Generation and Characterisation of Dimesitylphenylborane Dianions

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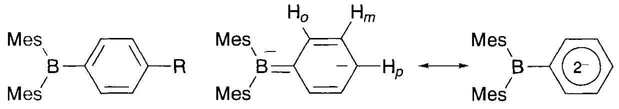
The reduction of dimesitylphenylborane and its substituted analogues with Na–K alloy or K-mirror in THF produces their dianions, the spectral data of which suggest novel structures possessing boron–carbon double bonds with negative charges on the boron and carbon at the *para*-position in the phenyl ring.

Anionic species possessing B=C[1] or B=B[2] structures have recently attracted growing interest in the field of organoborane chemistry. The trimesitylborane anion radical may have a partial B=C structure. According to X-ray analysis by Power *et al.*, however, the anion radical was shown to have a similar B–C bond length to that in neutral trimesitylborane and no evidence for double bond character was obtained.[3] A similar situation may also be expected for the hitherto elusive triarylborane dianions.

Leffler and coworkers observed that prolonged reaction of triphenylborane anion radical with alkali metals converts the EPR spectrum of triphenylborane anion radical to that of biphenyl anion radical,[4] suggesting instability of the dianion species. Later, Dupont and Mills reported a detailed electrochemical study of several triarylboranes.[5] They found a second irreversible reduction wave at −3.57 V *vs.* Ag/Ag$^+$ in the cyclic voltammogram of triphenylborane in THF, which they attributed to the dianion. The unstable dianion was speculated to be converted to tetraphenylborate and diphenylborate anions by disproportionation. We now report the first successful measurement of electronic and NMR spectra of dimesitylphenylborane dianions **1a–c**. These dianions have novel B=C structures as determined from ^{1}H, ^{13}C, and ^{11}B NMR spectra.

When dimesitylphenylborane **1a** is reduced by Na–K alloy in THF at room temperature, the solution turns blue (660 nm). The blue solution shows a well-resolved EPR spectrum, indicating that the blue species is the anion radical **1a**$^{-}$. However, the solution turns purple (581 nm) after further contact with the Na–K alloy (Fig. 1). The purple species quantitatively reverted to **1a** on exposure to air. The purple species is also generated when K-mirror is used as a reducing agent; however, the reduction with Na-mirror gives only the blue species and further reduction is very sluggish. Similar treatment of **1a** with Na–K alloy in [^{2}H$_8$]THF in an NMR tube gives a broad NMR spectrum at room temperature and a well-resolved spectrum at −40 °C (Fig. 2). Rotation of the mesityl group is restricted at this temperature, and two kinds of *o*-methyl [δ 1.54 (s, 6 H), 2.69 (s, 6 H)] and aromatic protons [δ 6.20 (s, 2 H), 6.56 (s, 2 H)] in the mesityl group are observed. Aromatic protons (H_o, H_m, H_p) in the phenyl group appear at δ 3.92 (d, 2 H, *J* 8.1 Hz), 4.92 (dd, 2 H, *J* 8.1, 5.7 Hz), and 3.26 (t, 1 H, *J* 5.7 Hz), respectively. These chemical shifts of aromatic protons are roughly comparable with the aromatic proton of the recently reported 1,2,4,5-tetrakis(trimethylsilyl)benzene dianion (δ 5.11 in [^{2}H$_8$]toluene).[6] The chemical shifts of the corresponding carbons (C_o, C_m, C_p) are unequivocally determined to be δ 119.8, 128.4, and 79.0, respectively, by CH-COSY methods.† These ^{13}C chemical shifts clearly indicate that the negative charge is mostly localised in the C_p position. The ^{11}B signal of the dianion appears at δ 10.4, whereas that of neutral **1a** is at δ 66.2 (BF$_3$–Et$_2$O standard). The upfield shift of δ 55.8 strongly suggests the expected B=C structure. From these chemical shift values, the regeneration of **1a** on exposure to air, and clean conversion from the anion radical species as recognised by electronic and NMR spectra, the purple species is established to be dianion **1a**$^{2-}$. In particular, the ^{13}C and ^{11}B chemical shifts are in accordance with the formulation **A** as a main canonical structure. The fact that the H_o and H_m signals appear considerably upfield compared to the normal sp^2-carbon chemical shifts of C_o and C_m can be explained by the paramagnetic ring current effect of an 8π-electron system in the six-membered ring, as represented by the structure **B** as a minor contributor.



