An Isolable Radical Anion Based on the Borole Framework**

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The element boron is known to have a variety of ways to relieve its inherent electron deficiency. The acceptance of an electron pair (Lewis acidity) has applications in catalysis^[1] and activation of element-element bonds (frustrated Lewis pairs).^[2] The combination of boron with π -donating substituents (e.g. BF₃) and its incorporation into organic π -conjugated systems allows the empty p_z orbital of boron to participate in π bonding and π conjugation, respectively, and the latter enables the use of boron in optoelectronic materials with unique properties.^[3] The absence of π -donating substituents at the boron center may result in multiple-center bonding to form nonclassical frameworks (e.g. B₂H₆ or clusters). In addition, organoboranes and -diboranes(4) are prone to accept a single electron by chemical reduction.^[4] Likewise, hydrogen atom abstraction from N-heterocyclic carbene (NHC)-stabilized boranes (NHC-BH₃) can lead to neutral, persistent^[4f] boryl radicals of the type NHC-BH₂;^[5] which have been studied by means of cyclic voltammetry, EPR, and UV/Vis spectroscopy as well as trapping reactions.^[4-6] However, examples of isolated boron radicals are rare owing to the reactive nature of the species, and only little is known about their structural properties. Steric protection of the boron center combined with spin delocalization over the organic substituents, both achieved by substitution with mesityl groups (Mes = 2,4,6-trimethylphenyl), has occasionally enabled isolation and structural characterization of radical anions such as [Li([12]crown-4)₂][BMes₃] (1) or [K([18]crown-6)- $(thf)_{2}$ [Mes₂BB(Ph)Mes] (2).^[7]

Our group has recently studied a persistent radical anion as an intermediate in the stepwise reduction of 1-ferrocenyl-2,3,4,5-tetraphenylborole (**3**).^[8] Boroles are a class of antiaromatic compounds with interesting chemical and photophysical properties^[9,10] that are well-known for their ability to accept two electrons with formation of an aromatic borole dianion.^[11,12] Encouraged by these recent results on the radical anion [**3**]⁻⁻, which indicated the presence of a highly

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unusual $C_4B \pi$ system bearing five electrons,^[8] we set out to isolate and characterize a stable borol radical anion. As we report here, this was possible by choice of steric protection and an appropriate reducing agent.

The synthesis of MesBC₄Ph₄ (1-mesityl-2,3,4,5-tetraphenylborole, **4**) by means of the commonly employed tin-boron exchange reaction^[11-14] was unsuccessful because of the low reactivity of dihalo(mesityl)boranes (MesBX₂; X = Cl, Br). However, **4** was obtained in 41 % yield by functionalization of the boron center in 1-chloro-2,3,4,5-tetraphenylborole (**5**) through nucleophilic displacement of the chlorine ligand with LiMes (Scheme 1).^[14b] A more efficient alternative was found to be the salt-elimination reaction of MesBCl₂ with 1,4-



Scheme 1. Synthesis of 1-mesityl-2,3,4,5-tetraphenylborole (4) and its single-electron reduction with $[CoCp*_2]$ to give the radical anion 8 as well as its two-electron reduction to yield the dianion 9.

dilithio-2,3,4,5-tetraphenylbuta-1,3-diene (6) which provided 4 in 66% yield. Formation of a Lewis acid-base adduct with Et₂O, as previously reported for 1,2,3,4,5-pentaphenylborole (7), was not observed,^[13] already indicating the desired enhanced steric shielding of the boron atom. Both methods afforded 4 as a dark green crystalline solid containing one equivalent of benzene according to ¹H NMR spectroscopy and elemental analysis. The ¹¹B NMR resonance of 4 ($\delta =$ 79.4 ppm) is shifted significantly downfield shifted relative to that of 7 ($\delta = 65.4$ ppm).^[14a] In addition, the green color of 4 is rather unexpected for pentaarylboroles, which are usually blue (7: $\lambda_{\text{max}} = 560 \text{ nm}$), and arises from the lowest-energy electronic absorption at $\lambda_{\text{max}} = 578 \text{ nm} (\varepsilon = 871 \text{ Lmol}^{-1} \text{ cm}^{-1})$, a less well-separated absorption at about $\lambda = 425$ nm, and a second maximum at $\lambda_{max} = 365 \text{ nm}$ ($\varepsilon = 8181 \text{ Lmol}^{-1} \text{ cm}^{-1}$; see the Supporting Information).

