Inorg. Chem. **2008**, *47*, 7631−7637

Inorganic Chemistry
Article

Hydrogenation of Molecular Cyclic Diborane(4) Compounds Featuring B−B Bonds and Olefinic or Aromatic Bridges: a Quantum Chemical Study

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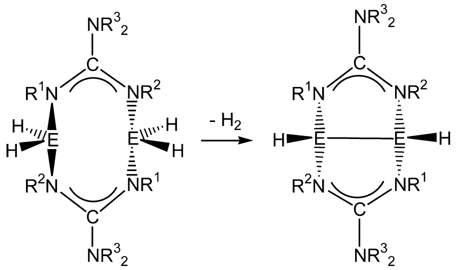
Received March 26, 2008

Hydrogenation reactions starting with di- or oligonuclear boron compounds featuring direct B−B bonds with the B atoms in the formal oxidation state +II are analyzed with the aid of ab initio quantum chemical (RI-MP2) calculations. The products of these reactions are B(III) hydrides which might be useful starting reagents for stoichiometric hydrogenation reactions and possibly in special cases also for hydrogen storage. Several different isomers of these B(III) hydrides featuring either terminal or bridging H atoms were considered. The results are compared to hydrogenation reactions of related molecules.

Introduction

In the past we have studied experimentally dehydrogenation reactions of guanidinate and amidinate complexes of boron[1,2] and gallium[3] hydrides. In these experiments we especially used the guanidine derivative hppH (hppH = 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine). The reactions lead to cyclic E(III) hydrides which could eliminate a second H_2 to give E(II) hydrides (E = B or Ga, see eq 1).



(1)

The Gibbs free energy change $\Delta_R G°$ (at 1 bar and 298 K) for dehydrogenation of $[H_2B(hpp)]_2$ and the model compound $[H_2B(NH)_2CNH_2]_2$ was calculated to be −30 and +19 kJ mol^{-1}, respectively.[4] For the model amidinate compound $[H_2B(NH)_2CH]_2$ dehydrogenation comes out to be associated with a $\Delta_R G°$ value of +28 kJ mol^{-1}.[5] Thus, the reaction Gibbs free energy is mildly negative or positive. If the reaction barrier is sufficiently low, the reaction could be driven reversibly. Interestingly, the hydrogenation of the Ga_2 dimer (which can be stabilized with the aid of the matrix isolation technique) was shown to be associated with a hydrogenation barrier of not more than about 30 kJ mol^{-1}.[6,7] It was shown impressively recently for the Ge alkyne analogue Ar′GeGeAr′ [Ar′ = C_6H_3-2,6(C_6H_3-2,6-*i*Pr_2)$_2$] that dihydrogen activation is possible by breaking a main group element-element bond under mild conditions (1 bar, room temp.).[8]

In ongoing research we are addressing the question to which extent the thermodynamic properties of such reactions change if the guanidinate or amidinate groups are replaced by other bridges. We apply quantum chemical calculations, which were shown to provide reliable information for this class of compounds,[4,5] to answer this question. Herein we analyze the dehydrogenation of diboryl compounds which are bridged by ethylene or an aromatic ring (compounds

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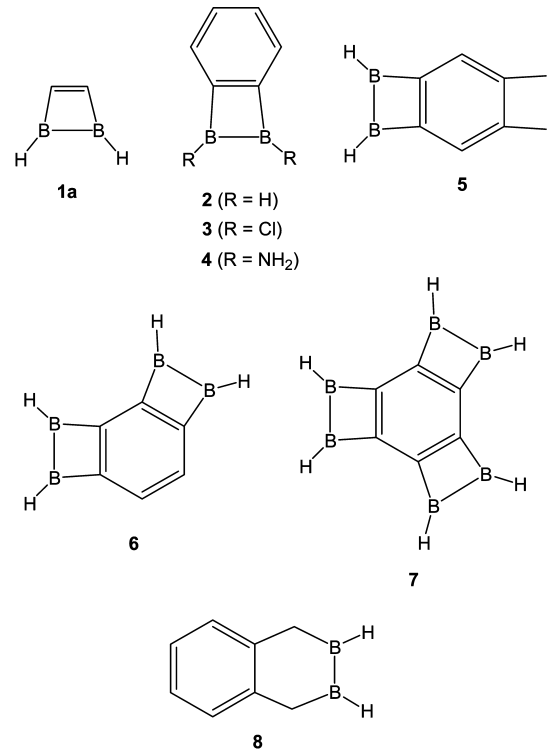
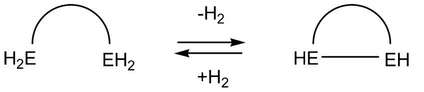
10.1021/ic800540z CCC: $40.75

Scheme 1



1a−**8**, see Scheme 1). In contrast to the previously studied compounds, only one bridge connects the two E atoms (see eq 2).



