.97, -2.76, -2.43, -1.91 V for X = F, Cl, Br, I respectively) in agreement with the enhanced rate of the photoreaction along the halogen series.

For biphenyl, naphthyl and anthracenyl halides, the rate constants for dissociation of the chloride and bromide anion

from the radical anions are available.<sup>33</sup> In all cases, the chlorinated systems show lower dissociation rate constants than the corresponding brominated species. For the naphthyl system, the rate constant for iodide dissociation from the radical anion was reported as well, being even higher than that of the brominated species. The increase of the reaction rate along the halobenzene series observed here is thus in agreement with available data and a SET mechanism.

The SET from 2 to a solvent molecule produces formally a radical anion, which is only in some cases persistent, but often spontaneously decomposes into a halide and the corresponding radical.<sup>34,35</sup> This leads to a stoichiometric production of halogen anions. These are able to attack one of the silicon atoms in  $2^{+\circ}$  under formation of the observed trimethylsilyl halides and nitrogen centered radical 5 (Scheme 2). Abstraction of a hydrogen atom generates 3 and concludes the first photodesilylation.<sup>22,36–38</sup> The second desilylation yielding 4 proceeds by the same mechanism.

The mechanistic scenario outlined above is supported by computations at the B3LYP/6-311+G\*\* level of theory using a polarizable continuum model (PCM) for taking solvent effects into account. According to these calculations, the first step of the SET from 2 to DCM directly followed by spontaneous decay of DCM into chloride and chloromethyl radical is endergonic by 54.3 kcal mol<sup>-1</sup>. The N-Si bonds in the radical cation  $2^{+\bullet}$  are weak (16.1 kcal mol<sup>-1</sup>), and formation of trimethylsilylchloride from the  $2^{+\bullet}$  and chloride ion is exergonic (-48.7 kcal mol<sup>-1</sup>). Hydrogen abstraction of the resulting radical from dichloromethane is exergonic by -1.6 kcal mol<sup>-1</sup>. Overall, the reaction is endergonic by 20.1 kcal mol<sup>-1</sup> but can proceed easily after photoinduction.

The final product of the photolysis, which we have not discussed so far, has a signal at 1 ppm in the <sup>11</sup>B NMR. This shift indicates a tetracoordinated boron center. In addition, the signal for the nitrogen-bonded protons experienced a high-field shift from 4.65 ppm in 4 to 4.29 ppm, while the other signals in the hydrogen and carbon NMR shifted only marginally. This suggests that the last step does also not affect the borafluorene system, but only the BN unit. The high resolution electron impact mass spectrometry (EI-MS) revealed that 4 was still detectable. Other ionization methods (ESI, APCI, MALDI) were not successful due to hydrolysis, or similarly gave 4 (LIFDI). Therefore, we assume that 4 underwent dimerization to 6 or trimerization to 7 in the course of the photoreaction (Scheme 3). The dimers and trimers could well be labile under the conditions of MS precluding the detection of the molecular ion peaks. Systems including a B<sub>2</sub>N<sub>2</sub> or a more stable B<sub>3</sub>N<sub>3</sub> core are known



Scheme 2 Proposed mechanism of desilylation of 2



Scheme 3 Dimerization and trimerization product of 5.



**Scheme 4** Synthesis of bisilylated aniline **8**. Its photolysis at  $\lambda = 254$  nm in DCM leads to **9**. A monosilylated intermediate could not be observed.

and their <sup>11</sup>B NMR chemical shifts are in the range of the one measured by us.<sup>39,40</sup> The NMR shifts calculated at the B3LYP/ 6-311+G\*\* level of theory for the trimer and dimer are too similar to allow an assignment. While dimerization is computed to be an endothermic and endergonic process by 1.2 kcal mol<sup>-1</sup> and 15.1 kcal mol<sup>-1</sup>, respectively, trimerization is exothermic ( $-0.8 \text{ kcal mol}^{-1}$ ) but more endergonic (27.0 kcal mol<sup>-1</sup>). Although both dimerization and trimerization are energetically unfavorable, we favor dimerization because it is less endergonic and can mechanistically in principle proceed as a photoreaction similar to the [ $\pi 2s + \pi 2s$ ] cycloaddition of isoelectronic olefins.

Finally, we investigated whether the boron center is essential for successful photodesilylation. Therefore, *N*,*N*-bis(trimethyl-silyl)aniline **8** was synthesized by treating aniline **9** first with two equivalents of *n*-BuLi at -78 °C followed by addition of two equivalents of trimethylsilyl chloride at the same temperature (Scheme 4).<sup>41</sup>

To ensure comparability to the above described experiments, irradiation of **8** was performed in dichloromethane solution at  $\lambda = 254$  nm. Again, trimethylsilyl chloride was detectable in the measured NMR spectra indicating successful photodesilylation. With the help of GC-MS measurements, formation of **9** as product of irradiation could be proven. Obviously, the boron center is not required for photodesilylation reactions to occur.

As the reaction most likely is initiated by SET, the size of the ionization potential (IP) may be decisive. Therefore, the IP for both the systems under investigation were calculated (2: 6.0 eV, 8: 5.9 eV) as well as those for 1-trimethylsilyloxycyclohex-1-ene 10 (5.8 eV) and trimethylsilyloxy-cyclohexane 11 (6.9 eV). While 10 is known to undergo photodesilylation, 11 cannot be desilylated photochemically.<sup>21</sup>

The IP of the compounds, which can be photolytically desilylated, is in the same range of energy, while the IP of **11** is significantly higher and thus photodesilylation is inhibited.

In summary, our study shows that the 9-amino-9-borafluorene, the first example of a  $NH_2$ -substituted borole, is accessible from the corresponding 9-bis(trimethylsilyl) derivative 2 by photoinduced twofold desilylation. The mechanistic analysis suggests that the photoreaction is initiated by a single electron transfer from 2 to the halogen containing solvent. The reaction is not limited to aminoboroles, but also proceeds upon irradiation of N,N-bis(trimethylsilyl)aniline **10**. The limited data that is currently available suggests that an ionization potential of around 6 eV is required for a substrate to undergo the SET mechanism. The target compound 9-amino-9-borafluorene is unstable under photoirradiation and undergoes cyclooligomerization, most likely to the dimer.

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### Conflicts of interest

There are no conflicts to declare.

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