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A Deceiving X-ray Single-Crystal Structure Determination: Amino-Hydrogen Exchange in Amino-alkynylboranes and ab initio Investigations of Alkynylboranes, Borirenes, and Boraallenes

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Dimeric(dimethylamino)(phenylethynyl)borane $(\mathbf{2})_2$ is formed by the reaction of bis(dimethylamino)(phenylethynyl)borane (**1**) with 9-BBN-H. An X-ray single-crystal diffraction study revealed a central B_2N_2 four-membered ring for $(\mathbf{2})_2$ with both alkynyl groups pointing to the same side in a *cisoid* arrangement. However, solution and solid-state NMR as well as ab initio calculations on model compounds show that the *cis* arrangement in the crystal chosen for X-ray diffraction is *not* representative of the bulk material, which consists of both *cis* and *trans* isomers. Further investigations of the competition between hydrogen-amino group exchange and hydroboration in the reaction of amino-alkynylboranes with hydroborating agents (9-BBN-H and catB-H) show the exchange to be much faster even in the presence of Wilkinson's catalyst and with cyclic amino-alkynylboranes such as 1,3-dimethyl-2-[(trimethylsilyl)ethynyl]-1,3,2-diazaborolidine (**3**). Ab initio calculations on alkynylboranes **I**, borirenes **II**, and boraallenes **III**, which are all geometrical isomers, show alkynylboranes to be the most stable isomers only if strongly π-donating groups X (X = NH_2, F) are attached to the boron atom. In any case, boraallenes are highest in energy.

The relative stability of classically bonded B–C compounds and their multicentre-bonded carborane isomers is strongly dependent on the electronic nature of the substituents at the boron atoms. For instance, whereas 1,4-difluoro-1,4-diboracyclohexa-2,5-diene (with π-donating fluorine atoms attached to the boron centres) retains the six-membered ring structure[2], 1,4-diboracyclohexa-2,5-diene itself rearranges to the *nido*-tetracarbadiborane $B_2C_4H_6$[3,4]. Possible mechanisms for this rearrangement have been suggested by Schleyer et al. on the basis of ab initio calculations[5]. When investigating the double hydroboration of dialkyl-alkynylboranes with dialkylboranes, Köster and coworkers found no borylated alkanes, but 1,5-dicarba-*closo*-pentaboranes(5) instead as the only products of the reaction[6]. This suggests that the classically bonded isomers are less stable than their corresponding multicentre-bonded isomers in the absence of π-donating groups at the boron centres. Since amino groups are especially effective π donors with respect to boron atoms, we were interested in the physical and chemical properties of amino-alkynylboranes[7–9] and in particular the competition between hydroboration of the C≡C bond and hydrogen-amino group exchange when amino-alkynylboranes were allowed to react with hydroborating agents. Furthermore, on the basis of ab initio calculations the factors responsible for the relative stability of alkynylboranes (**I**) and their isomeric borirenes (**II**) and boraallenes (**III**) are studied.

The reaction of 9-borabicyclo[3.3.1]nonane (9-BBN-H) with bis(dimethylamino)(phenylethynyl)borane (**1**) in THF at room temperature was monitored by ^{11}B-NMR spectroscopy. After 15 minutes, two new signals at δ = 47.2 and 29.6 were recorded (intensity 1:1). 16 h later, the signal at δ = 29.6 had vanished with the appearance of a new signal at δ = 0.5. Workup of the reaction mixture gave 9-BBN-NMe_2 ($\delta^{11}B$ = 47.2), which could be isolated by distillation, and dimeric (dimethylamino)(phenylethynyl)borane $(\mathbf{2})_2$ which was obtained from the residue by crystallisation from pentane (Eq. 1). Thus, instead of hydroboration a dimethylamino group-hydrogen exchange proceeded exclusively. An analogous amino group-hydrogen exchange reaction occrurred also between catecholborane and **1** [although somewhat slower, after 16 h only half of the catecholborane (catB–H) had been transformed into *B*-(dimethylamino)catecholborane]. The lack of hydroboration of the C≡C bond of **1** cannot be attributed to steric factors as the sterically less demanding bis(dimethylamino)propynylborane reacted in the same manner as **1**. It is well-known[10–13] that transition metal catalysts may increase the rate of hydroboration reactions considerably. But even when the above reactions were carried out in benzene in the presence of a small amount of Wilkinson's catalyst $Rh(PPh_3)_3Cl$, no alkenyl-

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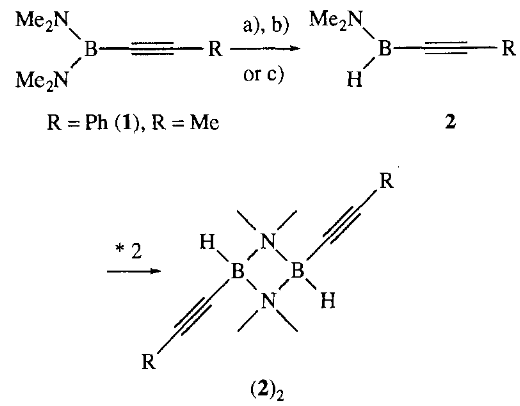
boranes could be detected by NMR spectroscopy (1). There was no difference at all in the NMR spectra from the reactions run with or without the rhodium catalyst.

