Boryl Radicals

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A Phosphine-Coordinated Boron-Centered Gomberg-Type Radical**

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***Abstract:** The P-coordinated boryl radical [Ph_2P-(naphthyl)BMes]$^•$ (Mes = mesityl) was prepared by (electro)-chemical reduction of the corresponding borenium salt or bromoborane. Electron paramagnetic resonance (EPR) analysis in solution and DFT calculations indicate large spin density on boron (60–70 %) and strong P–B interactions (P→B σ donation and B→P negative hyperconjugation). The radical is persistent in solution and participates in a Gomberg-type dimerization process. The associated quinoid-type dimer has been characterized by single-crystal X-ray diffraction.*

Over the last few years, significant progress has been achieved in boron chemistry with the isolation of a variety of compounds featuring original structures, exhibiting interesting properties, and displaying rich reactivity. These developments concern highly reactive diamagnetic species (such as boryl anions,[1] diborynes and oxoboryls,[2] 1,3-diboratacyclobutane-1,3-diyls,[3] boriniums,[4] and borylene adducts[5]) as well as radicals for which unusual bonding situations (such as one-electron B−B σ and π bonds)[6] have been uncovered and important synthetic applications have emerged.[7] In particular, boryl radicals ($L\rightarrow BR_2$)$^•$, which can be considered as neutral tricoordinate boron radicals, have attracted considerable attention.

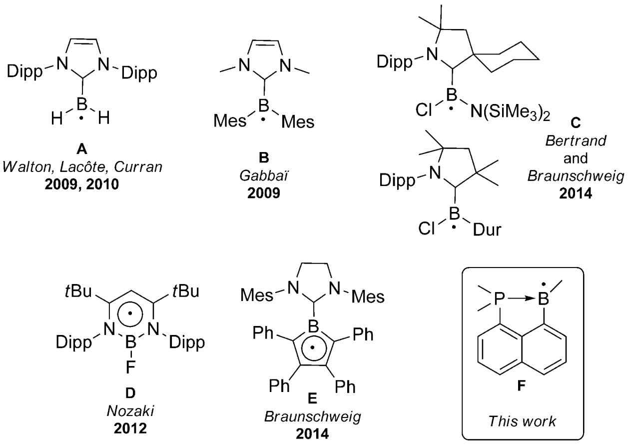

Figure 1. Different types of EPR-characterized/isolated boryl radicals **A**–**E** and the P-coordinated boryl radical **F** studied herein. Dipp = 2,6-diisopropylphenyl; Dur = 2,3,5,6-tetramethylphenyl.

Some reported examples of boryl radicals are shown in Figure 1. Basically, two different types can be distinguished: 1) acyclic systems, such as **A**,[8a,b] **B**,[8c] and **C**,[5c, 8d] in which a five-electron $BR_2^•$ radical is stabilized by a strong Lewis base, typically a N-heterocyclic carbene (NHC), and 2) cyclic compounds, such as **D** and **E**, which are stabilized by π delocalization.[9]

In this context, we report herein a persistent P-coordinated boryl radical. A compound of type **F** (Figure 1) has been prepared by (electro)chemical reduction. The structure of the radical has been thoroughly analyzed by electron paramagnetic resonance (EPR) spectroscopy and DFT calculations. Single-crystal X-ray diffraction analysis revealed that the molecule undergoes Gomberg-type dimerization by B–C coupling. This B-centered radical is a new member in the family of naphthyl-bridged P/B compounds,[10] and is a stable version of the transient phosphine–boryl radicals (R_3PBH_2)$^•$.[11]

Taking advantage of the strong P→B interaction enforced by the naphthyl bridge,[10c–e] we have recently isolated the P-coordinated borenium salt **1** (see Figure 2, inset).[10f] This prompted us to try to generate the corresponding boryl radical. The reduction of **1** was first assessed electrochemically. The cyclic voltammogram showed a quasi-reversible one-electron wave at −0.48 V (versus ferrocene/ferrocenium Fc/Fc^+) in fluorobenzene (Figure 2).[12] This reduction potential is significantly more positive than that of other borenium/boryl couples. For example, the NHC-stabilized radical **B** is formed at much lower potential ($E_{1/2} = -1.81$ V)[8c] and the lowest reported reduction waves occur at $E_{1/2} = -0.86$ V for 9-acridinyl $BMes_2$ derivatives.[13] As a result of its cationic

