The Pentaphenylborole–2,6-Lutidine Adduct: A System with Unusual Thermochromic and Photochromic Properties**

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Organoboranes have attracted great attention owing to their interesting photophysical properties, which enable promising applications as optoelectronics and colorimetric chemosensors.^[1,2] Three-coordinate boron has a low-lying empty p orbital, which bestows a strong Lewis acidity to the resulting substances and promotes electron transport through conjugated systems.^[3] The electron affinity of trivalent boron leads to the formation of various stable adducts of triaryl/alkyl boranes and Lewis bases. Remarkably, some of the boranepyridine adducts have interesting nonlinear optical properties.^[4] Recently, Wang and co-workers have demonstrated that irradiation of adducts such as A leads to the formation of B, which contains a boracyclopropane ring with the B-N linkage remaining intact (Scheme 1).^[5] Analogous rearrangement reactions have been found during photolysis of tetraphenylborates, where the generation of free radical species has also been observed (Scheme 1).^[6]



Scheme 1. Light-induced rearrangements of four-coordinate boron compounds.

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Detailed investigations regarding the photochemistry of Lewis base adducts of boracycles are however scarce, even though theoretical and experimental studies have shown that the incorporation of boron into a cyclic π system implicates a substantial impact on the electronic properties of the molecule.^[7]

Herein, we present the structure and the thermochromic behavior of Lewis base adducts of pentaphenylborole (PPB) with pyridine bases, and in particular an unusual photo-induced transformation to a borataalkene. To this end, the Lewis base adducts of pentaphenylborole^[8] with 4-picoline (**1a**) and 2,6-lutidine (**1b**) were prepared in a straightforward manner (Scheme 2). Interestingly, these two reactions substantially differ in their photophysical behavior. Treating a CD_2Cl_2 solution of PPB with 4-picoline resulted in an immediate color change from blue to yellow, and an upfield shift of the ¹¹B NMR signal from $\delta = 65.4$ ppm to $\delta = 3.5$ ppm

was observed in the ¹¹B NMR spectrum, thus suggesting the formation of **1a**.

However, upon addition of 2,6-lutidine to PPB, the color of the solution remained deep blue under the same conditions. Surprisingly, the ¹¹B NMR signal of **1b** detected at room temperature ($\delta =$ 21.0 ppm) is at much lower field than that of **1a**. Cooling a toluene solution of **1b** from room temperature to -40 °C resulted in a color change from deep blue

to light yellow. The UV/Vis spectrum of **1b** at ambient temperature features a broad absorption band at 578 nm (Supporting Information, Figure S5) that decreased in intensity upon cooling. At -40 °C, the ¹¹B NMR signal is shifted to $\delta = 3.3$ ppm, which clearly confirms the formation of a four-



Scheme 2. Syntheses of the Lewis base adducts 1a and 1b.

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coordinate boron center at low temperatures. In contrast, a high-temperature NMR study revealed a linear shifting of the ¹¹B NMR signal from $\delta = 21.0$ ppm at room temperature to $\delta = 56.0$ ppm at 70 °C (Supporting Information, Figure S1).

These observations most likely result from an equilibrium between **1b** and a significant amount of non-coordinated PPB (Scheme 2); this process is too fast to be resolved on the NMR timescale. Thus, the ¹¹B NMR chemical shift observed at room temperature is the average of free and coordinated PPB. However, with the faster UV/Vis spectroscopy, the free PPB can be detected by its absorption at 578 nm.

From the temperature-dependent shift of the ¹¹B NMR signal, values of ΔH and ΔS for the association process were calculated to be -81 kJ mol^{-1} and $-244 \text{ J mol}^{-1}\text{K}$, respectively. In comparison to the frustrated Lewis pair (FLP) system B(C₆F₅)₃/2,6-lutidine ($\Delta H = -42 \text{ kJ mol}^{-1}$, $\Delta S = -130 \text{ J mol}^{-1}\text{K}$),^[11] the equilibrium in this study is more on the side of the coordinated PPB, which is due to the higher Lewis acidity of boroles. At room temperature, about 29% of the PPB remain non-coordinated, and thus the characteristic blue color of this antiaromatic boracycle is retained. An association constant of 380 Lmol⁻¹ was determined for **1b** by means of UV/Vis titrations (Supporting Information, Figure S4).

At room temperature, a broad signal at $\delta = 2.52$ ppm in the ¹H NMR spectrum of **1b** was assigned to the two methyl groups on the pyridine ring. At -40 °C, this signal splits into two peaks at $\delta = 1.57$ and 3.29 ppm, respectively (Supporting Information, Figure S2). An explanation for this observation in solution can be drawn from the solid-state structure of the adduct. Yellow single crystals of **1b** that were suitable for an X-ray diffraction study were obtained by diffusion of hexane into a saturated toluene solution. In the molecular structure of **1b**, one of the methyl groups resides above the butadiene system of the borole, while the other one is situated in a position between two phenyl rings (Figure 1). The different environments of the methyl groups eventually result in different ¹H NMR shifts at low temperatures. The B–N bond in **1b** (1.6567(3) Å) is considerably longer than that in



Figure 1. Molecular structure of **1 b**, with ellipsoids set at 50% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: B–N 1.6567(3), B–C1 1.6524(3), B–C4 1.6210(3), B–C5 1.6345(3), C1–C2 1.3687(3), C2–C3 1.4908(2), C3–C4 1.3551(3); C1-B-C4 99.82(1), C1-B-C5 104.52(1), C1-B-N 116.59(1), C4-B-C5 116.73(2), C4-B-N 109.66(1), N-B-C5 109.55(1).