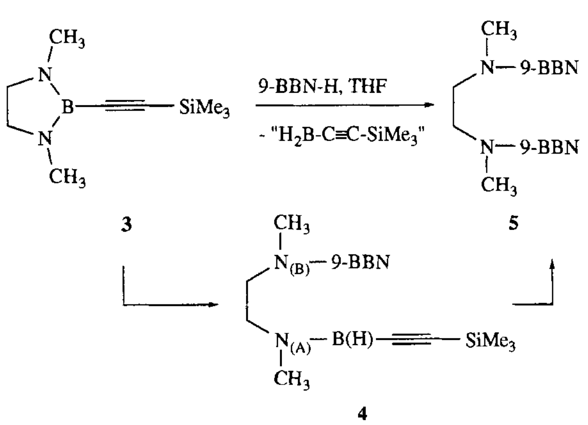


(1)

a) 9-BBN-H, THF, $-$9-BBN-NMe$_2$ (R = Ph, Me)
b) catB-H, THF, $-$catB-NMe$_2$ (R = Ph)
c) catB-H, Rh(PPh$_3$)$_3$Cl (5 mol%), C$_6$H$_6$, $-$catB-NMe$_2$ (R = Ph)

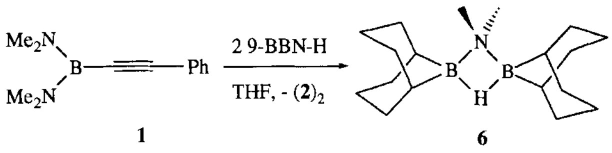
Since the five-membered ring in 1,3,2-diazaborolidines is often more stable than the corresponding bis(dimethylamino) derivatives[14] it was hoped that 1,3-dimethyl-2-[(trimethylsilyl)ethynyl]-1,3,2-diazaborolidine (3) might withstand ring opening and hence resist hydrogen-amino group exchange. Indeed, a ^{11}B-NMR spectrum of 3 mixed with 9-BBN-H (1:1) in THF showed only two signals at $\delta = 47.5$ (broad) and 23.7 (ratio 3:1) after 3 h. While the signal at $\delta = 23.7$ is attributable to unreacted 3, the hitherto unknown 1,2-bis[(9-borabicyclo[3.3.1]nonanyl)methylamino]ethane (5) (δ^{11}B = 47.9) could be isolated from the reaction mixture as colourless crystals (Eq. 2). This result does indeed prove the relative stability of the diazaborolidine ring system – although in an unexpected fashion: Once the five-membered ring is opened by attack of the first 9-BBN-H, amino group-hydrogen exchange at the remaining amino group (A) at the boron atom in the assumed intermediate 4 to yield 5 is apparently much faster than the B–N bond breaking reaction which would open the five-membered ring. As only one equivalent of 9-BBN-H was added, half the amount of 3 remained unchanged. There is no spectroscopic evidence of the suggested intermediate 4, nor could [(trimethylsilyl)ethynyl]borane H$_2$B–C≡C–SiMe$_3$ be detected. After removal of THF, 3, and 5 from the reaction mixture and methanolysis, the yellow waxy residue showed a ^{11}B-NMR signal at $\delta = 18.2$ attributed to B(OMe)$_3$[15]. This proves that the residue still contained boron. An elemental analysis was inconclusive due to varying amounts of THF which could not be fully removed, and neither an infrared nor a mass spectrum of the residue yielded further information on its nature.

By adding 9-BBN-H to 1 in a 2:1 molar ratio we hoped to achieve hydroboration of the C≡C triple bond in 2 with the second equivalent of 9-BBN-H. Instead, in addition to (2)$_2$ the µ-amino-diborane(6) derivative 6 is formed (Eq. 3).



(2)

Addition of catB–H to a solution of (2)$_2$ in THF or benzene (with and without Wilkinson's catalyst) led to a yellow waxy residue similar in appearance to that described for the reaction of 3 with 9-BBN-H (vide supra, Eq. 2) and to catB–NMe$_2$ (δ^{11}B = 26.4)[15], which was the only product to be isolated from the reaction mixture. Although the most obvious pathway for the Me$_2$N-hydrogen exchange in (2)$_2$ seems to be a dissociation of the B–N four-membered ring followed by attack of the borane at the Me$_2$N group and substituent exchange, no cleavage of the B–N ring in (2)$_2$ could be achieved by addition of an excess of *N,N,N',N'*-tetramethylethylenediamine (TMEDA) or trimethylphosphane to a solution of (2)$_2$ in benzene as evidenced by ^{11}B-NMR spectroscopy. Even in the presence of Wilkinson's catalyst, (2)$_2$, which could be a hydroborating agent in its own right, remained unchanged for several days at room temperature (sealed NMR tube, C$_6$D$_6$). However, heating the same sample to 60 °C for 24 h led to a complex mixture of products (^{1}H-, ^{11}B-, and ^{13}C-NMR analysis).



