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Stability of η2-H2 borane complexes – a theoretical investigation

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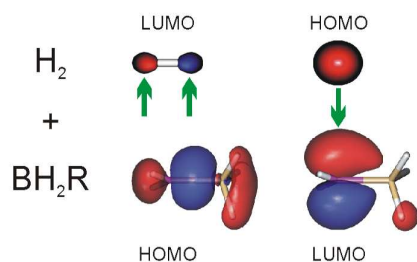# Stability of η^2-H$_2$ borane complexes – a theoretical investigation

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Comprehensive quantum chemical study reveals the electronic structure and stability of novel η^2-H$_2$ BR$_3$ complexes. The electronic effects of substituents are investigated using NBO analysis and MO theory. A new type of natural pentavalent borane compound is also presented.

Abstract

Non-metallic η^2-H$_2$ complexes are extremely rare, moreover in the case of boranes (with the exception of the BH$_5$ molecule) the existence of such structures were only indicated by computational studies. In a recent paper we have demonstrated that external electron donor groups can stabilize the η^2-H$_2$ complexes, similarly to the backdonation in case of transition metals. In this paper we present evidence of a new stabilizing effect: electron donation from the B−R bonds to the H$_2$ σ* orbital. The stability and electronic structure of several mono-, di-, and trisubstituted borane-H$_2$ complexes were investigated by *ab initio* calculations. SiR$_3$ groups were found to facilitate the σ(B−R)→σ*(H−H) interaction, increasing the stability of the η^2 complexes. Furthermore in the case of tris(trimethyl)silylborane the exceptional stability of a novel neutral pentavalent borane structure is shown.

Introduction

Theoretical investigations of the H$_2$ σ-complexes of boron are in the focus of attention currently because of the rapidly developing FLP chemistry for dihydrogen activation[1]. The first example of these complexes, BH$_5$ – that can also be regarded as a η^2-H$_2$ complex of BH$_3$ – was predicted as a possible intermediate on the hydrolysis pathway of the tetrahydroborate (BH$_4^-$) anion in the beginning of sixties[2-5]. These early experimental works suggested two possible geometries for BH$_5$: the H$_2$ molecule is oriented to the BH$_3$ molecule side-on or end-on. Fast isotope exchange reactions between sodium borohydride and D$_2$SO$_4$ also

indicated the possibility of a BH_5 intermediate. The earliest quantum chemical studies found no local minimum[6-8] or only a very shallow one[9,10] for BH_5 on the potential energy surface, however highly correlated calculations with extended basis sets predicted the stability of the BH_5 molecule at low temperatures[11,12] well before the experimental evidence. The existence of this elusive complex was experimentally proven in 1994 by infrared spectroscopy at 10 - 25 K in argon matrix[13].

The most stable geometry of the BH_5 complex was predicted by all high level quantum chemical studies[11,12,14,15] to be a side-on coordinated complex shown in Scheme 1. According to the highest level models[14,15] the distance between the boron atom and the H_2 unit is 1.399 ± 0.002 Å. Compared to the monomer the H^A-H^B distance in the H_2 unit was elongated by ~0.05 Å in BH_5 (0.800 ± 0.004 Å). The C_s symmetry of the complex results in two different B−H distances in the BH_3 unit, both of them slightly elongated compared to the BH_3 monomer, the longest one being the $B-H^2$ bond eclipsed by the H_2 unit (1.192 ± 0.003 Å).
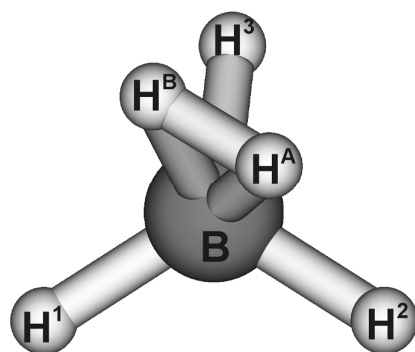
Scheme 1.: BH_3-H_2 side-on coordinated complex.

High level quantum chemical studies give -6.1^{14} and -6.6^{15} kcal/mol for the formation energy (E_d) of the BH_5 complex. Inclusion of the zero point energy decreases this value to -0.7 and -1.2 kcal/mol respectively, while the Gibbs free energy of the complex at room temperature is positive with respect to the monomers, indicating that BH_5 is only stable at low temperatures.

The origin of the attractive interaction between the H_2 and BH_3 molecules was determined to be a covalent 3c-2e bond[9,11,12a]. The pyramidal geometry of the BH_3 subunit, the short distance of the H_2 to the boron atom and the elongation of the H^A-H^B bond[12a,14] supports this bond structure. Molecular orbital studies and NBO analyses[12a] also show a charge transfer from the H^A-H^B sigma bond to the empty orbital of the boron atom.

