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VIP **Bond Theory**

Confirmation of an Early Postulate: B–C–B Two-Electron–Three-Center Bonding in Organo(hydro)boranes**

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Hydroboration reactions of alkyl(hydro)boranes are among the most useful methods in organic synthesis.[1] In contrast, the potential of aryl(hydro)boranes is only now starting to be exploited since they have been recognized as versatile building blocks for boron-doped π-conjugated systems. Owing to their exciting optoelectronic properties, boron-containing organic materials possess promising application potential as electron transporters and light emitters in organic light-emitting devices, organic solar cells, and chemosensors.[2,3]

The particular reactivity pattern displayed by aryl(hydro)boranes offers two fundamentally different access routes to organoboron materials,[4] either through the monohydroboration of alkynes,[5] or, as a more recent development, by substituent redistribution.[6] While substituent redistribution of organo(hydro)boranes is notorious as a generally undesirable process that leads from initially pure RBH_2 or R_2BH reagents to mixtures R_nBH_{3-n} ($n = 0$–3) upon storage, we have established preparatively useful variants in recent work. Specifically, we developed condensation reactions of the type $2\,ArBH_2 \rightarrow Ar_2BH + {}^1\!/_2\,B_2H_6$ as a generalizable strategy to prepare main-chain boron-containing polymers.[6] While some factors governing the product selectivity were obvious (for example, constant removal of B_2H_6 from the reaction equilibrium), other important boundary conditions had to be adjusted empirically (for example, the steric demand of the aryl groups necessary to avoid the formation of Ar_3B).[6] Aiming at a rise from an empirical to a targeted reaction design, a detailed understanding of the mechanistic background and the intermediates involved is thus crucial.

A valuable guiding principle has already been put forward in early work of Brown and Köster, who reported in the early 1960s that numerous mixed triorganoboranes $B(R^1)(R^2)(R^3)$ are stable even at moderately elevated temperatures, whereas organo(hydro)boranes R_nBH_{3-n} ($n = 1,2$) tend to form exchange equilibria with all four conceivable species ($n = 0$–3) present. Substituent scrambling was, in fact, found to be efficiently catalyzed even by trace amounts of hydroboranes.[7] Köster therefore proposed an exchange of R groups between boron atoms to proceed through the formation of dimeric intermediates with a bridging B–C–B fragment that has necessarily to be supported by an additional, thermodynamically more favorable B–H–B two-electron–three-center (2e3c) bond.[7] However, as of today, not a single example of a dimeric organo- or organo(hydro)borane with bridging B–C–B fragments has been confirmed to exist, let alone unequivocally identified.[8]

Herein we present the unique example of a fully characterized dimeric diorganylborane featuring a B–H–B-supported B–C(aryl)–B linker, which is the first solid evidence confirming Köster's 50-year-old postulate. Based on these findings, we address the following key questions of general relevance for organo-main-group chemistry: 1) What is the relative thermodynamic stability of a B–C(aryl)–B bond compared to a B–H–B bond in the light of Köster's postulate; and 2) How is the electronic structure of the B–C(aryl)–B bond to be seen in the context of, for example, Al–C(aryl)–Al species, bis(silyl)-substituted arenium ions, and the parent benzenium ion?

The starting point of our study was the observation of a peculiar transient species during the ring-opening oligomerization of 9*H*-9-borafluorene (**A**) to its pentamer $(\mathbf{A})_5$ (Scheme 1 a).[9] In situ NMR spectroscopy augmented by DFT calculations led us to assign a structure to this short-lived intermediate in which two molecules of **A** form an unusual C_1-symmetric dimer $(\mathbf{A})_2$ with a B-B-bridging aryl ring.[9,10] Even though the low stability of $(\mathbf{A})_2$ precluded any further characterization, we considered this species a stimulating lead structure in the quest for isolable B–C(aryl)–B-bridged molecules. Aiming at the kinetic stabilization of $(\mathbf{A})_2$, we introduced bulky *tert*-butyl substituents at the phenylene rings and prepared 2,7-di-*tert*-butyl-9-bromo-9-borafluorene (**1**; Scheme 1 b)[22] from 2,7-di-*tert*-butyl-9,9-dimethyl-9-silafluorene[11] and BBr_3.