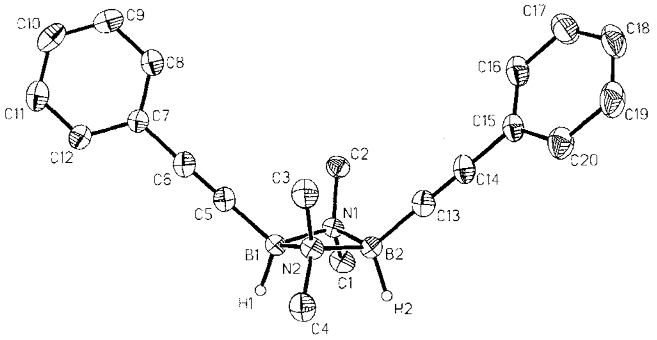
(3)

Spectroscopic Data and Solid State Structures of (2)$_2$ and 6

The dimeric nature of (2)$_2$ can clearly be deduced from mass spectroscopic data. The molecular ion, which loses a hydrogen atom, a methyl, or a phenyl group on fragmentation, is readily recognised. The most abundant ion, however, is the molecular ion 2$^+$, which demonstrates the high stability of monomeric Me$_2$NB(H)C≡C–Ph. In solution, ^{1}H- as well as ^{13}C-NMR data for the dimethylamino groups disclose the presence of both *cis* and *trans* isomers, although for the phenyl region shift differences for the two isomers are only detectable in the ^{1}H-NMR spectrum. In monomeric 2 the coupling constant $^1J_{\mathrm{BH}} = 133$ Hz is larger than expected for an amino-alkylborane and even larger than in bis(amino)boranes [e.g. Me(Me$_2$N)BH: $^1J_{\mathrm{BH}} = 120$, (Me$_2$N)$_2$BH: $^1J_{\mathrm{BH}} = 126$ Hz][15], indicative of the comparable electronegativity of N(sp^2) and C(sp).

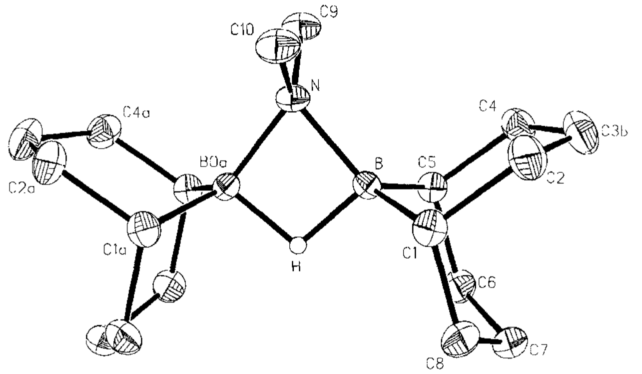
In order to get more information on the molecular structure of (2)$_2$, an X-ray structure determination was performed. The result is presented in Figure 1. The most striking feature is the *cisoid* arrangement of the alkynyl groups, resulting in an almost C_{2v} symmetrical molecule with a folding angle of 13.8° at B1B2 of the B_2N_2 ring. All B−N and N−C bond lengths are comparable to those observed for $[X_2B-NMe_2]_2$ molecules, where X = H[16], F[17], Cl[18]. Little if any significant changes in the C≡C bond lengths are observed when comparing alkynylboranes with three-coordinate boron atoms (1.20 to 1.22 Å)[8,9,19–23], **(2)**$_2$ [1.196(6) and 1.200(7) Å] and a borate anion as in $Ph_3B-C{\equiv}C-PR_3$ [1.216(5) Å][24], thus indicating that any boron-carbon π interaction is too weak to cause substantial changes in bond lengths. We attribute the remarkable lengthening of the B−C(alkyne) bond in the same series [about 1.53 to 1.559(7)/1.547(7) to 1.593(5) Å] to rehybridisation (sp^2 to sp^3) and increased negative charge on the boron atom rather than B−C double bonding. Ab initio calculations on the model compound $[(H_2N)_2B-C{\equiv}C-H]_2$ show the energy difference between the *cis* and *trans* form (C_{2v} and C_{2h}, respectively) to be only 0.1 kcal/mol (MP2/6-31G*//6-31G*). Furthermore, the geometrical parameters (i.e. bond lengths and angles) of both isomers as given by the ab initio calculations are almost identical. Prolonged heating of a solution of **(2)**$_2$ in C_6D_6 lead only to decomposition without any change in the ratio of the two isomers, and this would be compatible with the negligible difference of their heats of formation. Finally, a solid-state ^{13}C-CPMAS NMR confirmed that the bulk material in the solid state contained both isomers in roughly the same ratio as in solution. It hence appears that the crystal chosen for X-ray diffraction was *not* representative of the bulk sample.

Figure 1. ORTEP plot of **(2)**$_2$, thermal ellipsoids at 25% probability, most H atoms omitted for clarity. Selected bond lengths [Å] and angles [deg]: B1−H1 1.10(3), B2−H2 1.10(3), B1−N1 1.612(6), B2−N1 1.608(6), B1−N2 1.604(6), B2−N2 1.608(6), B1−C5 1.559(7), B2−C13 1.547(7) ,C5−C6 1.196(6), C13−C14 1.200(7), C6−C7 1.442(6), C14−C15 1.439(7); H1−B1−C5 114(2), H2−B2−C13 111(2), B1−N1−B2 85.9(3), B1−N2−B2 86.2(3), N1−B1−N2 92.3(3), N1−B2−N2 92.2(3), B1−C5−C6 177.3(4), B2−C13−C14 176.9(5), C5−C6−C7 177.5(5), C13−C14−C15 178.5(5)[41]