the chloroborole 4-picoline adduct (1.6022(3) Å),^[9b] and the sterically highly hindered borafluorene systems (1.638(3) Å).^[10] In fact, the value in **1b** is much more comparable to that observed in the aforementioned FLP of $B(C_6F_5)_3$ and 2,6-lutidine, which dissociates at room temperature in solution.^[11] In comparison with PPB, the molecular structure of 1b reveals significant strain, as shown by the torsion angles of the borole.^[9a] The steric demand of the Lewis base is also emphasized by the two B-C non-equivalent bonds within the C₄B unit (B–C1 1.6524(3) Å, B–C4 1.6210(3) Å). This observation is very different from other four-coordinate borole derivatives,^[9,12] which all feature symmetric B-C bonds. The steric crowding of 1b is also reflected in the outward bending of the ortho-methyl groups of lutidine by 0.339 Å and 0.266 Å with respect to the plane defined by the NC₅ ring. This deformation of the pyridine base is more pronounced in **1b** than in other FLPs.^[11]

Irradiation of toluene solutions of **1a** and **1b** at -50 °C reveals that **1a** shows no visible change in absorption bands and chemical shift. However, a significant color change from yellow to dark green was observed in the case of **1b**. NMR spectroscopic investigations show a clean conversion of **1b** into another species upon irradiation. The ¹H NMR spectrum of the green compound at room temperature contains one sharp signal at $\delta = 1.76$ ppm for the two methyl groups of lutidine and a new multiplet at $\delta = 5.92-5.96$ ppm for two protons associated with the 2,6-lutidine. A new set of signals for the phenyl groups of PPB is also present (Figure 2). Excess 2,6-lutidine is observed as a singlet at $\delta = 2.41$ ppm for the two



Figure 2. ¹H NMR spectroscopy study of the rearrangement from compound **1b** (†) to **2** (\pm); \Box excess 2,6-lutidine. The photoconversion was carried out at -50°C, but NMR spectra were recorded at room temperature to prevent the splitting of the methyl groups in **1b** (see text for details).

methyl groups. The detection of a ¹¹B NMR signal at $\delta =$ 41 ppm suggests the formation of a B=C bond.^[13] This reaction pattern is without precedent, and, to the best of our knowledge, the light-induced formation of a borataalkene has never been reported. While **1b** shows no detectable ¹⁵N NMR signal owing to the direct attachment of the nitrogen atom to the quadrupolar boron nucleus, a

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¹⁵N NMR signal at -153.0 ppm was observed for the new species, which suggests the shifting of the Lewis base from boron to carbon.^[14] Again, excess 2,6-lutidine gives rise to an additional ¹⁵N NMR signal at $\delta = -63.2$ ppm.

Monitoring the reaction by NMR spectroscopy showed that the conversion of a toluene solution of one equivalent of PPB and 1.4 equivalents of 2,6-lutidine was complete after 24 h of light exposure (mercury lamp P = 180 W) at -50 °C (Scheme 3). The reaction was found to be totally reversible at room temperature (Supporting Information, Figure S3). To



Scheme 3. Lewis adducts 1a and 1b and the light-induced rearrangement of 1b.

provide information as to whether the excess of 2,6-lutidine might influence the course of the reaction, a control experiment was carried out. To this end, a crystalline sample of the adduct **1b** was dissolved in $[D_8]$ toluene and irridiated at -50 °C. Likewise, under these strictly stoichiometric conditions (1:1), the new compound was formed, which leads us to consider an intramolecular rearrangement reaction from **1b** to compound **2** or **3** upon irradiation (Scheme 3).

To improve our understanding of these processes, we performed theoretical calculations on 1b and on two potential rearrangement products, 2 and 3. Geometry-optimization and single-point-energy calculations suggest 2 to be the favored photoreaction product over 3. The NMR calculations of 2 also compare very well with the experimental findings (NMR calculations can be found in the Supporting Information). A potential-surface calculation shows that 2 is 40 kcal mol⁻¹ higher in energy than 1b. It also shows that 2 resides in a shallow energy well, with an energy barrier of only 4 kcal mol⁻¹ for the reverse reaction path. The computational results are consistent with the poor stability of 2 under ambient conditions. In the dark, 2 is fully converted into 1b without decomposition at room temperature, with $t_{1/2} = 9.3$ h. After 3 days, 1b was the only detectable compound in solution. Regeneration of 2 was readily accomplished by irradiation at −50°C.

In summary, the thermochromic Lewis base adduct of pentaphenylborole with 2,6-lutidine, **1b**, has been prepared and characterized. Both thermochromism and photochromism are totally reversible and perfectly understood. The thermochromism can be ascribed to a fast equilibrium between free PPB (blue) and **1b** (yellow). The molecular structure of **1b** revealed a strongly distorted ring system. Irradiation of a toluene solution of 1b at low temperature caused a shift of the base from boron to the adjacent carbon atom with the formation of a B=C bond. NMR spectroscopic investigations and also theoretical calculations fully support the assigned structure of the rearrangement product. The computational results also suggest a very small barrier for the back-reaction; for this reason, compound **2** must be handled at low temperatures. Further investigations on the mechanism of the rearrangement are now in progress.

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