1a R = H
b R = Me$_3$Si
c R = Ph
(Mes = Mesityl)

A

B

Similar dianions are successfully generated from dimesityl(*p*-trimethylsilylphenyl)borane **1b** and 4-biphenylyldimesi-

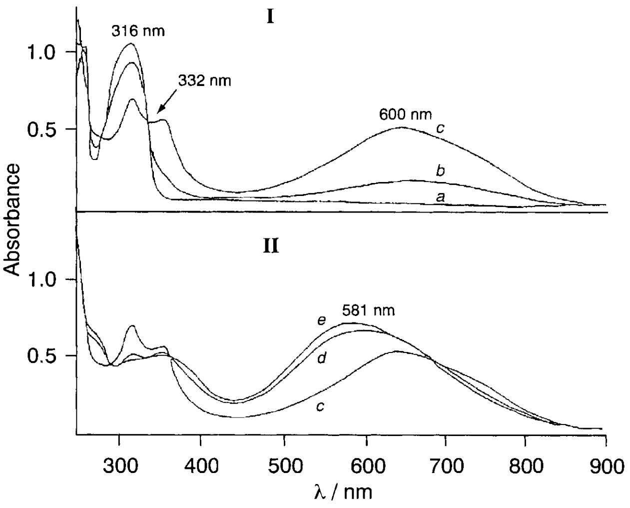


Fig. 1 Electronic spectral change in the reduction of **1a** with Na–K alloy in THF; each spectrum is recorded as a function of contact time with the Na–K alloy and the change separates into two stages: **I**, formation of anion radical; and **II** formation of dianion. (*a*) 0, (*b*) 15, (*c*) 30, (*d*) 45, (*e*) 60 s.

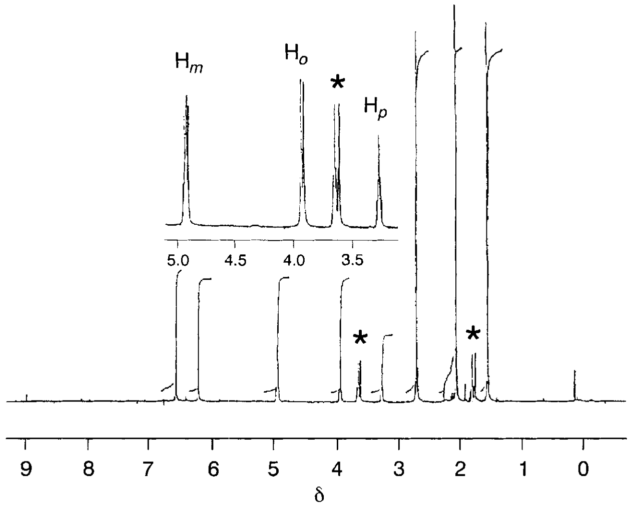


Fig. 2 ^{1}H NMR spectrum of dimesitylborane dianion **1a**$^{2-}$ in [^{2}H$_8$]THF at −40 °C (* shows signals of THF in [^{2}H$_8$]THF)

Table 1 ^{11}B chemical shifts of dianions and absorption maxima in electronic spectra (VIS region) of anion radicals and dianions

Compound	^{11}B chemical shift of dianion (δ)	λ_{max} (log ε)^a of anion radical/nm	λ_{max} (log ε)^a of dianion/nm
1a	10.4	660 (3.78)	581 (3.90)
1b	16.6	681 (3.54)	558 (3.91)
1c	25.2	412 (4.35), 852 (4.17)	644 (4.67)

^{a} Estimated from spectral change assuming clean conversion.

