

Preparation and Characterization of Novel High-Spin Organoborane Dianions

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Abstract: New borane-chelates, 2,4,6-tribenzoyl-1,3,5-tris(diethyl- or diphenylboryloxy)benzenes were synthesized. These borane-chelates showed multi-step reduction behavior. The metal-reduction with a Na-K alloy in THF produced the dianionic species whose ground state was shown to be a triplet for the diphenylboryl derivative. © 1998 Elsevier Science Ltd. All rights reserved.

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1. Introduction

High-spin organic compounds have recently received intense attention in view of the implications for material science and basic research on the spin alignment. So far, several unique high-spin molecules containing silicon [1] and phosphorus [2] elements have also been reported. Organoboranes have electron-deficient centers based on the empty p-orbital of the boron atom. Recently, Rajca and co-workers reported an interesting 1,3-dimesitylborylbenzene dianion with a triplet ground state. [3] In connection with our previous study of organoboranes [4,5] and heteroatomic high-spin molecules [6,7], we are interested in the organoborane chelates where borane moiety is used as a binder of spin building blocks. We report herein preparation and detection of novel organoborane high-spin compounds, **1a**²⁻ and **1b**²⁻.

2. Results and Discussion

2-1. Reduction of 2-diphenylboryloxybenzophenone **2**: A model study

In order to obtain insight into the stability of the anion radical of borane-chelates, we first examined reduction of the known borane-chelates **2** [8]. The borane-chelate **2** has reduction potentials at [-0.97 (reversible), -1.66 (irreversible) V vs SCE in DMF]. When **2** was

reduced by a Na-K alloy in THF at room temperature under degassed conditions, the solution turned blue ($\lambda_{\text{max}} = 590 \text{ nm}$). Further contact with Na-K led to a reddish-purple species which has a stronger absorption maximum at the shorter wavelength of 511 nm. The blue species was ESR active (Figure 1)¹ and assignable to the anion radical of **2**⁻ which was stable for a long time at room temperature under degassed conditions. The reddish-purple species was ESR silent and assigned to the dianionic species by the reduction of the benzylic carbon, although evidence regarding the structure was not pursued.

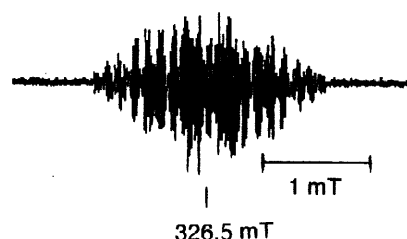
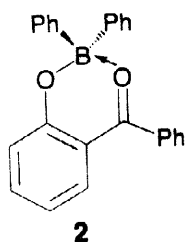
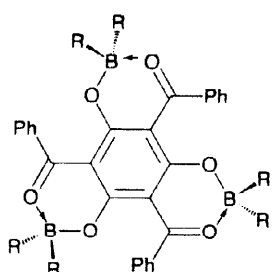


Figure 1. ESR spectrum of the blue species (590 nm) observed for the reduction of **2** in THF.

2-2. Syntheses and Reduction of **1a** and **1b**

The new borane-chelates **1a** and **1b** were synthesized by the condensation of 2,4,6-tribenzoylphloroglucinol and butyl diphenylborate or triethylborane in benzene (under reflux for 3 h for **1a**, at room temperature for 4 h for **1b**).² These yellow compounds are air-stable but moisture-sensitive.



1a,b a; R = Ph, b; R = Et

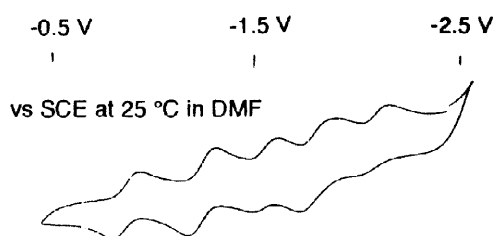


Figure 2. Cyclic voltammogram of **1a** in DMF in the presence of 0.1 M tetrabutylammonium perchlorate.

The borane-chelate **1a** should have six reduction waves of which five (reversible or pseudo-reversible) were observed in its cyclic voltammogram (-0.88, -1.25, -1.56, -1.81, -2.16 V vs SCE in DMF) (Figure 2). The first two reduction potentials are well below the second reduction potential (-1.66 V) of the model compound **2**, suggesting that the reduction of benzylic carbons of **1a** may occur at the third or the fourth reduction potential range. The reduction of **1a** was achieved by a Na-K alloy in THF and monitored by the electronic spectrum. The spectral change can roughly be separated into two stages I (fast process) and II (slow) (Figure 3). The initial stage I increased the 550-572 nm absorption which would be due to the formation of the mono(anion radical), bis(anion radical) or even tris(anion

radical), although the above CV data suggest that the tris(anion radical) formation may compete with the reduction of the benzylic carbons. Further reduction (stage II) decreased this absorption and increased the absorption of the shorter wavelength. This spectral change would correspond to the reduction of the benzylic carbons. The color of the solution is described in the figure.