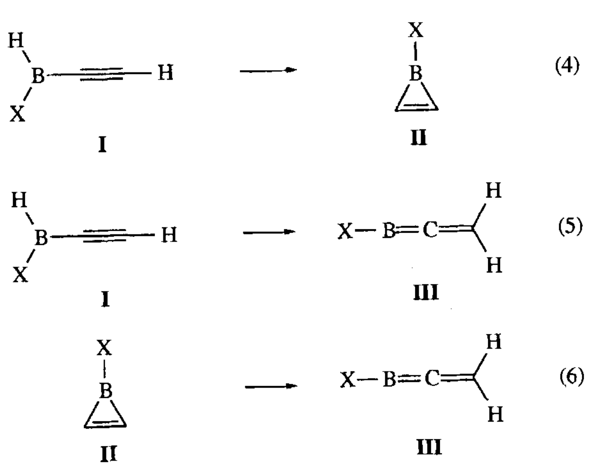
Although the constitution of the μ-amino-diborane **6** can be deduced from its analytical data we performed an X-ray structural analysis in order to obtain more detailed information on its molecular geometry. The result is shown in Figure 2. The molecule has almost C_{2v} symmetry with a crystallographic mirror plane passing through C9, C10, N, and H. A disorder in the 9-BBN ring could be resolved by splitting the positions of C3, the main conformer (70%, as shown in Figure 2) having C3 bent towards the B−B axis, the second conformer (30%) with C3 bent away from the B−B axis. As expected, the B−B distance [1.976(5) Å] is about 15% longer than in diborane(4) compounds with a two-centre two-electron B−B bond[21,25–27] (B−B: 1.77 Å in B_2H_6[28]). The B−N bond length in **6** is only slightly shorter than in **(2)**$_2$ [1.591(3) Å in **6**, 1.608(6) and 1.612(6) Å in **(2)**$_2$] but the difference in the B−H bond lengths in **(2)**$_2$ [1.10(3) Å] and **6** [1.25(3) Å] nicely reflects the different nature of the hydrogen atoms in both compounds [bridging in **6**, terminal in **(2)**$_2$].

Figure 2. ORTEP plot of **6** (main conformer only, see text), thermal ellipsoids at 25% probability, most H atoms omitted for clarity. Selected bond lengths [Å] and angles [deg]: B−H 1.25(3), B−B 1.976(5), B−N 1.591(3); C1−B−C5 109.0(2), N−B−H 90(2), B−N−B 76.7(2), B−H−B 104(4), C9−N−C10 108.7(3)[41]



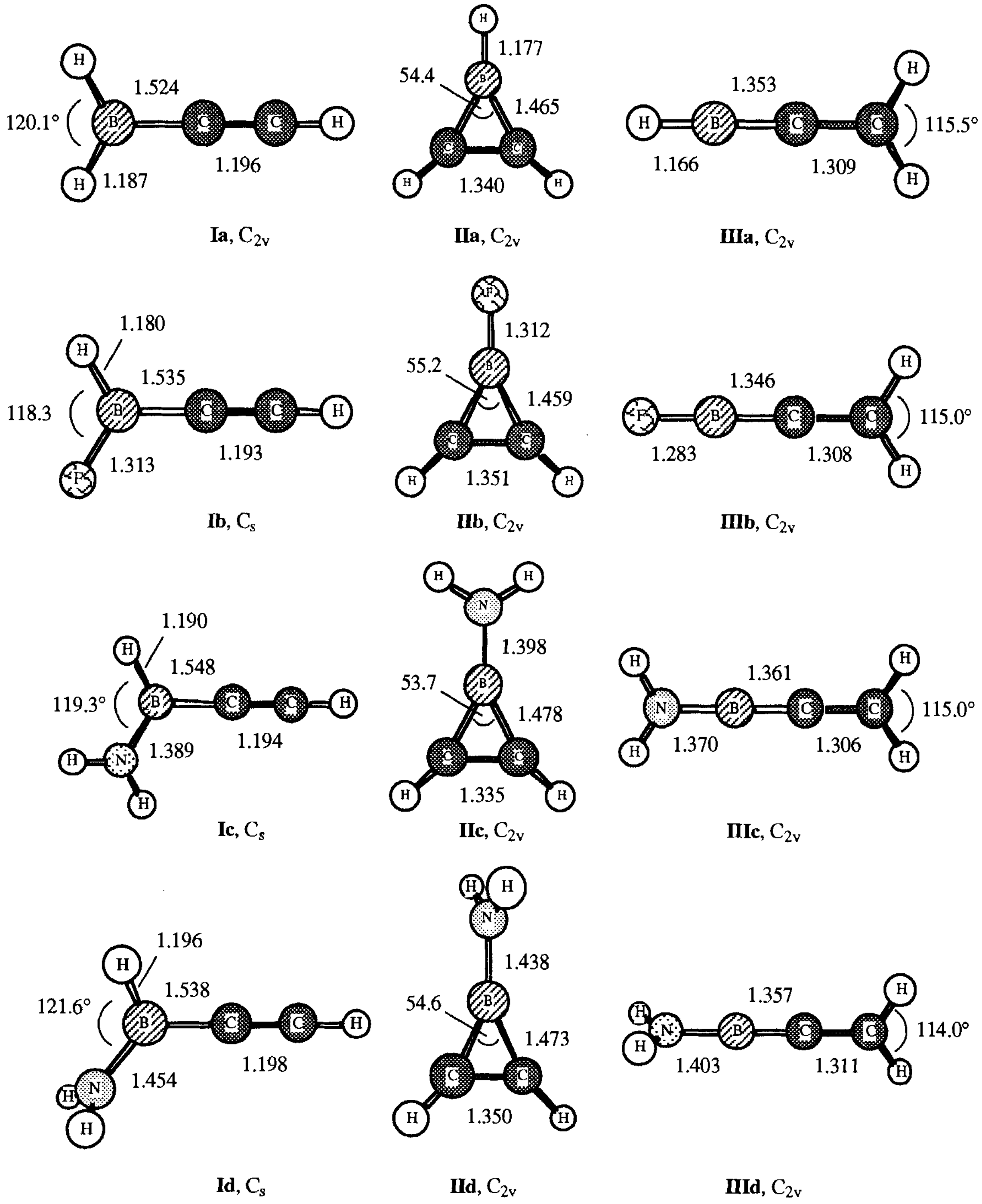
Ab initio Calculations on the Alkynylborane − Borirene Rearrangement