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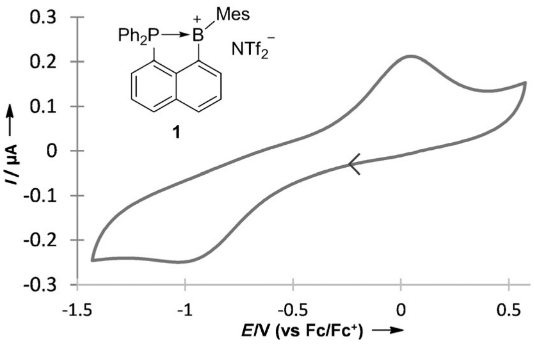
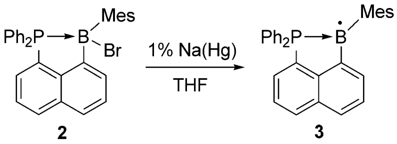


Figure 2. Cyclic voltammogram of **1** in a fluorobenzene solution containing [nBu$_4$N][NTf$_2$] (0.06 M) as the electrolyte. Scan rate: 500 mV s^{-1}; potential reported against Fc/Fc$^+$ as the internal standard.

character, **1** can also be reduced much more easily than boranes, including the highly electrophilic tris(pentafluorophenyl)borane ($E_{1/2} = -1.17$ V).[14]

Encouraged by the electrochemical reduction of **1**, we then explored the chemical reduction of its precursor, the P-coordinated bromoborane **2** (Scheme 1). Using zinc powder or 1% Na(Hg) amalgam in THF, a dark-red solution was formed from which compound **3** could be isolated by filtration and precipitation over pentane (83% yield).



Scheme 1. Synthesis of radical **3** by reduction of bromoborane **2**.

The X-band EPR spectrum of **3** in THF/toluene solution at room temperature shows a complex but nicely resolved signal centered at an isotropic g value of $g_{iso} = 2.0026$ (Figure 3). No change was observed over days at room temperature, indicating the highly persistent character of this boryl radical. The hyperfine structure could be resolved by simulation,[15] taking into account couplings to the ^{31}P and ^{11}B/^{10}B nuclei, as well as to two ^{1}H nuclei. The coupling constants to ^{31}P and ^{11}B nuclei (31 and 11 G, respectively) fall in the same range as those of transient phosphine–boryl radicals (R$_3$PBH$_2$)$^•$.[11] Delocalization of the unpaired electron over the organic substituents (in particular the naphthyl moiety, see DFT calculations described below) is indicated by the necessity to include two ^{1}H nuclei in the simulation with couplings of 4 and 5 G. However, the large $a(^{11}B)$ coupling indicates that the spin density at boron is unusually high in **3**.[16] The value measured for **3** falls in the upper range of those reported for persistent/isolable boryl radicals (7.3–13.2 G).[5c,8] It is also higher than those of the triphenylboron and trimesitylboron anion radicals ($a(^{11}B) = 7.8$ and 9.9 G, respectively), which have approximately 60% spin density on boron.[17]

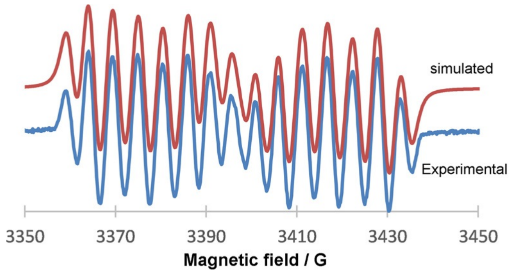


Figure 3. Experimental (gray) and simulated (black) X-band EPR spectra of **3** in toluene/THF solution at room temperature. G = gauss.

To gain more insight into the structure of **3**, DFT calculations were performed.[18] The geometry was optimized at the UB3PW91/6-31G** level of theory and the hyperfine coupling constants were then computed at the B3PW91/IGLO-II(P),EPR-II(H,B,C) level (see the Supporting Information, Tables S1 and S2).[15] The obtained values (35.3 and 10.3 G for ^{31}P and ^{11}B nuclei, respectively) match remarkably well with those determined experimentally. DFT also nicely reproduces the two couplings to ^{1}H nuclei (5.7 and 5.5 G) and enables us to assign the nuclei as the protons on the naphthyl ring in the *ortho* and *para* positions with respect to boron (suggesting some delocalization of spin density). The optimized structure of **3** (Figure 4a) is also informative. The boron center is in a trigonal planar environment (the sum of the bond angles $\Sigma B_\alpha = 359.6°$) and the Mes group is twisted by 68.3° from the (naphthyl,P,B) plane, suggesting very little, if any, delocalization of spin density over the mesityl ring. Consistently, the B−C$_{Mes}$ bond (1.571 Å) is longer than the B−C$_{naphthyl}$ bond (1.534 Å). Bond lengths in pm changed to Å to correspond to Figure 4a and throughout the manuscript for