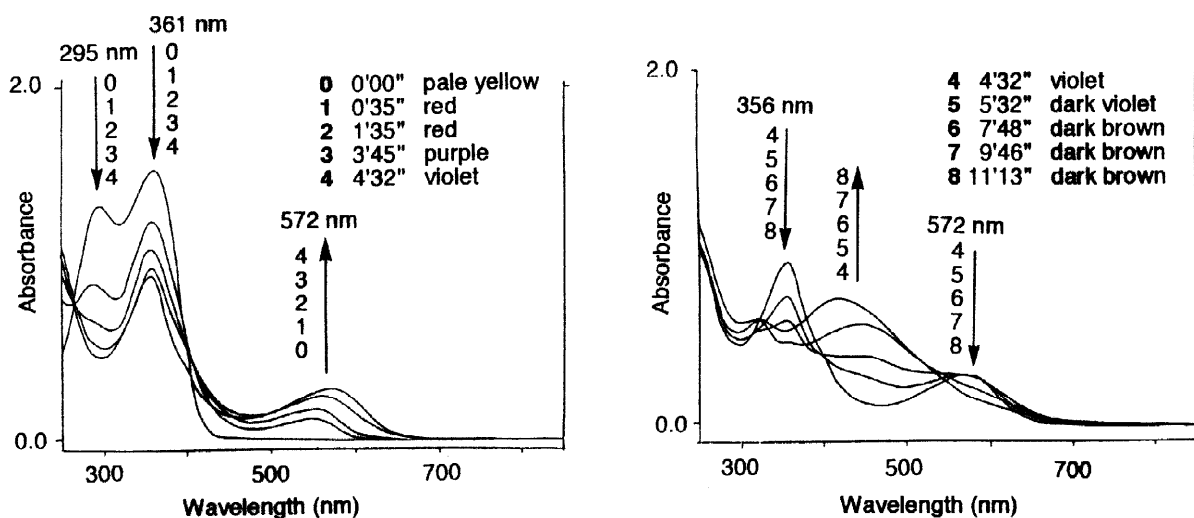


Figure 3. Change in electronic spectrum during the reduction of 1a in THF at room temperature; left: stage I, right: stage II (see text).

2-3. ESR spectra of the dianions $1a^{2-}$ and $1b^{2-}$

The violet species (572 nm) obtained from the stage I (after ca. 4 min) showed a wide and broad zero-field splitting (zfs) (Figure 4, left). The observed pattern is explicable as a triplet or a quartet pattern. We also observed a weak signal due to the $\Delta m_S = \pm 2$ transition in the half-magnetic field region. A quartet species should have a split pattern in the signal due to the $\Delta m_S = \pm 2$ transition and such an example has been reported. [9] From the shape of the $\Delta m_S = \pm 2$ transition [a relatively strong triplet signal and two very weak split signals (*)

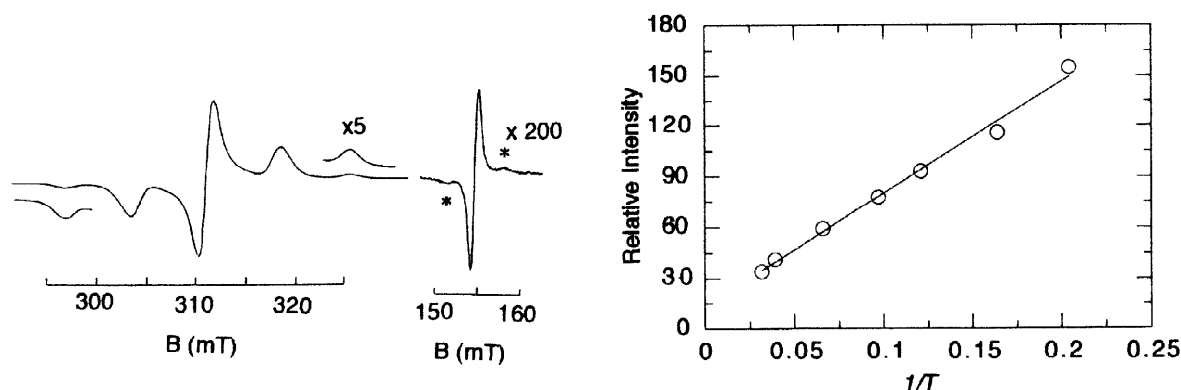


Figure 4. ESR spectrum (left) of the violet species (572 nm) at 5 K and Curie plots (right) of the signal intensity using the central signal due to the $\Delta m_S = \pm 2$ transition observed for the reduction of 1a.