The three-membered borirenes (**II**) are geometrical isomers of alkynylboranes (**I**), and Eisch and coworkers showed that an alkynylborane − borirene rearrangement could be induced photochemically[20]. Whereas spectroscopic and structural investigations as well as ab initio calculations (vide infra) provide evidence that alkynylboranes are best described by classical formulae (i.e. B−C single and C≡C bond) without much electron delocalisation, borirenes may be formally envisaged as three-vertex *closo*-carboranes



X = H (**a**), F (**b**), NH_2(i) (in plane, **c**), NH_2(o) (orthogonal, **d**) with 8 ($2n + 2$, n = number of vertextes, in this case n = 3) core electrons[29,30]. We therefore decided to investigate further the factors influencing the stability of either isomers by quantum-chemical methods. Included in this comparison were also the isomeric boraallenes $H_2C{=}C{=}B{-}X$ (**III**)[31].

Figure 3. Calculated geometries of **Ia**–**IIId** (RHF/6-31G*) with the imposed symmetry restrictions



Ia, C_{2v} **IIa**, C_{2v} **IIIa**, C_{2v}

Ib, C_s **IIb**, C_{2v} **IIIb**, C_{2v}

Ic, C_s **IIc**, C_{2v} **IIIc**, C_{2v}

Id, C_s **IId**, C_{2v} **IIId**, C_{2v}

The structures of a series of alkynylboranes $X(H)B{-}C{\equiv}C{-}H$ **Ia** to **Id**, their isomeric borirenes $XB(CH)_2$ **IIa** to **IId**, and boraallenes $H_2C{=}C{=}B{-}X$ **IIIa** to **IIId** were optimised at the 6-31G* level of theory and their energies evaluated with the inclusion of electron correlation (Møller-Pleset) up to fourth order (MP4SDTQ/6-31G*//6-31G*) and corrected for zero point energy (zpe) [X = H (**a**), F (**b**), NH_2 in plane (**c**) and NH_2 orthogonal (**d**) to the plane around the boron atom]. Geometrical details are presented in Figure 3. All structures represent local minima on the energy surface as confirmed by vibrational analysis, except those with orthogonal NH_2 groups. These

Table 1. Calculated energies of **Ia**−**IIId** (au, MP4SDTQ/6-31G*//RHF/6-31G*) and zero point energy zpe (kcal/mol) in parentheses

	I	II	III
a	-102.4428751 (25.95)	-102.4573144 (28.14)	-102.4136906 (27.18)
b	-201.5448068 (23.05)	-201.5440591 (24.67)	-201.4953744 (23.75)
c	-157.7157149 (39.82)	-157.705175 (40.73)	-157.6718149 (40.30)
d	-157.6584742 (37.19)	-157.6741603 (39.14)	-157.6364808 (38.25)

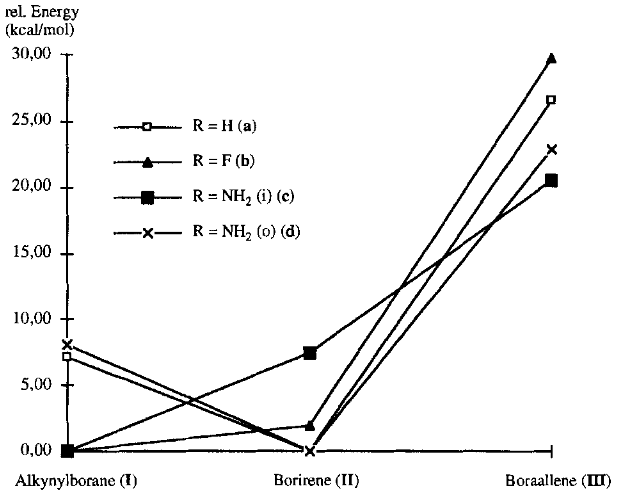
have two negative frequencies corresponding to pyramidalisation of the nitrogen atom and rotation of the NH_2 group into the plane around the boron atom.

In **Ia**−**d** very little changes of either the B−C or the C≡C bond lengths are calculated, again indicating little if any π interaction. However, in borirenes **IIb** and **IIc** there is a strong competition between X−B π bonding and interaction of the empty orbital at the boron atom with the π system of the double bond (hereafter denoted C→B π interaction). This not only lengthens the B−N bond (**IIc**) but is also apparent in the distance between the boron atom and the centre of the double bond only in **IIc** (1.32 Å) and **IId** (1.31 Å), whereas – contrary to expectation – the boron atom in **IIb** (1.30 Å) is *further* away from the double bond than in **IIa** (1.29 Å). This suggests that the geometrical changes in the H and F derivatives **a** and **b** are caused by overlapping σ and π effects, which are difficult to separate[32]. For a proper comparison, the pair NH_2(i)/NH_2(o) with the same electronegativity seemed more appropriate.