Treatment of **1** with Et_3SiH in C_6H_6 at room temperature leads to the quantitative formation of one product. X-ray diffraction analysis of single crystals of the compound revealed a dimer $(\mathbf{2})_2$ of 2,7-di-*tert*-butyl-9*H*-9-borafluorene (**2**; Scheme 1 b).[21,22] Its outstanding attributes are the aimed-for B-B-bridging aryl ring and a supporting B–H–B 2e3c bond (Figure 1, top), as already predicted for the transient parent species $(\mathbf{A})_2$.[9] Correspondingly, both species exhibit closely related NMR features: Each of them contains four magnetically inequivalent aromatic rings, one of which

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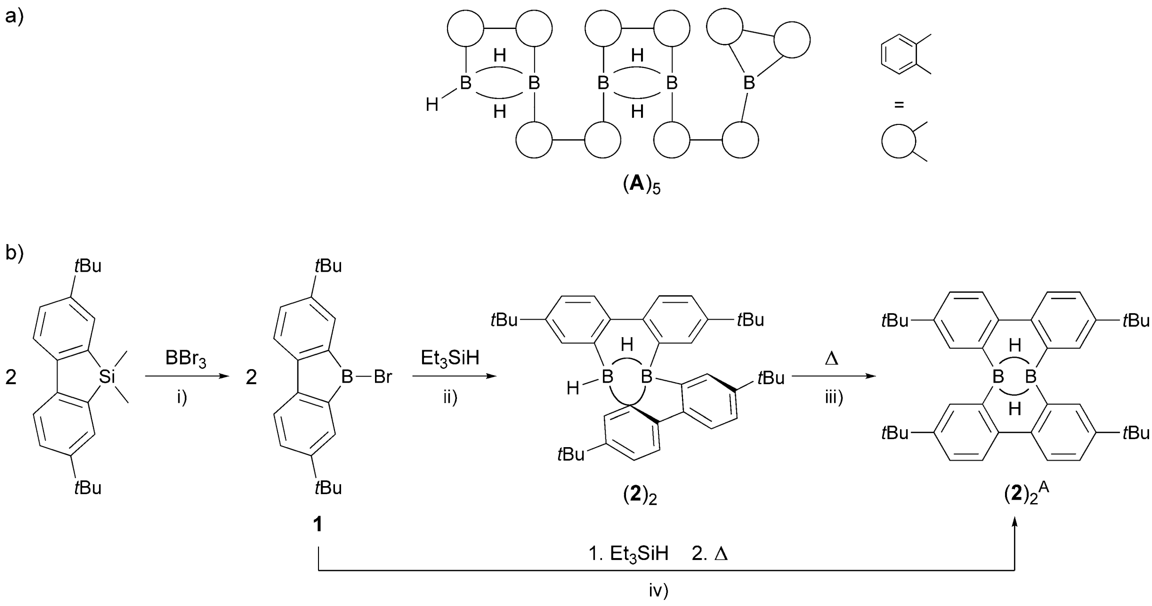


Scheme 1. a) Pentamer $(\mathbf{A})_5$ resulting from the ring-opening oligomerization of 9*H*-9-borafluorene **A**. b) Synthesis of the 9-bromo-9-borafluorene **1** and its conversion to the B–C–B/B–H–B-bridged dimeric 9*H*-9-borafluorene $(\mathbf{2})_2$; thermal isomerization of $(\mathbf{2})_2$ to the doubly B–H–B-bridged species $(\mathbf{2})_2^{A}$. Conditions: i) 6 equiv, 6 d, 70 °C; ii) 5 equiv, C_6H_6, 5 h, RT; iii) hexane, 30 min, 140 °C; iv) 4 equiv, hexane, 30 min, 150 °C.