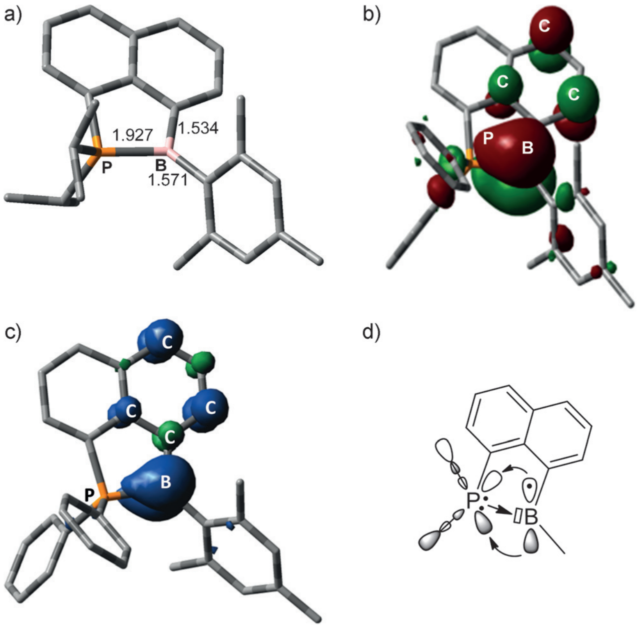


Figure 4. DFT analysis of compound **3**: a) optimized geometry (distances in Å); b) SOMO (cutoff = 0.04); c) spin density distribution (isovalue = 0.005 au); d) representation of the PB donation/back donation. H atoms are omitted for clarity.

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consistency. The presence of a strong P→B interaction is apparent from the short P–B distance (1.927 Å). Comparison with the corresponding borenium salt **1** (2.006 Å) is interesting and reveals some shortening of the bond in **3**. This is rather counterintuitive given that the boron center is less electrophilic in the boryl radical **3** than in the borenium **1**, and thus reduction of **1** to form **3** would be expected to weaken the P→B interaction.

The electronic structure of **3** was then carefully analyzed by DFT calculations.[15] The singly occupied molecular orbital (SOMO; Figure 4b) and the total spin density distribution (Figure 4c) are mainly localized on the B atom (60–70% spin density) with small contributions of the P atom as well as the C_{ipso}, C_{ortho}, and C_{para} atoms of the naphthyl ring. Most noticeable are the overlaps of the 2p(B) orbital with 1) the adjacent 2p(C_{ipso}) orbital (π bonding) and 2) the neighboring σ*(PC) orbitals (negative hyperconjugation). This picture is corroborated by natural bond orbital analysis (NBO), which gives at the first order a π(BC_{ipso}) orbital centered on boron (62%) with an occupancy of $0.86\,e^-$. Stabilizing interactions with $\pi^*(C{=}C)_{naphthyl}$ and σ*(PC) orbitals are found at the second-order perturbation level (with NBO delocalization energies $\Delta E_{int} = 15.3$ and $9.5\,kcal\,mol^{-1}$, respectively).[15] Interaction of the singly occupied 2p(B) with adjacent vacant σ*(PC) orbitals is reminiscent of the negative hyperconjugation occurring within P ylides (Figure 4d). The effect of the negative hyperconjugation is probably to contribute to the shortening of the PB distance in **3** (P→B donation/B→P back donation) compared to borenium **1**.

The stability and high spin density of **3** at the B atom encouraged us to try to crystallize it. Our attempts were finally rewarded and suitable crystals were obtained from a THF solution layered with pentane at room temperature. According to X-ray diffraction, the molecule adopts in fact a dimeric quinoid-type structure [**3**]$_2$ in the solid state (Figure 5).[19] The dimerization occurs at the boron atom of one boryl unit and the C_{para}(naphthyl) atom of the other boryl unit. The length of the resulting B–C bond (B2–C4 = 1.670(7) Å) is typical of a single B–C bond. The two boron atoms are in different environments. The B atom directly involved in the dimerization (B2) becomes tetrahedral and its bond to phosphorus is elongated (2.115(5) Å) due to steric shielding. The other boron atom (B1) remains trigonal planar. Atom B1 is engaged in a strong P→B interaction (1.933(6) Å)[20] and the bond towards C_{ipso}(naphthyl) is significantly shortened (1.463(7) Å), indicating that the bond has double bond character.