(2)

Whereas molecules **2**−**8** represent global energy minima for the corresponding overall formula, there are three isomers of $C_2B_2H_4$, and **1a** defines not the global energy minimum. In the light of the available literature data, the synthesis of most of the species (or at least derivatives) appears to be possible. Thus, an example of a derivative of **1a** which has already been synthesized is 1,2-bis(diisopropylamino)-1,2-dihydro-1,2-diborete (R = N*i*Pr$_2$).[9] However, in this form the species tends to rearrange to the more stable 1,3-dihydro-1,3-diborete isomer (**1b**) at increased temperatures (exceeding 120 °C in this special case). Hexaboryl-benzene derivatives $C_6(BR_2)_6$ (e.g., R = CH_3 or C_2H_5) were also prepared[10] and possibly can be transformed to the corresponding derivatives of **7** by reductive coupling. In addition, quantum chemical calculations (using the B3LYP method) for **2**, **7**, and one isomer of $C_2H_2(BH)_4$ (**6**) have already been reported.[11] However, this theoretical study deals exclusively with the strain-induced bond localization of the aromatic C_6 ring.[11,12] Herein the hydrogenation reactions and the structures of the reactants and reaction products for **1**−**8** are analyzed in quantum chemical calculations using RI-MP2.

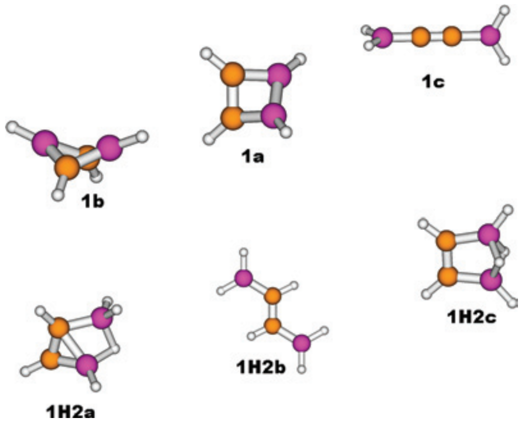


Figure 1. Structures of **1** and its hydrogenation products $C_2B_2H_6$.

Results and Discussion

In the following we discuss in turn for each of the systems illustrated in Scheme 1 the structures of the hydrides before and after hydrogenation and the thermodynamics for hydrogenation. Details of the structural properties of the hydrogenation products can be obtained from the Cartesian coordinates included for all species in the Supporting Information.

According to our MP2 calculations, 1,2-diborete **1a** is by 40.6 kJ mol^{-1} less stable than 1,3-diborete **1b** (adopting a puckered, C_{2v} symmetric structure as illustrated in Figure 1a), and the difference in the Gibbs energy $\Delta_R G°$ amounts to 39.8 kJ mol^{-1}. Our results are in agreement with previous ab initio calculations. Thus, for example, HF/6-31G* calculations predicted the energy difference to be 41 kJ mol^{-1},[13] and recent MP4 calculations argue for an energy difference of 34 kJ mol^{-1}.[14] Figure 1 illustrates their structures (see the Supporting Information for structural parameters). McKee showed (by MP2 and MP4 calculations) that the energy difference between the 1,2- and the 1,3-diborete decreases to not more than 3 kJ mol^{-1} if the H atoms at the B atoms are replaced by NH_2 groups.[14] More importantly, the barrier separating these two forms increases by as much as 45 kJ mol^{-1} relative to the parent compounds. This increase in the barrier height can be made responsible for the success in the preparation of amido-substituted 1,2-diborete.[9,15,16] The D_{2d} symmetric acetylene derivative **1c** defines a third minimum on the potential energy hypersurface of $C_2B_2H_4$. $\Delta_R E$, $\Delta_R E_{ZPE}$, and $\Delta_R G°$ relative to **1a** amount to +26.4, +15.0, and +11.2 kJ mol^{-1}, respectively, according to MP2.