exhibits a remarkably broad spread of its $^{13}C\{^1H\}$ NMR resonances (here, 114.1–167.7 ppm), and both molecules show two signals assignable to boron-bonded protons. The ^{11}B NMR spectrum of $(\mathbf{A})_2$ is characterized by two well-resolved resonances at 8.5 and 10.3 ppm, whereas one extremely broad resonance at 9.1 ppm is observed for $(\mathbf{2})_2$ (still testifying to the presence of tetracoordinate boron nuclei). Similar to $(\mathbf{A})_2$, $(\mathbf{2})_2$ isomerizes to the 1,2-(2,2′-biphenylylene)diborane(6) $(\mathbf{2})_2^{A}$ upon thermolysis at 140 °C (Scheme 1 b).[22] Contrary to $(\mathbf{A})_2$, however, solutions of $(\mathbf{2})_2$ do not undergo ligand redistribution/ring-opening oligomerization reactions at room temperature over days.

We next compared the reactivity of $(\mathbf{2})_2$ and of $(\mathbf{2})_2^{A}$ toward the Lewis base pyridine. Addition of pyridine to a solution of $(\mathbf{2})_2$ in C_6H_6 results in the quantitative formation of **2**·py, the pyridine adduct of 2,7-di-*tert*-butyl-9*H*-9-borafluorene.[22] The reaction starts immediately and requires several days for completion. In case of $(\mathbf{2})_2^{A}$, no interaction with pyridine is observable under similar experimental conditions within 1 h; however, over a period of several weeks, a gradual transformation to **2**·py also takes place (NMR spectroscopy control).[22] Correspondingly, $(\mathbf{2})_2^{A}$ persists in non-dried $CDCl_3$ for weeks, whereas $(\mathbf{A})_2$ and $(\mathbf{2})_2$ are prone to hydrolysis (NMR spectroscopy control). According to DFT calculations,[12] the reaction $(\mathbf{2})_2 \rightarrow (\mathbf{2})_2^{A}$ is exoergic by only $\Delta_r G° = -2.8\ \mathrm{kcal\,mol^{-1}}$, but both isomers are separated by a substantial barrier ($\Delta^{\ddagger} G° = 28.6\ \mathrm{kcal\,mol^{-1}}$). We therefore conclude that the significantly higher stability of $(\mathbf{2})_2^{A}$ is mainly of kinetic origin, in line with the concept of stabilization by structural constraint.[4,13]

The X-ray crystal structure analysis of $(\mathbf{2})_2$ together with DFT calculations on $(\mathbf{2})_2$ and selected simplified model systems allowed us to gain a comprehensive picture of the bonding situation in this molecule.[21,22] If we neglect those features of $(\mathbf{2})_2$ present only for practical reasons (that is, the four *t*Bu substituents and the bonds between the rings I/II and III/IV, which render the molecule sufficiently stable for isolation), we are essentially left with dimeric $(Ph_2BH)_2$ (Figure 1, top; phenyl rings marked in red). In contrast to all other structurally characterized diorganyl(hydro)boranes $(R_2BH)_2$ (including R = mesityl, C_6F_5),[14] $(\mathbf{2})_2$ does not establish the common structural motif $R_2B{-}(\mu\text{-}H)_2{-}BR_2$ but features only one B–H–B bond together with a B-B-bridging aryl ring. The two bridging $B{-}C_b$ bonds are significantly longer than the mean terminal $B{-}C_t$ bonds ($a = 1.786(3)$ Å, $b = 1.736(3)$ Å; c–$e = 1.569(3)$–$1.593(3)$ Å; see Figure 1, top). Interestingly, the B···B distance in $(\mathbf{2})_2$ is longer by only 0.025 Å compared to the doubly B–H–B-bridged congener $(\mathbf{2})_2^{A}$ (1.805(3) Å vs. 1.780(6) Å). As a first experimental indication of an essentially unperturbed π-electron system in the bridging ring I, we find no C–C bond length alternation.