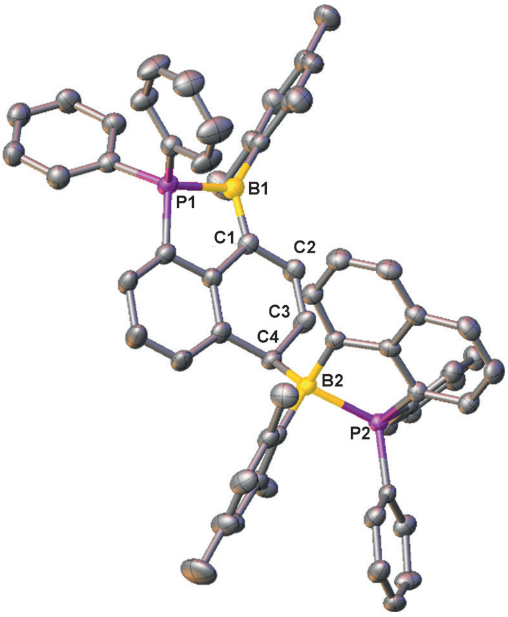
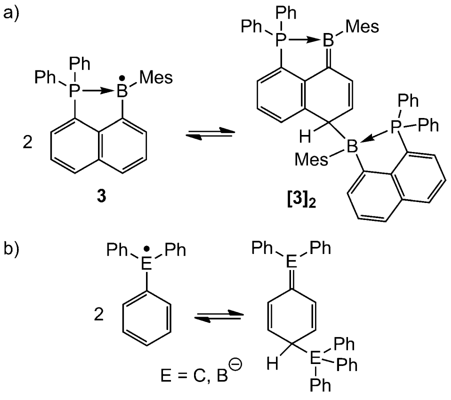


Figure 5. OLEX2 plot of [**3**]$_2$ with thermal ellipsoids set at 50% probability. For clarity, the hydrogen atoms have been omitted. Selected bond lengths [Å] and angles [°]: B1–C1 1.463(7), B1–P1 1.933(6), B2–C4 1.670(7), B2–P2 2.115(5), C1–C2 1.434(7), C3–C4 1.509(7), C2–C3 1.338(6); C1-B1-C11 131.4(5), C1-B1-P1 101.0(4), C11-B1-P1 127.5(3).



Scheme 2. a) Monomer–dimer equilibrium of **3** and b) the Gomberg-type dimerization of the triphenylmethyl radical (E = C) and the triphenylboron anion radical (E = B^-).

The formation of [**3**]$_2$ is reminiscent of the dimerization of the trityl radical $Ph_3C^{\bullet}$ as reported by Gomberg (Scheme 2).[21] Dimerization of triarylmethyl radicals is a particularly fascinating transformation in organic chemistry. The reaction has always attracted significant interest and undoubtedly represents a founding principle of radical chemistry.[22] Comparatively, very little is known about related transformations with main-group radicals. Monomer/dimer interconversions have been observed with p-block radicals (in particular with E = Si, Sn, P, Sb, Bi),[23] but they usually involve E–E bond formation/cleavage. In a recent study on aryl-substituted silyl radicals, Sekiguchi et al. proposed a Si–C_{para} dimerization process to rationalize the decrease of the EPR signal intensity observed upon cooling.[24] In the case of boron compounds, Ph_3B was reported early on to dimerize under reductive conditions (Na).[25] The ionic nature and instability of the transient triphenylboron anion radical prevented detailed analysis of the dimerization process, but a Gomberg-type dimeric structure could be proposed based on NMR spectroscopic data.[26] The dimerization process observed with the boryl radical **3** is unique among persistent/isolable boryl radicals[27] and the B–C_{para} coupling is probably favored by the same factors as for the trityl radical: B–B coupling suffers from strong steric congestion whereas C–C coupling is disfavored by a) the low spin density at the C_{para} position (20–25% versus

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60–70 % at B according to DFT) and b) high loss of aromatic character (the two naphthyl units would adopt quinoid structures).

Further characterization of $[\mathbf{3}]_2$ indicated complete dimerization of **3** in the solid state, as demonstrated by the fact that the red powder obtained by crystallization is EPR silent. Additionally, in the cross-polarization magic angle spinning (CP-MAS) NMR spectrum, relatively sharp signals for ^{31}P and ^{11}B nuclei were detected at expected chemical shifts ($\delta(^{31}\mathrm{P}) = +11.5$ and -3.9 ppm; $\delta(^{11}\mathrm{B}) = 25.0$ and 5.2 ppm). Finally, the equilibrium between **3** and $[\mathbf{3}]_2$ was analyzed by variable-temperature EPR spectroscopy in solution. From the variation of the integral of the EPR signal, the Gibbs free energy associated with the dimerization of **3** was estimated to $-15\ \mathrm{kcal\,mol^{-1}}$.[15] This value is slightly larger than that of the trityl radical ($\Delta G = -11\ \mathrm{kcal\,mol^{-1}}$)[28] which may be attributed, at least in part, to the lower aromaticity of the naphthyl unit (versus phenyl).

In summary, a new P-coordinated boryl radical has been prepared. According to EPR data and DFT calculations, the spin density is mainly localized on the boron center, with small contributions of the P atom and naphthyl unit. The radical is persistent in solution and exists in equilibrium with a head-to-tail B–C dimer, which has been characterized by X-ray crystallography. Gomberg-type dimerizations of this type are extremely rare with main-group radicals and future work will seek to explore further the chemistry of P-coordinated boryl radicals.

Keywords: boron · cyclic voltammetry · EPR spectroscopy · phosphorus · radicals

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