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Derivatives of **1c** have also been synthesized[17] and represent potential starting reagents for a future preparation of hexaboryl benzene derivatives and derivatives of **7.** Addition of H_2 to $C_2B_2H_4$ leads to three possible products of the overall formula $H_2C_2B_2H_4$, in which the H atoms bind to the B atoms and adopt either bridging or terminal positions. The energy difference between the three isomers is very small. **1H2a** features three terminal and one bridging H atom, **1H2b** only terminal H atoms, and **1H2c** two terminal and two bridging H atoms. All three forms exhibit slightly larger C−C bond distances than C_2H_4 (133.0 pm). Thus, in **1H2a**, **1H2b**, and **1H2c** the C−C bond distances are 135.3, 136.0, and 134.9 pm, respectively. A distinction of **1H2a** is that one of the B atoms is bound not only to one C atom but establishes also an interaction with the second C atom (resulting in a short C−B distance of 149.8 pm and a much longer one of 173.7 pm). **1H2b** is a planar molecule with π-interactions being established between the C and B atoms and with the largest C−C bond distance of 136 pm (versus 135.3 pm for **1H2a** and 134.9 pm for **1H2c**) of all isomers. The B−C bond distance in **1H2b** is 155.0 pm. For comparison, a B═C double bond distance of 144.4(8) pm has been determined experimentally for $[Mes_2BCH_2]^-$, and in Mes_2BCH_3, the B−CH_3 single bond distance measures 156.2 pm.[18] The thermodynamic properties calculated for the hydrogenation reactions starting with 1,2-diborete, **1a**, to give one of the forms **1H2a**−**1H2c** are included in Table 1. Δ_RE without and including ZPE (zero-point energy, only vibrational contributions are considered) corrections are −112.6 and −85.8 kJ mol^{-1}, respectively, and $\Delta_RG°$ amounts to −54.7 kJ mol^{-1} for the reaction to give **1H2a**.

The knowledge of the barrier height for hydrogenation is of course important for judging the potential use of these compounds (e.g., as hydrogen transfer reagents). Therefore, we have calculated the transition state TS1 for the hydrogenation of compound **1a** leading to product **1H2a** (see Figure 2 and Table 1). The energy of the transition state is 157.6 kJ mol^{-1} higher than that of product **1H2a**, and the standard Gibbs free energy barrier for hydrogenation of **1a** according to eq 3 amounts to 86.9 kJ mol^{-1}.

$$\mathbf{1a} + H_2 \rightarrow \mathbf{1H2a} \qquad (3)$$

Next we studied $C_6H_4B_2H_2$, **2**, featuring a benzene instead of an ethylene bridge. Selected dimensions of this molecule and its derivatives $C_6H_4B_2Cl_2$ and $C_6H_4B_2(NH_2)_2$ are summarized in Table 2. The aromatic ring prevents the molecule from rearrangements. This is a very important simplification with respect to ethylene bridges. In all three species the C−C bond distances differ, with the longest bond being established between the C atoms in position 1−2 (endo) to which the B atoms are bound (142.6, 143.3, and 142.4 pm for **2**, **3**, and **4**, respectively) and the shortest bond between the C atoms in the exo positions 3−4 and 5−6 (138.1, 138.7, and 139.0 pm for **2**, **3**, and **4**, respectively). The values calculated herein are in good agreement to those calculated earlier for **2** with B3LYP/6-31G*, where the extremes were found to be 143.2

Table 1. Relative Energies (E_{rel}, in kJ mol^{-1}) of the Located Minima for the Hydrogenation Products of **1**–**8**, Reaction Energies (with and without ZPE Corrections, Δ_RE and Δ_RE_{ZPE}, in kJ mol^{-1}), and Gibbs Free Energies ($\Delta_RG°$, in kJ mol^{-1}) for the Hydrogenation Reactions Starting from the Corresponding Diborane