Three borderline cases are conceivable as a rationale for the bonding situation within the B–C(aryl)–B fragment (Scheme 2). Case 1: C_b forms a σ bond to one B atom but acts as π donor toward the other. Such disparate interactions have been observed in dimeric alkynylalanes[15] and $[Et_3Si(toluene)]^+$.[16] Case 2: $(\mathbf{2})_2$ is a σ complex in which an sp^3-hybridized C_b forms two two-electron–two-center (2e2c) bonds with the B atoms. Ring I would act as four-electron donor and in turn abandon the cyclic conjugation of its π system (compare with the bonding in benzenium and bis(silyl)-substituted arenium ions[17]). Case 3: Ring I contributes a $C_b(sp^2)$ hybrid orbital and one electron pair to a $B{-}C_b{-}B$ 2e3c bond; the aromaticity of the π system remains largely unperturbed. As an example, the bonding situation in the higher homologue $(AlPh_3)_2$ has been classified as intermediate between cases 2 and 3.[18]

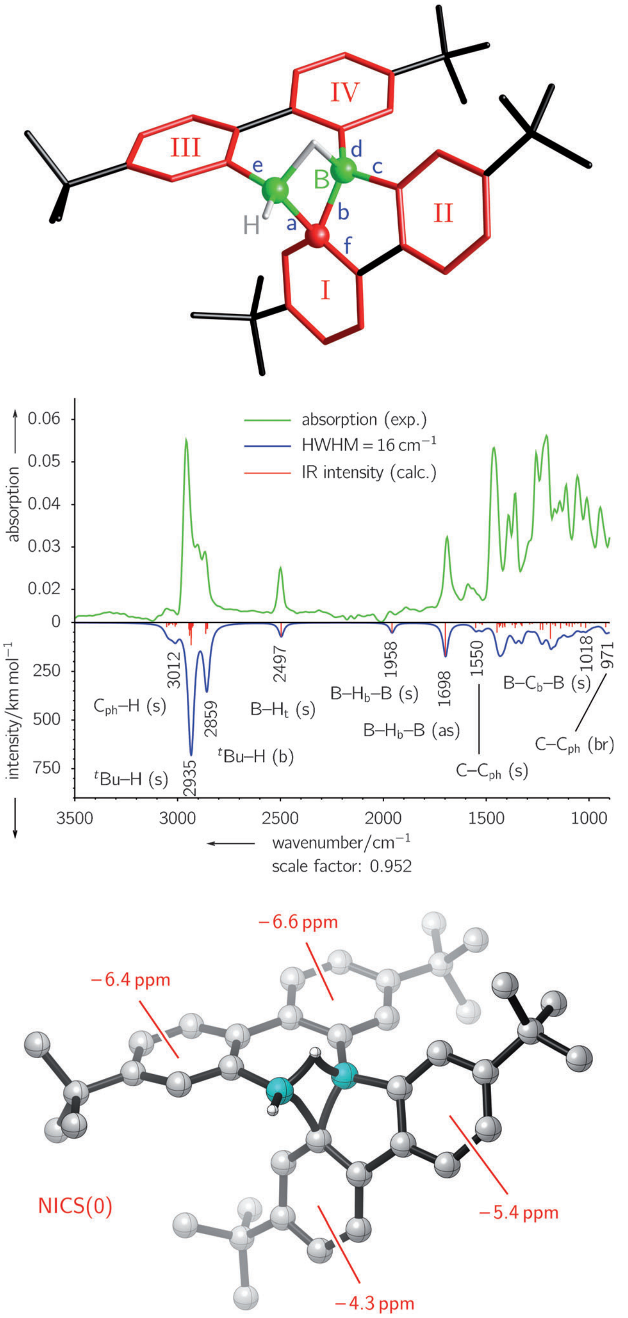
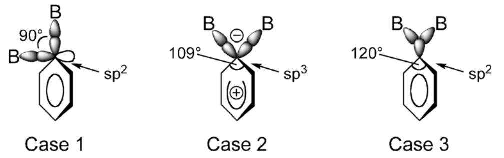


Figure 1. Experimental (top) and calculated (bottom) structures and IR spectra of $(\mathbf{2})_2$. The frequency values given in the lower half of the Figure correspond to the maxima of the Gaussian curve folded over the computed peaks at a half width at half maximum (HWHM) of 16 cm^{-1}. For the calculated structure, interatomic connectivities are represented by AIM bond paths.