In the solid-state structure of 4 determined by X-ray diffraction the bond lengths and angles (see Table 1) of the central C_4B moiety are consistent with those of other

Table 1:	Selected	bond	lengths	[Å]	and	angles	[°]	of 4	8,	and	9
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Bond	4	8	9
B1–C1	1.586(2)	1.553(4)	1.531(4)
B1–C4	1.575(2)	1.553(4)	1.527(4)
B1–C5	1.560(2)	1.585(4)	1.609(4)
C1–C2	1.356(2)	1.393(3)	1.468(4)
C2–C3	1.537(2)	1.480(3)	1.427(4)
C3–C4	1.351(2)	1.397(3)	1.443(4)
Angle	4	8	9
C1-B1-C4	105.2(1)	104.4(2)	104.7(2)
C1-B1-C5	127.7(1)	127.9(2)	129.3(2)
C4-B1-C5	126.8(1)	127.4(2)	126.0(2)
B1-C1-C2	106.0(1)	107.4(2)	107.5(2)
C1-C2-C3	110.7(1)	110.4(2)	109.2(2)
C2-C3-C4	111.3(1)	110.5(2)	110.7(2)
C3-C4-B1	105.9(1)	107.2(2)	107.9(2)

boroles,^[12,14a] and no close contacts between neighboring molecules are evident in contrast to the solid-state structure of **7**,^[14a] which further proves the effective steric shielding in **4**. As expected, the torsion angle formed by the mesityl group with respect to the C₄B plane (68.7(1)°) is increased in comparison to that of less bulky aryl groups.

For a closer insight into the redox properties of **4**, cyclic voltammograms in CH_2Cl_2 were recorded which showed two well-separated reduction waves (Figure 1). The first reduction event was identified at $E_{1/2} = -1.69$ V (referenced against the



Figure 1. Cyclic voltammogram of 4 in 0.1 $\[Mathbb{M}]$ [PF₆]/CH₂Cl₂ at room temperature. Scan rate: 150 mVs⁻¹; potential reported versus Fc/Fc⁺ as the internal standard. The inset (dashed) displays the reversibility of the single-electron reduction.

ferrocene/ferrocenium (Fc/Fc⁺) couple) as a reversible process associated with the formation of the radical anion [**4**]⁻. It is noteworthy that this reduction potential is considerably less negative than that observed for **3** ($E_{1/2} = -1.96$ V)^[8] and for 9-borafluorenes ($E_{1/2} = -2.04$ V to -2.28 V).^[15] A similar reduction potential has recently been reported for a polycyclic thiophene-fused borole system ($E_{1/2} = -1.72$ V).^[16] The second reduction process is centered at $E_{1/2} = -2.54$ V and irreversible. It corresponds to formation of the aromatic dianion [**4**]²⁻ and its redox potential is close to that found for **3**

 $(E_{1/2} = -2.56 \text{ V})$. The irreversibility is most likely due to subsequent reactions with the halogenated solvent.

Chemical single-electron reduction of **4** was accomplished by using decamethylcobaltocene ($[CoCp_2]$; $E^0(Fc/Fc^+) =$ -1.9 V) as a reducing agent (Figure 1).^[17] Reaction of a slight excess of **4** with $[CoCp_2]$ in benzene at ambient temperature smoothly generates $[CoCp_2][MesBC_4Ph_4]$ (**8**), which was obtained as an analytically pure reddish brown solid in 85% yield. Under an inert atmosphere, **8** shows no signs of decomposition in the solid state at room temperature and is moderately stable in THF solution at -30 °C. The UV/ Vis spectrum in THF shows an absorption maximum at $\lambda_{max} =$ 560 nm,which is slightly blue-shifted compared to that of the neutral borole **4** and similar to that observed for [**3**]⁻⁻ ($\lambda_{max} =$ 541 nm).

EPR spectroscopy confirmed that **8** is a radical. The EPR signal of **8** was detected in THF at 295 K as a four-line resonance (centered at $g_{iso} = 2.0025$; Figure 2). The experi-



 $\it Figure 2.$ Experimental and simulated EPR spectrum (X-band) of 8 in THF solution at 295 K.

mental spectrum was reproduced by a simulation (see the Supporting Information for details) which included the coupling of one unpaired electron with the nuclear isotopes of ¹¹B (I = 3/2; abundance: 80.1 %) and ¹⁰B (I = 3; abundance: 19.9 %). The resulting hyperfine coupling constants A for ¹¹B and ¹⁰B are 3.43 G and 1.08 G, respectively. This is comparable to what has been reported for [**3**]⁻⁻ (A(¹¹B) = 3.73 G) and is consistent with a pronounced degree of spin delocalization over the borole framework.^[4f]