	E_{rel}	Δ_RE	Δ_RE_{ZPE}	$\Delta_RG°$
TS1	157.6	45.0	53.2	86.9
1H2a	0.0	−112.6	−85.8	−54.7
1H2b	22.8	−89.8	−69.3	−44.6
1H2c	51.8	−60.8	−33.5	−2.4
TS2	155.3	19.7	27.5	61.2
2H2a	0.0	−135.6	−108.8	−76.9
2H2b	0.1	−135.5	−107.2	−74.6
2H2c	3.8	−131.8	−112.9	−85.8
3H2a	0.0	−156.3	−133.9	−100.7
3H2b	2.0	−154.2	−131.8	−102.6
3H2c	60.6	−95.6	−74.1	−37.9
3H2d	80.0	−76.2	−51.2	−17.1
4H2a	0.0	−187.7	−160.2	−127.1
4H2b	14.9	−172.7	−148.5	−120.0
4H2c	15.3	−172.4	−148.1	−119.6
5H4a	0.0	−298.3	−240.3	−174.3
5H4b	8.3	−290.0	−250.0	−193.8
6H4a	0.0	−318.2	−275.5	−221.4
6H4b	22.7	−295.6	−253.9	−200.1
6H4c	23.5	−294.8	−252.0	−197.9
7H6a	0.0	−398.0	−316.2	−220.3
7H6b	10.4	−387.6	−303.1	−205.6
7H6c	17.1	−380.8	−322.6	−237.5
8H4a	0.0	−198.1	−183.9	−153.1
8H4b	37.5	−160.5	−150.1	−119.5
8H4c	154.4	−43.6	−40.9	−17.0
8H4d	567.0	369.0	367.4	388.9
8H4e	572.5	374.5	374.2	397.2
8H4f	581.1	383.1	381.1	402.3

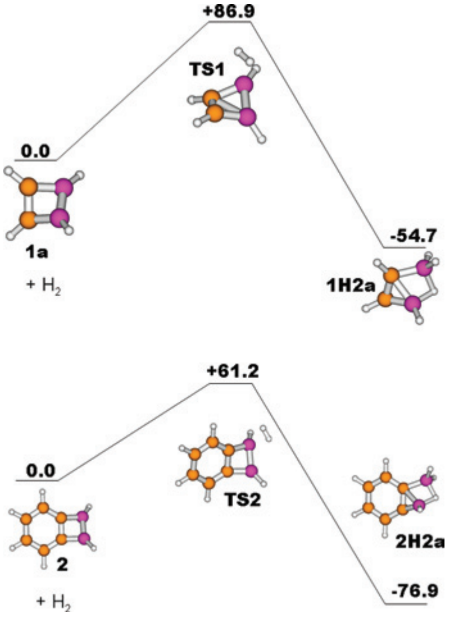

Figure 2. Transition states for the hydrogenation of **1a** leading to **1H2a** and of **2** leading to **2H2a**. The $\Delta G°$ values (at 298 K, 1 bar) are also given.

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[17] See, for example: Schulz, H.; Gabbert, G.; Pritzkow, H.; Siebert, W. *Chem. Ber.* **1993**, *126*, 1593–1595.

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Table 2. Selected Parameters (Distances in pm, Angles in Degrees) for **2**, **3**, and **4** (X = H, Cl, or NH_2)

	2	3	4
C1−C2	142.6	143.3	142.4
C2−C3	140.7	139.9	139.9
C3−C4	138.1	138.7	139.0
C4−C5	141.4	140.9	140.3
C−B	153.4	154.9	157.4
B−B	166.2	170.7	172.3
B−X	118.2	173.7	139.3
C1−C2−B	90.0	95.1	95.4
B−B−C	81.8	84.9	84.5
C−B−X	130.1	131.1	131.2
B−B−X	145.3	144.0	144.2

and 138.7 pm).[11] The shortest C−C distances are even slightly shorter than those of benzene, which were calculated to be 139.2 pm. Strain-induced bond localizations are responsible for these differences.[11] Three minima were found for the hydrogenation product $C_6H_4B_2H_4$ (see Figure 3). They differ by the number of bridging H atoms, which is two for isomer **2H2a** but only one for isomer **2H2b.** Hydrogenation of **2** to give **2H2a**, **2H2b**, or **2H2c** is associated with $\Delta_R G°$ values of −76.9, −74.6, and −85.8 kJ mol^{-1}, respectively (see Table 1). Thus, the C_6H_4 bridge leads to slightly higher hydrogenation Gibbs energies than the C_2H_2 bridge. In **2** larger values are adopted for the B−B distance and the C−C−B bond angles (166.2 pm and 90.0°, see Table 2) than in **1a** (164.3 pm and 87.8°). This is caused by the stronger resistance of the C_6H_4 bridge to change the bond angles which are optimized for aromaticity in the C_6 ring. Therefore, the higher hydrogenation energy of **2** in comparison with **1a** is presumably caused by the relative instability of **2.**

We also calculated the barrier for hydrogenation of **2** to give **2H2a**. The energy of the transition state TS2 (Table 1 and Figure 2) is 155.3 kJ mol^{-1} higher than that of **2H2a.** With 61.2 kJ mol^{-1} the standard Gibbs free energy barrier for hydrogenation is smaller than in the case of **1b.** Thus, the calculations suggest that hydrogenation of **2** is possible under mild conditions.