Scheme 2. Illustration of the three conceivable borderline cases for the bonding situation within a B–C(phenyl)–B fragment.

For $(\mathbf{2})_2$, case 1 can be safely ruled out on structural grounds, because both B–C$_b$–COG angles are similar and none of them comes close to 90° (145.3°, 152.5°; COG = centroid of ring I). The distinction between cases 2 and 3 is more challenging and, in addition to the critical evaluation of experimental data, requires an explicit quantum-chemical treatment. Structural characteristics of case 2 (case 3) are the presence (absence) of a C–C bond-length alternation in the bridging phenyl ring together with a C–C$_b$–C angle close to 109.5° (120°). As mentioned above, we observe no systematic C–C bond-length alternation in I; the C–C$_b$–C angle amounts to 118.0(2)°. The latter structural parameter fits well to the sp^2 hybridization of C$_b$ obtained from natural localized molecular orbitals (NLMO) by natural bond orbital (NBO) analysis.[12] The NLMO analysis yields an optimized Lewis structure with a 2e3c bond for both the B–H–B and the B–C$_b$–B bridges, in line with corresponding Wiberg bond indices of 0.62 and 0.51. Being aware of the fact that bond lengths are not strictly correlated with bond strength, we recapitulate in this context that the average B–C$_b$ bond is longer by 0.18 Å than the average B–C$_t$ bond. The experimental and calculated geometries as well as the IR spectra are in faithful agreement, and a detailed analysis of relevant aromatic vibrational modes supports the equivalence of all four phenyl rings and thus further confirms the aromatic character of ring I (see Figure 1 and the Supporting Information for an assignment of selected bands). NMR characteristics of case 2 would be a marked shielding of C$_b$ accompanied by a deshielding of the *ortho*- and *para*-C atoms. In the present discussion, this criterion is of limited value because of the unsymmetrically substituted nature of ring I. However, calculations of nucleus-independent chemical shifts (NICS(0))[19] contribute a quantum-chemical NMR criterion confirming that the aromatic character of ring I (NICS(0) = −4.3 ppm) is only slightly more perturbed than in the cases of II–IV (−5.4 ppm to −6.6 ppm; Figure 1, bottom).

To characterize the bridging phenyl ring I in structure $(\mathbf{2})_2$ in more detail, we computed the benzenium cation and the $(PhBH_2)_2$ model system $(\mathbf{3})_2$ (Figure 2),[22] which comprises both a bridging as well as a terminal phenyl fragment for direct comparison.

In $(\mathbf{3})_2$ both phenyl rings also show clear NICS(0) diagnostics of aromaticity (bridging phenyl ring: −6.0 ppm; terminal ring: −7.3 ppm), which compare well with those of benzene (−8.2 ppm) and monomeric phenylborane (**3**; −6.9 ppm). In contrast, the computed NICS(0) value of the benzenium cation is close to zero (see the Supporting Information), as is to be expected for a nonaromatic molecule. Moreover, the C–C bond length alternation is quite pronounced in the computed benzenium cation structure (1.37–1.47 Å), whereas both phenyl rings in $(\mathbf{3})_2$ have C–C bonds of more or less equal length (1.39–1.40 Å in the terminal and 1.38–1.41 Å in the bridging phenyl fragment). The actual system $(\mathbf{2})_2$ shows the same features in this regard.