The rotation barrier about the B−N bond provides another means of investigating a concurring C→B π interaction. These are indeed in borirenes **IIc** and **IId** much smaller than in alkynylboranes **Ic**/**Id** (18.0 and 33.5 kcal/mol, respectively) because of the competition between C→B and N→B π donation in the planar isomer of **II**. Not unexpectedly, the value of 20.3 kcal/mol for boraallenes **IIIc**/**IIId** is smaller than the 33.5 kcal/mol for the corresponding amino-methyl-boranes $H(H_2N)BCH_3$ **IVc** and **IVd** (MP4SDTQ/6-31G*//RHF/6-31G*). In our eyes, this again proves that there is very little if any B−C≡C π interaction in alkynylboranes as long as there are strongly π-donating substituents attached to the boron atom. In fact, although the boron atom in alkynylboranes is closer to the C≡C π system, the B−C=C π interaction in vinylboranes is estimated to be more substantial than in alkynylboranes (ca. 4 kcal/mol)[33].

The energies for the rearrangement reactions (4)−(6) are represented graphically in Figure 4. Most noteworthy, strongly π-donating substituents at the boron atom stabilise the alkynylborane with respect to the borirene. Thus, for X = F (**b**) and NH_2(i) (**c**) reaction (4) is endothermic (1.9 and 7.4 kcal/mol), but for X = H (**a**) and NH_2(o) (**d**) exothermic (−7.1 and −8.1 kcal/mol, respectively). In all cases, the boraallenes (**III**) are highest in energy. Finally, the shortening of the B−X bond in boraallenes **III** (sp-hybridised boron atom) as compared to **I** and **II** (sp^2-hybridised boron atom) by about 3 pm compares favourably to the value derived from X-ray crystallography in our recent studies[8,27].

Figure 4. Graphical representation of the relative stability of **Ia**−**IIId** (kcal/mol, at MP4SDTQ/6-31G*//RHF/6-31G* + zpe)



This work shows that amino group-hydrogen exchange in amino-alkynyl-boranes is much faster than even transition metal-catalysed hydroboration of the triple bond. Spectroscopic data as well as reactivity studies hold strong evidence that the alkynyl moiety is a strongly electron-withdrawing ligand to the boron atom without much π-donating abilities. This view, which is to some extent in contrast to earlier work[22,34−37], is supported by ab initio calculations on the structure and relative stability of alkynylboranes, borirenes, and boraallenes. A more comprehensive study of the orbital situation in alkynylboranes including MO calculations and photoelectron spectroscopy is in preparation.

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Experimental

All manipulations described were carried out under dry nitrogen in Schlenk glassware that was dried in vacuo. Solvents were made anhydrous by standard procedures, distilled and stored under nitrogen. Chemicals: $(Me_2N)_2BC{\equiv}CPh$[38], 2-chloro-1,3-dimethyl-1,3,2-diazaborolidine[39], catB-H (1 M in THF, Aldrich), 9-BBN-H, $Me_3SiC{\equiv}CH$ (Fluka), *n*BuLi (1.6 M in hexane, Chemetall). – NMR: Jeol EX 400 (^1H, ^{13}C; Me_4Si or internal C_6D_6 or $CDCl_3$ as secondary standards), Jeol GX 270 (^{27}Si; ext. Me_4Si), Bruker AC-P 200 (^{11}B; ext. $BF_3 \cdot OEt_2$), Bruker 300 (solid state, 5500 Hz spinner frequency). A positive sign indicates a downfield shift relative to the standard. – IR: Varian FT IR spectrometer. – MS: Varian ATLAS CH7 (EI, 70 eV). – Elemental analyses: Microanalytical laboratory of the institute. – Melting points (uncorrected) were measured in sealed glass capillaries under nitrogen. – *Computational details:* All calculations were carried out with a CRAY Y-MP8 computer with the Gaussian 92 program[40]. Equilibrium geometries were computed within the restricted Hartree-Fock (RHF) approach on the split-valence d-polarised 6-31G* basis set. Symmetry restrictions were imposed as shown in Figure 3. Minima on the potential hypersurface were verified by analysis of the harmonic vibrational frequencies at the RHF/6-31G* level. Final electronic energies were obtained by single-point calculations including electron correlation at the MP4SDTQ level with the optimised 6-31G* geometries (MP4SDTQ/6-31G*//RHF/6-31G*). Zero point energies were multiplied by 0.89 to correct for anharmonicity and these zero-point vibrational contributions were included in all energy data.