besides the triplet signal], we conclude that the observed species is a mixture of the triplet [major, $|D/hc| = 0.014 \text{ cm}^{-1}$ and $|E/hc| = 0.000 \text{ cm}^{-1}$] and the quartet [minor, $|D/hc| = 0.0069 \text{ cm}^{-1}$ and $|E/hc| = 0.000 \text{ cm}^{-1}$] species.³ The triplet $|D/hc|$ value is larger than the value of *m*-xylylene (0.011 cm^{-1}) [10] and considerably larger than Schlenk's hydrocarbon (0.0064 [11], 0.0079 cm^{-1} [12]) or its planar analogue **3** (0.0061 cm^{-1}) [13]. This is probably due to the contribution of the dianionic character of the central benzene ring as shown in **A**. This consideration is supported by the larger $|D/hc|$ values of the silicon-substituted benzene dianion **4** (0.0963 cm^{-1}). [1] Similar reduction of **1b** produced a triplet species (538 nm) with $|D/hc| = 0.013 \text{ cm}^{-1}$ and $|E/hc| \leq 0.001 \text{ cm}^{-1}$. However, in this case, the signal due to the $\Delta m_s = \pm 2$ transition was too small to be detected.

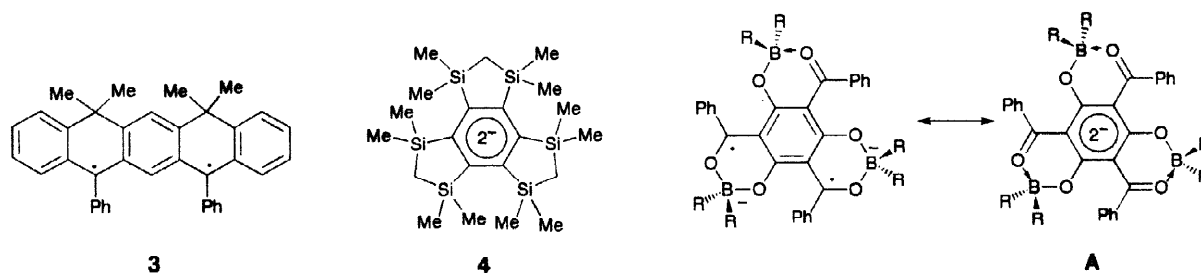


Figure 4 (right) shows temperature dependence of the signal intensity using the triplet signal due to the $\Delta m_s = \pm 2$ transition for **1a**²⁻. The signal intensity linearly increases to the reciprocal temperature. This indicates that **1a**²⁻ has a triplet ground state.³

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Footnotes

1. The analysis has not been successful because of so many hyperfine structures.
2. Spectral and physical data of **1a** and **1b**: **1a**: mp 235 °C, MS (FAB) m/z 931 (MH)⁺, ¹H NMR (CDCl₃) δ 6.85-6.88 (m, 12H), 6.97-7.04 (m, 12H), 7.08-7.14 (m, 6H), 7.47-7.53 (m, 6H), 7.69-7.74 (m, 3H), 7.95-7.99 (m, 6H); **1b**: mp 141 °C, MS (FAB) m/z 643 (MH)⁺, ¹H NMR (CDCl₃) δ 0.22-0.32 (m, 12H), 0.53 (t-like, 18H), 7.46 (t-like, 6H), 7.57-7.63 (m, 9H).
3. The weak signals [with split of ca. 6.2 mT, marked by * in Figure 4 ($\Delta m_s = \pm 2$)] besides the triplet $\Delta m_s = \pm 2$ transition signal is attributable to the quartet signals (x, y component signals, z component signals are too weak to observe even at 5 K). The expected $\Delta m_s = \pm 3$ transition was not observed. The simulated spectrum ($\Delta m_s = \pm 1$ region) for the quartet species (with $|D/hc| = 0.0069 \text{ cm}^{-1}$) has a stronger (ca. 2 times stronger than the observed intensity) central signal, suggesting that the observed species is a mixture of the triplet and quartet species. The quartet signals are only observable at low temperature (< 6 K), which suggests that the tris(anion radical) **1a**³⁻ is in a quartet ground state.