The solid-state structure of **8** was determined by X-ray diffraction, revealing a separated ion pair with no interaction between neighboring radical centers (Figure 3). The C_4B framework is essentially planar with a propeller-like orientation of the four phenyl groups similar to that in **4**. The interplanar torsion angle of 68.4(1)° formed by the mesityl group and the borole ring is almost identical to that in **4**. Upon reduction, the B1–C, B1–C4, and C2–C3 single bonds shorten slightly, whereas the C1–C2 and C3–C4 double bonds



Figure 3. Molecular structure of **8** in the solid state with hydrogen atoms and solvent molecule (THF) omitted for clarity. Thermal ellipsoids are set at 50% probability.

lengthen (see Table 1). Hence, the borole moiety of **8** shows a slight decrease in bond-length alternation as a result of increased delocalization of the π system which is consistent with the EPR spectrum. In contrast to **1**, where all three B–C bonds are shorter than those in the parent borane (Mes₃B),^[7a] the exocyclic B1–C5 bond of **8** is somewhat longer than in the neutral borole **4**. This is in agreement with an enhanced electron density at the boron center and delocalization of the additional electron into the C₄B ring rather than over the external mesityl group.

In order to get a better understanding of the electronic structure of **8**, DFT calculations were performed at the PBE0/ 6-311 + G(d,p) level (see the Supporting Information for further details). The optimized geometry of the radical anion moiety of **8** is in good agreement with the experimental data. Inspection of the electron density distribution of the SOMO indicates that the charge is predominantly located at the boron center. Furthermore, the electrostatic potential mapping shows that the overall charge density resides on the borole fragment but mainly in the butadiene backbone. Analysis of NBO charges of the atoms forming the central borole ring shows increasing electron delocalization in the π orbitals when the number of electrons added to the system increases (from **4** over [**4**]⁻ to [**4**]²⁻).

Dianionic borole systems have been known for more than 30 years and solid-state structural analyses have been reported.^[11,12] Nevertheless, we prepared the borole dianion 9 to obtain a system that is comparable to 8 concerning the periphery of the borole scaffold. Borole 9 (δ (¹¹B) = 30.2 ppm) was synthesized by reduction of 4 with potassium graphite yielding single crystals suitable for X-ray diffraction. As expected, the structural analysis shows a further decrease of bond alternation in 9, compared to that in 8 (see Table 1), when borole 4 takes up two electrons. This is in agreement with a high degree of charge delocalization within the π system which is typical for a compound with aromatic character.^[12] It should be considered, however, that the structures of 9 and all hitherto known examples of borole dianions may be influenced by the pronounced coordination of the counterions to the system and do not reflect a free aromatic moiety.

The reactivity of the open-shell species 8 was examined by using a trapping reagent. For this purpose, 8 was reacted with dibenzoyl peroxide (DBPO) which is known to undergo homolytic cleavage of the O–O bond by thermal or photolytical activation enabling its use as a radical initiator.^[18] Indeed, **8** readily reacts with DBPO at ambient temperature in a heterogeneous slurry. The selectively formed product is a borate species (**10**; Scheme 2) resulting from the formal recombination of the borole radical anion **8** with a benzoyloxy radical.



Scheme 2. Trapping reaction of 8 with dibenzoyl peroxide to form 10.

Compound **10** was characterized by means of multinuclear NMR spectroscopy, elemental analysis, and X-ray crystallography. The ¹¹B NMR resonance was found at δ = 4.9 ppm in the typical range of four-coordinated boron. The solid-state structure confirms a distorted tetrahedral geometry around the boron center and is comparable to that observed for borole-based Lewis acid–base adducts reported earlier (Figure 4).^[10,14b–d] These results indicate a boroncentered reactivity of the radical anion even though the



Figure 4. Molecular structure of **10** in the solid state with hydrogen atoms and solvent molecule omitted for clarity. Thermal ellipsoids are set at 50% probability.

boron atom resides at the sterically most hindered position of the heterocycle. The observed selectivity of the reaction reflects the calculated spin density of the SOMO. Consequently, **8** can be classified as a boron-centered radical anion, mainly stabilized by charge delocalization into the fivemembered borole unit and less by the steric protection of the mesityl group.

In summary, we have described the synthesis and oneelectron reduction of 1-mesityl-2,3,4,5-tetraphenylborole (4) along with the full characterization of the resulting radical anion 8. The obtained structural and EPR spectroscopic data $(g_{iso} = 2.0025; A(^{11}B) = 3.44 \text{ G})$ as well as DFT calculations are in agreement with a planar geometry with significant delocalization of the five π electrons within the borole ring. In addition, the radical anion 8 was successfully trapped by dibenzoyl peroxide to give the borate 10. The boron-centered reactivity shows that despite its substitution with a bulky

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mesityl group the boron atom remains accessible. Further studies of related radical species and their reactivity are currently in progress.

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