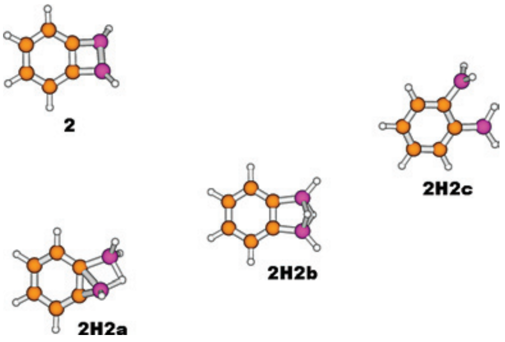

Figure 3. Structures of **2** and its hydrogenation products $C_6H_4B_2H_4$.

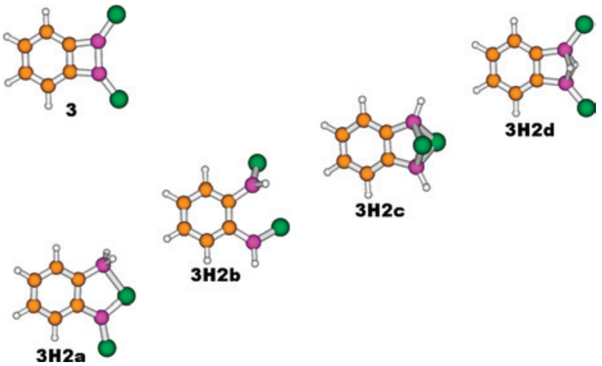

Figure 4. Structures of **3** and its possible hydrogenation products $C_6H_4B_2Cl_2H_2$.

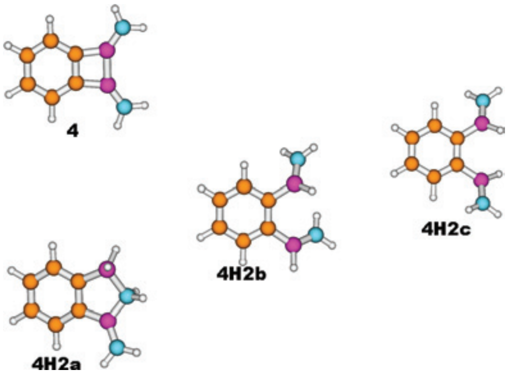

Figure 5. Structures of **4** and its hydrogenation products $C_6H_4B_2(NH_2)_2H_2$.

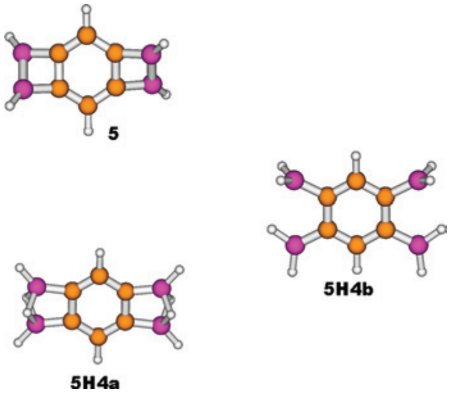

Figure 6. Structures of **5** and its hydrogenation products $C_6H_2B_4H_8$.

The effect of substitution on the hydrogenation reaction has also been studied. To this end, hydrogenation of the parent compound $C_6H_4B_2H_2$, **2**, was compared with that of $C_6H_4B_2Cl_2$, **3**, and $C_6H_4B_2(NH_2)_2$, **4** (see Table 2 for some geometric parameters of the reactants). Again, several structures had to be considered for the hydrogenation products $C_6H_4B_2Cl_2H_2$ and $C_6H_4B_2(NH_2)_2H_2$. Four forms **3H2a−3H2d** of $C_6H_4B_2Cl_2H_2$ and three forms **4H2a−4H2c** of $C_6H_4B_2(NH_2)_2H_2$ with the structures visualized in Figures 4 and 5 resulted from our RI-MP2 calculations. As anticipated, structures in which Cl adopts a bridging position between the two B atoms (**3H2a** and **3H2c**) are energetically preferred over that with bridging H atoms (**3H2d**). For **4**, only one structure contains a bridging NH_2 unit (**4H2a**). Structures with no bridging atoms and two three-coordinated B atoms are minima in both cases (**3H2b**, **4H2b**, and **4H2c**). The presence of B−N π-interactions leads to a planarization at the N atoms. As anticipated, substitution of the H atoms by the weak π-donor Cl increases the hydrogenation energy and standard Gibbs free energy (see Table 1). Substitution by the stronger π-donor NH_2 leads to further increase (see Table 1).