A natural bond orbital (NBO) analysis[12] of the wavefunction of $(\mathbf{3})_2$ reveals the same characteristics for the natural localized molecular orbitals (NLMOs) of the B–H–B and the B–C$_b$–B bridges (Figure 2a): They are represented by one

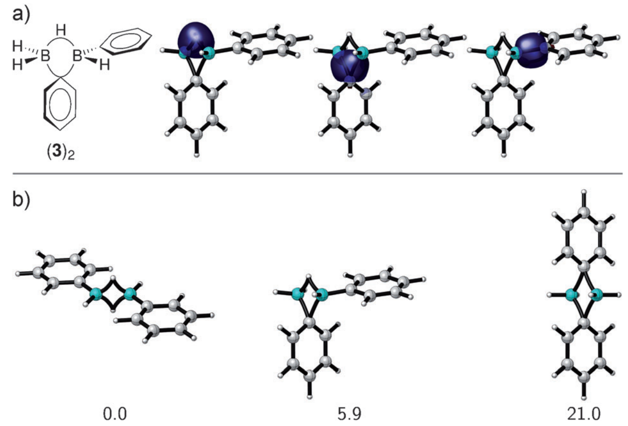


Figure 2. a) NLMO isosurfaces (B3LYP-D/def2-TZVP) illustrating the common properties of bridging and terminal B–C bonding in $(\mathbf{3})_2$ (plotted at an isovalue of $0.1\,a_0^{-3/2}$). b) Relative stabilities (ΔG in kcal mol^{-1}) of three different isomers of $(\mathbf{3})_2$, calculated at the coupled-cluster level of theory. Interatomic connectivities are represented by AIM bond paths.

single NLMO that matches a 2e3c bond in analogy to the NLMOs of B_2H_6. The B–C_t bond is instead clearly associated with a 2e2c σ-type NLMO. Furthermore, both phenyl rings carry three π-NLMOs, with all correspondent orbitals of the same shape (see the Supporting Information), which renders both phenyl rings equivalent. In clear contrast, the benzenium cation exhibits two distinct σ-NLMOs and only two π-NLMOs, which therefore favors an interpretation of the bonding in $(\mathbf{3})_2$ according to case 3, but not to case 2 (similar arguments hold for $(\mathbf{2})_2$; see the Supporting Information for a detailed discussion). According to an atoms-in-molecules (AIM) analysis[12] of the wavefunction of $(\mathbf{3})_2$, both boron centers possess distinct positive partial charges and all neighboring atoms bear similar negative charges of about −0.6 e. Conjointly, all remaining carbon centers of both phenyl fragments carry essentially no partial charge (as opposed to positive partial charges expected for a bridging phenyl ring in case 2). The two bridged units also share the common feature of curved AIM bond paths (as shown in the figures), which is indicative of 2e3c bonds.

We further examined the relative stabilities of terminally bound and bridged phenyl moieties in isomers of $(\mathbf{3})_2$ (Figure 2 b).[20] Unsurprisingly, the *trans* isomer with two terminal phenyl rings is lowest in energy. Moving one phenyl ring into a bridging position raises the corresponding isomer energy by merely 5.9 kcal mol^{-1}. Only if the second phenyl ring also adopts a bridging position, the bonding situation becomes prohibitively disfavored ($\Delta G = 21.0$ kcal mol^{-1}). The latter finding clearly carries Köster's early postulate,[7] which states that substituent scrambling does not occur for triorganylboranes, but that the presence of already one B–H–B bridge suffices to render the migration of organyl groups a viable process. When all of the experimental and theoretical evidence is taken together, the bridging phenyl ring of $(\mathbf{2})_2$ possesses a largely unperturbed π system and acts as a two-electron donor in a 2e3c bridge (case 3).

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[21] CCDC 899964 (**1**), 899965 ((**2**)$_2$), 899966 ((**2**)$_2^{A}$), and 899967 (**2**·py) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[22] The Supporting Information contains all experimental procedures, the ^{1}H and ^{13}C{^{1}H} NMR spectra of **1**, (**2**)$_2$, and (**2**)$_2^{A}$, details of the X-ray crystal structure analyses of **1**, (**2**)$_2$, (**2**)$_2^{A}$, and **2**·py, as well as computational details of the molecular properties of (**2**)$_2$, (**3**)$_2$, **3**, the benzenium cation, benzene, and diborane, together with the optimized molecular geometries, including (**2**)$_2^{A}$ and TS((**2**)$_2$→(**2**)$_2^{A}$).