tylborane **1c**.[‡] Table 1 gives the ^{11}B chemical shifts of the dianions as well as the absorption maxima (VIS) of the anion radicals and dianions. In all cases, the absorption maximum of the dianions is blue-shifted in comparison with the anion radicals at the longest absorption. From Table 1, ^{11}B chemical shifts are seen to be considerably substituent dependent. The ^{11}B chemical shift of the dianions can be considered as a measure of B=C character; a more upfield chemical shift would indicate stronger B=C character. In general, unstable dianionic π-systems must be stabilised by the B=C structure, whereas stable dianionic π-systems would not require high B=C character. In a series of dimesitylphenylborane dianions (**1a–c**)$^{2-}$, it is therefore reasonable that the ^{11}B chemical shift of the most unstable **1a**$^{2-}$ appears upfield (δ 10.4) to those of the slightly stabilised **1b**$^{2-}$ and the more stabilised **1c**$^{2-}$ (δ 16.6 and 25.2, respectively).[§]

In summary, dimesitylphenylborane dianions are characterised by electronic and NMR spectra for the first time. The dimesitylphenylborane structure seems to be important for the detection of dianions, since the two bulky mesityl groups would prevent the disproportionation proposed by DuPont and Mills.[5] The presence of the phenyl group would also be important for giving good coplanarity between the boron *p*-orbital and phenyl π-orbitals. The reduction of trimesitylborane is interesting in this context; similar reduction of trimesityborane produces an equilibrium mixture of the dianion and the anion radical, and a clean NMR spectrum of the dianion could not be obtained. Further studies are in progress.

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Footnotes

[†] The boron-substituted carbons appeared as weak and broad signals (δ 127.8, 153.5). Judging from signal intensity, the signal at δ 127.8 can be assigned as the boron-substituted carbon in the phenyl group.

[‡] *Spectroscopic data* for dianion **1b**$^{2-}$: ^{1}H NMR (400 MHz, [^{2}H$_8$]THF −40 °C) δ −0.21 (s, 9 H), 1.61 (s, 6 H), 2.08 (s, 6 H), 2.66 (s, 6 H), 4.21 (d, 2 H, *J* 9.2 Hz), 5.00 (d, 2 H, *J* 9.2 Hz), 6.25 (s, 2 H), 6.59 (s, 2 H). ^{13}C NMR (100 MHz, [^{2}H$_8$]THF, −40 °C) δ 0.81, 21.5, 21.7, 24.9, 75.5, 122.3, 126.7, 127.2, 127.7, 129.7, 138.4, 142.2, 153.0 (weak); (one boron-substituted sp^2-carbon was too weak to observe). ^{11}B NMR (86.6 MHz, [^{2}H$_8$]THF) δ 16.6. For dianion **1c**$^{2-}$: ^{1}H NMR (400 MHz, [^{2}H$_8$]THF, −40 °C) δ 1.75 (s, 6 H), 2.13 (s, 6 H), 2.66 (s, 6 H), 5.12 (d, 2 H, *J* 9.5 Hz), 5.19 (t, 1 H, *J* 6.6 Hz), 5.50 (d, 2 H, *J* 9.5 Hz), 5.93 (d, 2 H, *J* 8.4 Hz), 6.30 (dd, 2 H, *J* 6.6, 8.4 Hz), 6.36 (s, 2 H), 6.67 (s, 2 H). ^{13}C NMR (100 MHz, [^{2}H$_8$]THF, −40 °C) δ 21.4, 23.4, 24.5, 93.4, 102.7, 110.6, 117.6, 119.2 (weak), 126.0, 127.3 (two carbons), 128.5, 129.8, 134.1, 139.3, 142.2, 151.5 (weak). ^{11}B NMR (86.6 MHz, [^{2}H$_8$]THF) δ 25.2. Attempts to obtain a good crystal for X-ray analysis of the dianions were unsuccessful.

[§] The reduction potentials of **1a–c** were determined by cyclic voltammetry [E_{red}(1) = −2.00 V for **1a**, −1.93 V for **1b**, −1.86 V *vs.* SCE for **1c**, all reversible] in DMF containing tetrabutylammonium perchlorate (0.1 mol l^{-1}) with a sweep rate of 100 mV s^{-1} at 25 °C. The second reduction waves could not be observed in these conditions. Assuming a parallel relation between the first and second reduction potentials, the stabilities of the dianions were estimated to increase in the order **1a** < **1b** < **1c** as expected.

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