Further substitution of H atoms of benzene by BH groups leads to the molecule $C_6H_2B_4H_4$, for which two structures have to be considered (see Figures 6 and 7), with the second set of BH groups being either in 4 and 5 (structure **5**) or 3 and 4

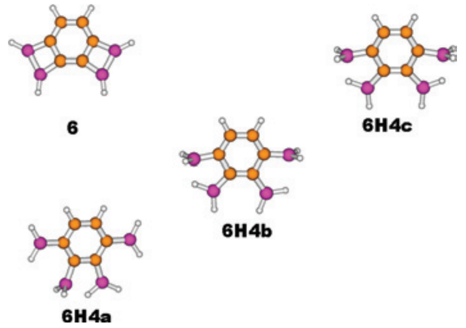

Figure 7. Structures of **6** and its hydrogenation products $C_6H_2B_4H_8$.

(structure **6**) positions. Isomer **5** comes out to be slightly more stable (by 11.7 kJ mol^{-1}). For the hydrogenation products of **5** our MP2 calculations found the two minima **5H4a** and **5H4b**. **5H4a** with four bridging H atoms is slightly preferred (by 8.3 kJ mol^{-1}) over **5H4b** featuring only terminal H atoms. Three minima were found for the products of hydrogenation starting with isomer **6**. The two forms **6H4b** and **6H4c** differ only very slightly in energy and structure. Thus, **6H4b** exhibits one short (158.7 pm) and one long (225.2 pm) B−H···B distance, while in **6H4c** both B−H···B distances are similar (164.7 and 165.5 pm). The changes in energy with and without ZPE corrections and in the Gibbs energy for hydrogenation of **5** and **6** are included in Table 1. The values calculated for the energy changes upon hydrogenation are in both cases more than twice as large as that calculated for **2.** The increased distortion of the C_6 ring in **5** and **6** is presumably an important factor at work here.

Table 3. Comparison of Selected Parameters (Distances in pm, Angles in Degrees) for **2**, **5**, **6**, and **7**

	2	**5**	**6**	**7**
C−C	138.1−142.6	139.8−144.4	138.2−142.4	142.8−143.8
C−B	153.4	154.6	155.9−156.3	151.3−152.0
B−B	166.2	166.8	172.2	166.3−167.2
B−H	188.2	118.2	118.4−118.6	117.8−117.9
C−C−B[a]	90.0	90.4	95.2−95.8	86.8−90.0
B−B−C[a]	81.8	82.6	84.4−84.6	78.8−81.9

[a] Atoms within a C_2B_2 ring.

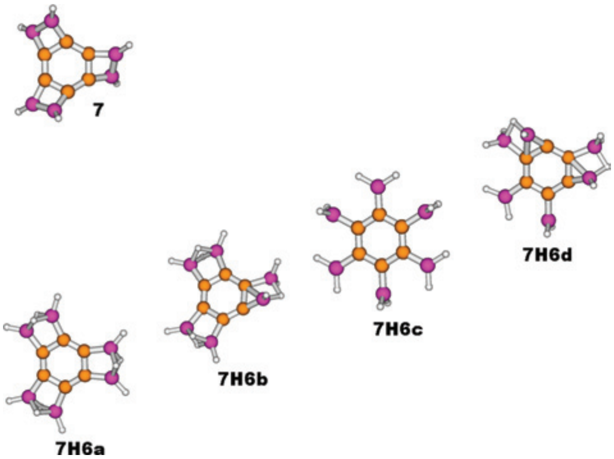

Figure 8. Structures of **7** and its hydrogenation products $C_6B_6H_{12}$.

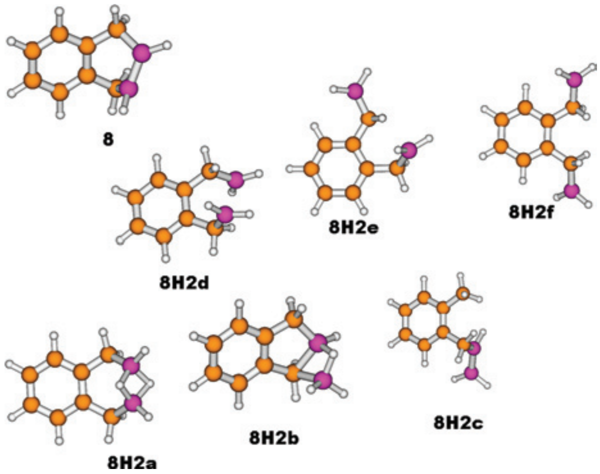

Figure 9. Structures of **8** and its hydrogenation products $C_6H_4(CH_2)_2B_2H_4$.