Dimeric (Dimethylamino)(phenylethynyl)borane **(2)**$_2$: A solution of 9-BBN-H (1.12 g, 9.2 mmol) in 15 ml of THF was added to bis(dimethylamino)(phenylethynyl)borane (**1**) (2.0 ml, 2.0 g, 10 mmol) at ambient temp. After stirring for 14 h all volatile components were removed in vacuo, the residue was dissolved in pentane and the clear, colourless solution was cooled to −78 °C. White crystals of **(2)**$_2$ precipitated and were isolated by decanting the solvent and then dried in vacuo (0.59 g, 3.8 mmol, 75%). From the decanted solution pentane was removed by distillation leaving behind a clear, colourless liquid, from which 9-BBN-NMe$_2$ (0.47 g, 2.9 mmol) was condensed into a trap (cooled to −78 °C) at 32 °C (10^{-2} Torr). **(2)**$_2$: m.p. 99 °C. – ^{1}H NMR (C_6D_6): δ = 7.54–7.49 [m (pseudo-t), 4H, H_m], 7.06–6.97 [m (2 pseudo-t), 6H, $H_{o,p}$], 3.3 (q, $^1J_{BH}$ = 80 Hz), 2.53 (s, 3H), 2.41 (s, 6H), 2.25 (s, 3H). – ^{11}B NMR (C_6D_6): δ = 0.5 (d, $^1J_{BH}$ = 80.8 Hz). – ^{13}C NMR (C_6D_6): δ = 132.0, 131.9 (C_p), 128.5, 125.6 (C_i), 104.0, 103.1, 51.3, 48.7, 44.8. – ^{13}C CPMAS NMR: δ = 134.3, 132.1, 130.5, 129.3, 125.1, 124.3, 103.8 (br, C_β), 95 (br, C_α), 94 (br, C_α), 53.0, 49.8, 45.2. – IR ($\tilde{\nu}$, cm^{-1}): 2422.0 (st), 2190.0 (st). – MS, *m/z* (%): 314 (17) [$M^{+\cdot}$], 313 (18) [$M^{+\cdot}$ − H], 298 (19) [313 − CH_3, m* = 283.7], 237 (6) [$M^{+\cdot}$ − Ph], 157 (100) [$M^{+\cdot}$/2], 156 (89) [157 − H], 142 (28) [157 − CH_3]. – $C_{20}H_{24}B_2N_2$ (314.05): calcd. C 76.49, H 7.70, N 8.92; found C 75.67, H 7.72, N 8.81.

Crystal Structure Determination of **(2)**$_2$: Crystal size 0.2 × 0.2 × 0.4 mm^3, orthorhombic space group *Pbca*, a = 11.518(4), b = 11.974(9), c = 28.40(2) Å, V = 3916(4) Å^3, Z = 8 for $C_{20}H_{24}B_2N_2$ (314.05 g/mol) and ρ_{calc} = 1.065 Mg/m^3. Data collection was carried out with a Siemens-Nicolet R3m/V four-circle diffractometer by using Mo-K_α radiation (graphite monochromator) at 193 K. 2 check reflections were measured after every 48 intensity measurements and did not change significantly during data collection. With ω scans, 0.74° scan width, 2Θ = 3° to 48° and scan speed 1.5 to 29.3°/min in ω, 3491 reflections were collected in h, $\pm k$, $\pm l$, of which 3073 were independent and 1676 considered observed [$F > 3.0\sigma(F)$]. The structure was solved by direct methods, and full-matrix least-squares refinement on $\Sigma w(|F_o| - |F_c|)^2$ converged at a final R = 7.41%, R_w = 6.78% with $w^{-1} = \sigma^2(F) + 0.0004F^2$ (all hydrogen atoms were found but refined as riding model with fixed isotropic U, except H1 and H2, which were refined isotropically in free positions, all other atoms were refined anisotropically), 225 parameters refined, data:parameter ratio = 7.4:1. GOOF 1.58. The remaining difference Fourier analysis was featureless (0.24/−0.23 eÅ^3)[41].

μ-9-(Dimethylamino)-(9-borabicyclo[3.3.1]nonan-9-yl)-9-borabicyclo[3.3.1]nonane (**6**): Borane **1** (2.0 ml, 2.0 g, 10 mmol) in 10 ml of THF was allowed to react with 9-BBN-H (2.45 g, 22 mmol) in 35 ml of THF at ambient temp. After 1 h all volatile components were removed in vacuo from the clear, yellow solution. The nonvolatile residue was dissolved in 5 ml of toluene and the solution cooled to −78 °C. After filtration **6** was isolated as clear colourless rhombic crystals (0.1 g, 0.35 mmol). No effort was made to isolate further **6** from the remaining toluene solution. M.p. 75–77 °C (gas evolution). – ^{1}H NMR (C_6D_6): δ = 2.05 (s, 6H), 2.0–1.25 (several m, 25H), 0.83 (m, 4H). – ^{11}B NMR (C_6D_6): δ = −2.7. – ^{13}C NMR (C_6D_6): δ = 39.9 (NCH_3), 35.9, 30.5 ($CH-CH_2$), 24.4, 22.7 (CH_2), 20 (b, BCH). – IR ($\tilde{\nu}$, cm^{-1}): 1673.9 (m), 1653.9 (sh), 935 (s), 636.6 (s). – MS, *m/z* (%): 287 (14) [$M^{+\cdot}$], 167 (100) [$M^{+\cdot}$ − 9-BBN + H], 124 (53) [167 − 43]. – $C_{18}H_{35}B_2N$ (287.1): calcd. C 75.30, H 12.29, N 4.88; found C 74.62, H 12.29, N 5.54.