Finally, all six H atoms of benzene were replaced by BH groups. As anticipated, three B−B bonds are established. One could think of another form, a [6]radialene-type structure (replacement of the CH_2 groups of the parent [6]radialene by BH groups) featuring six C═B double bonds and only C−C single bonds. This form is, however, destabilized by the loss of aromaticity in the C_6 ring, which cannot be compensated by the formation of the C═B double bonds. The calculations did not find any minimum for this structure in contrast to the success in the preparation of a huge variety of [6]radialene species $C_6(CR_2)_6$.[19] Previous calculations suggest the π-bond contribution to a C═B double bond to be about 16 kJ mol^{-1} weaker than that of a C═C double bond.[20] Therefore the C═CH_2 double bonds can better compete with the aromatic stabilization than the C═BH double bonds. The C−C bond distances in $C_6B_6H_6$ fall within the range 142.8−143.8 pm (Table 3). The endo C−C distances (C atoms being part of the four membered C_2B_2 ring) are shorter than the exodistances, in agreement with previous B3LYP calculations.[11] The C−B and B−B bond distances were calculated to be 151.3−152.0 pm and 166.3−167.2 pm, respectively. Addition of three H_2 molecules leads to hexaboryl benzene with four minimum structures (see Figure 8). Structure **7H6a**, in which the number of bridging H atoms is maximized (6 H bridges), is energetically slightly favored over the other forms. Thermodynamic data for the hydrogenation of **7** are summarized in Table 1. Although **7H6a** has the lowest energy, reaction to give **7H6c** is associated with the largest change in the standard Gibbs free energy (−237.5 kJ mol^{-1}). This value is about 20 kJ mol^{-1} less negative than three times the Gibbs free hydrogenation energy for **2** to give **2H2c.**

Finally, we calculated the structure of $C_6H_4(CH_2)_2B_2H_2$, **8**, and its hydrogenation products (see Figure 9). In **8** a six-membered ring is established which might be favored over a four-membered ring as in all other compounds discussed herein.

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(19) See, for example, (a) Hopf, H.; Maas, G. *Angew. Chem.* **1992**, *104*, 953–977*; Angew. Chem., Int. Ed.* **1992**, *31*, 931−954, and references given therein. (b) Höpfner, T.; Jones, P. G.; Ahrens, B.; Dix, I.; Ernst, L.; Hopf, H. *Eur. J. Org. Chem.* **2003**, 2596–2611.

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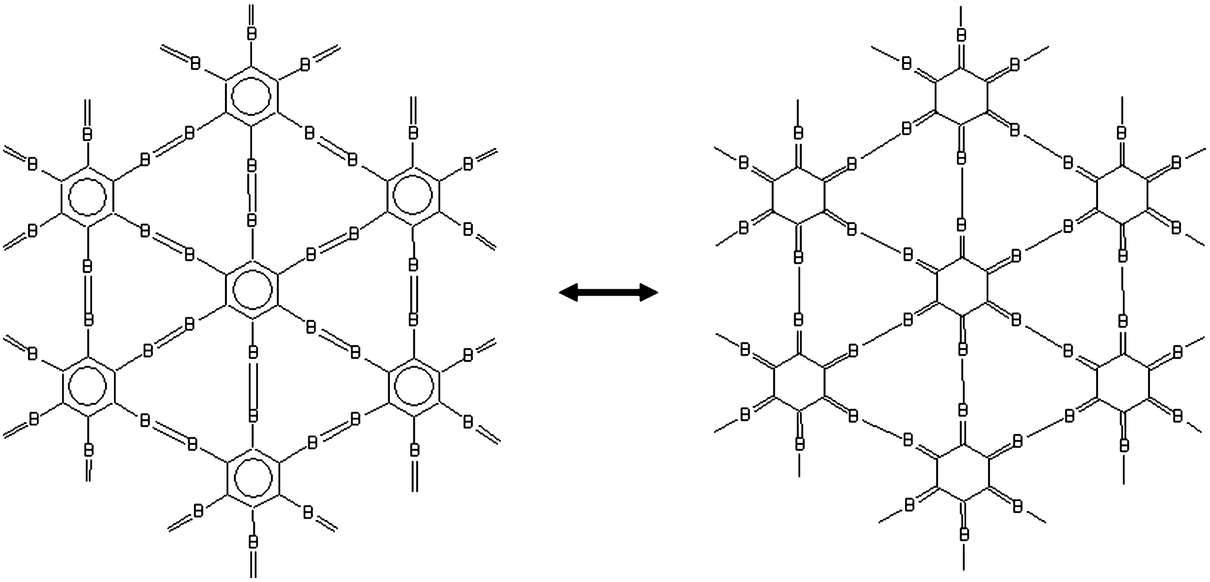

Figure 10. Possible structure of C_6B_6. Of the two shown resonance formulae, the first is likely to be the most important one.

However, the Gibbs free energy change $\Delta_R G°$ for hydrogenation of **8** (−153.1 kJ mol^{-1}, see Table 1) comes out to be significantly larger than for compounds **1a** and **2** (−54.7 and −85.8 kJ mol^{-1}, respectively).

Conclusions

In this work the hydrogenation reactions of eight different diborane(4) molecules in which the two B atoms are bridged by ethylene or aromatic groups are analyzed. The synthesis of most of these compounds (or at least derivatives) appears to be possible on the basis of the available literature (see Introduction). All hydrogenation reactions come out to be exothermic. The calculated $\Delta_R G°$ values are significantly more negative than those calculated previously (with density functional theory, BP86) for the guanidinates $[HB(hpp)]_2$ (+30 kJ mol^{-1}) and $[HB(NH)_2CNH_2]_2$ (−19 kJ mol^{-1})[4] and the model amidinate $[HB(NH)_2CH]_2$ (−28 kJ mol^{-1}).[5] Of these compounds, $[HB(hpp)]_2$ and $[H_2B(hpp)]_2$ have already been synthesized.[1,2] The hydrogenation reactions also differ remarkably in their thermodynamic properties from the hydrogenation of the parent diborane(4) $H_2B–BH_2$, for which hydrogenation to give two separated BH_3 molecules was calculated (with MP2) to be associated with a $\Delta_R H°$ value of not more than −4.1 kJ mol^{-1}.[21] The barriers for hydrogenation were also calculated for two systems. The results suggest that hydrogenation should be possible under mild conditions. Some derivatives of the species discussed herein were already synthesized and shown to be stable. The examples include the hexaboryl benzene derivatives $C_6(BR_2)_6$ (R = Me or Et), which were made by cyclotrimerization of acetylene precursors. In the light of these results, it should be possible to prepare other hexaboryl benzene derivatives, especially $C_6(BF_2)_6$, which are possible precursors to the corresponding hydrides.

It should be mentioned that additional hydrogen loss from the diborane(4) species could also be possible and might lead to interesting compounds. For example, hydrogen elimination from compound **7**, $C_6B_6H_6$, gives a compound of the formula C_6B_6 which is likely to form a network structure as sketched in Figure 10 in which the C_6 rings are linked by −B=B− bridges. A second resonance structure in which B−B single bonds and C=B double bonds are formed at the expense of the aromatic systems is likely to play a minor role. A material C_6B_6 could take up 6 equiv of H_2 to give $C_6(BH_2)_6$ and might therefore be of interesting for hydrogen storage although its 6 mass % of usable hydrogen bonded to boron might not be completely satisfying.

Computational Details

Details of the Quantum Chemical Calculations. The quantum chemical calculations were performed with the aid of the TURBOMOLE program package.[22] For all calculations, the resolution-of-identity-MP2 (RI-MP2)[23] method was used in combination with the TZVPP basis set.[24] The RI-MP2 method is based on an approximate representation of products of orbital basis functions as a linear combination of atom-centered auxiliary basis functions. It allows the replacement of each four index integral by a sum of three index integrals and thus reduces the computational cost. It is faster than traditional MP2 calculations with an insignificant loss in accuracy.[25] The auxiliary basis set used in this work is optimized for TZVPP.[25] Vibrational analysis was carried out for all structures, and the absence of any

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imaginary frequency confirmed that all structures represent minima on the potential energy hypersurface. The freeH module (an auxiliary FORTRAN code of the TURBOMOLE program calculating thermodynamic functions by standard statistical thermodynamics) was applied for calculating the zero point energies and the Gibbs free energy changes (at 298 K and 1 bar). The harmonic vibrational frequencies were scaled by 0.9496 as suggested by Scott et al.[26]

Acknowledgment. The authors thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for their continuous financial support.

Supporting Information Available: Selected structural parameters for compounds **1a**–**1c** and calculated coordinates and vibrational properties for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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