Crystal Structure Determination of **6**: Crystal size 0.3 × 0.3 × 0.2 mm^3, monoclinic space group $P2_1/m$, a = 6.594(3), b = 19.269(6), c = 7.429(2) Å, β = 113.26(2)°, V = 867.2(5) Å^3, Z = 4 for $C_{18}H_{35}B_2N$ (287.1 g/mol) and ρ_{calc} = 1.099 Mg/m^3. Data collection was carried out with a Siemens-Nicolet R3m/V four-circle diffractometer by using Mo-K_α radiation (graphite monochromator) at 293 K. 2 check reflections were measured after every 48 intensity measurements and did not change significantly during data collection. With ω scans, 0.8° scan width, 2Θ = 3° to 49° and scan speed 1.5 to 29.3°/min in ω, 1525 reflections were collected in $-h$, k, $+l$ $-l$, of which 1500 were independent (R_{int} = 0.0843). The structure was solved by direct methods and full-matrix least-squares refinement on F^2 (SHELXL 93) and converged at a final R_1 = 6.68% [$F > 4.0\sigma(F)$], wR_2 = 19.80% (all data) with $w^{-1} = \sigma^2F_o^2 + (0.0993P)^2 + 0.3203P$, where $P = (F_o^2 + 2F_c^2)/3$ (all hydrogen atoms were refined as riding on the C atoms with fixed isotropic U, $U_H \approx 1.2 \cdot U_C$, all other atoms were considered anisotropic), 111 parameters refined, data:parameter ratio = 13.5:1. GOOF on F^2 = 1.085. A disorder in one of the borabicyclonane rings (C3) could be resolved, and the two conformers were refined with a 70:30 occupancy. The remaining difference Fourier analysis was featureless (0.24/−0.23 eÅ^3)[41].

1,3-Dimethyl-2-[(trimethylsilyl)ethynyl]-1,3,2-diazaborolidine (**3**): (Trimethylsilyl)ethyne (2.76 ml, 1.97 g, 20 mmol), dissolved in 30 ml of hexane, was lithiated at 0 °C with *n*BuLi (12.64 ml, 20 mmol) in hexane (1.58 M solution). Stirring for 14 h at room temp. and for 2 h at reflux was followed by addition of 2-chloro-1,3-dimethyl-1,3,2-diazaborolidine (2.64 ml, 20 mmol) in 10 ml of hexane at −30 °C. After stirring for 14 h at room temp. all insoluble material was removed under nitrogen, and all volatile components were removed from the clear, colourless filtrate under reduced pressure. Distillation of the liquid residue at 40 °C (10^{-2} Torr) yielded 1.98 g of **3** (10.2 mmol, 51%). From the distillation residue, a small amount (<1 mmol) of bis(1,3-dimethyl-1,3,2-diazaborolidin-2-yl)ethyne[42] was isolated by sublimation at 100 °C (10^{-3} Torr), m.p. 104 °C. – **3**: ^{1}H NMR ($CDCl_3$): δ = 3.12 (s, 4H), 2.65 (s, 6H), 0.17 (s, 9H, $^1J_{CH}$ = 120, $^2J_{SiH}$ = 7.3 Hz). – ^{11}B NMR ($CDCl_3$): δ = 23.5. – ^{13}C NMR ($CDCl_3$): δ = 112.6, 106 (b, $^1J_{BC}$ ≤ 110 Hz), 51.5, 34.2, −0.1 ($^1J_{SiC}$ = 56.4 Hz). – ^{29}Si ($CDCl_3$): δ = −18.4. – Raman ($\tilde{\nu}$, cm^{-1}) = 2143.9. – MS, *m/z* (%): 194 (100) [$M^{+\cdot}$], 179 (31) [$M^{+\cdot}$ − CH_3], 121 (6) [$M^{+\cdot}$ − $SiMe_3$], 83 (95). – $C_9H_{19}BN_2Si$ (194.2): calcd. C 55.70, H 9.87, N 14.43; found C 54.78, H 9.99, N 14.28.

N,N'-Bis(9-borabicyclo[3.3.1]non-9-yl)-N,N'-dimethylethylenediamine (**5**): 9-BBN-H (0.24 g, 2.0 mmol) in THF was added at ambient temp. to a solution of **3** (0.39 ml, 0.39 g, 2.0 mmol) in 10 ml of THF. Some gas evolution was observed while the reaction mixture turned yellow. No 9-BBN-H was detectable by ^{11}B-NMR spectroscopy after 1 h. Since the ^{11}B-NMR spectrum remained unchanged after stirring at ambient temp. for 14 h, the volume of the reaction mixture was reduced to 3 ml at 200 Torr. Then the mixture was cooled to −78 °C. Colourless crystals of **5** were isolated after 24 h, m.p. 110 °C. – ^{1}H NMR (C_6D_6): δ = 3.02 (s, 4H), 2.60 (2, 6 H), 2.06–1.91 (m, 12 H), 1.84–1.76 (m, 8 H), 1.52–1.45 (m, 8 H). – ^{11}B NMR (THF): δ = 47.9. – ^{13}C NMR (C_6D_6): δ = 51.0, 36.6, 33.9, 33.5, 23.9, 23.8 (b). – IR (ṽ, cm^{-1}): 1411.9 (s), 667.2 (s), 404.5 (m). – MS, *m/z* (%): 327 (64) [M$^{+\cdot}$ – H], 218 (2) [328 – C_8H_{14}], 164 (100) [327 – cyclo-CH_2CH_2N-9-BBN]. – $C_{20}H_{38}B_2N_2$ (328.2): calcd. C 73.20, H 11.67, N 8.54; found C 69.71, H 10.93, N 8.89.

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