According to ref[11] the elongation of the B−H bond compared to BH_3 can be attributed to the repulsion of the two hydrogen atoms, or possibly backdonation from the B−H bonds to the H_2 unit. This additional bonding mode however − although possibly contributing to the stability of the BH_5 molecule − was not investigated further. A similar backdonation effect[16] was identified in the rate determining transition state of the hydrogenolysis of $CyB(C_6F_6)_2$.

Besides the single example of BH_5, no other BR_3-H_2 complex was ever synthesised according to the literature. Theoretical indications of similar complexes are also extremely rare. Mo *et al.* found a η^2-H_2 complex intermediate on the PES of the hydrogen addition reaction of the phosphine-borane $[(CF_3)_3B][PH_3]^{17}$. Interaction from the lone electron pairs of the nearby fluorine atoms were assumed to play a role in the stabilization of the complex. Another fluorinated boron derivative, perfluoro-

pentaphenylborole was also shown to form a reactive complex with H_2[18]. In case of BF_3 and BCl_3 however no minimum corresponding to a side-on H_2 complex could be found[19]. An η^2-H_2 complex intermediate was also identified on the $BH_4 + CF_3OH = BH_3OCF_3 + H_2$ reaction profile[20].

In a very recent work we have shown that a new type of interaction − donation of electron from external Lewis bases to the H_2 unit − can stabilize an η^2-H_2 borane complex in diphospine-borane systems[21].

In this paper we present a theoretical investigation with the aim of identifying the possible stabilizing factors in BR_3−H_2 complexes and finding synthetic targets of new complexes of this type.

Computational methods

The formation energy of BH_5 was calculated very accurately (CCSDTQ/CBS limit[15]), but further calculations with bigger substituents on boron this method is no longer feasible. In order to find a cheap and adequate *ab initio* computational level the reaction $BH_3 + H_2 = BH_5$ was calculated at different levels of theory (see Table 1.). The long-range and dispersion corrected ωB97X-D functional with the aug-cc-pVTZ basis set resulted in formation energies close to the CCSDTQ energies at the CBS limit[15] showing the eligibility of the former for the description of the potential surface of this reaction. Throughout this paper the ωB97X-D/ aug-cc-pVTZ method was used.

All calculations were carried out using Gaussian 09 program package[22]. At all the optimized structures vibrational analysis was performed to check the nature of the stationary point (at a minimum all the eigenvalues of the Hessian matrix are positive, at the transition states there is exactly one negative eigenvalue. For NBO analysis the NBO 5.9. − implemented in Gaussian 09 − program was used[23]. The molecular geometries and orbitals were visualized by the MOLDEN[24] program.

Method		E
MPW1K	6-31+G(d)	-5.4
	6-31+G(d,p)	-7.7
	6-31+G(d,2p)	-8.4
	6-311+G(d,2p)	-8.5
	aug-cc-pVDZ	-9.3
	aug-cc-pVTZ	-8.9
	aug-cc-pVQZ	-8.9
ωB97X-D	6-31+G(d)	-3.9
	6-31+G(d,p)	-6.1
	6-31+G(d,2p)	-6.8
	6-311+G(d,2p)	-6.8
	aug-cc-pVDZ	-7.8
	aug-cc-pVTZ	-7.2
	aug-cc-pVQZ	-7.2
MP2	aug-cc-pVTZ	-5.9
Kim *et al.*[14]		-6.1
Allen *et al.*[15]		-6.6

Table 1.: Formation energies of the BH_3−H_2 side-on complex with different methods (energies in kcal/mol).

Results and discussion

In previous studies the interaction between the H_2 and BH_3 units was analysed extensively using the geometry of the complex and the formation energy. To determine the nature of the interaction however other bonding descriptors can be used as well. With the help of NBO analysis the interactions between orbitals can be identified. Although in Ref[12a] NBO analysis of BH_5 was carried out, no interaction besides the one between the $\sigma(H^A−H^B)$ orbital and the empty $2p(B)$ orbital was mentioned. According to our previous calculations[21], in addition to this interaction a backdonation from the $\sigma(B−H)$

orbitals to the $\sigma^*(H^A-H^B)$ orbital can be detected. Since these previous NBO studies used different theoretical methods, in order to provide consistent reference for the substituted H_2-BR_3 complexes we carried out NBO analysis of BH_5 at the ωB97X-D/aug-cc-pVTZ level.

The best Lewis structure for description of the electron density of the H_2-BH_3 complex (99.1% of the electron density is accounted for in the Lewis structure) is found to be a structure containing a 3c-2e covalent bond involving the boron atom and the H_2 unit.
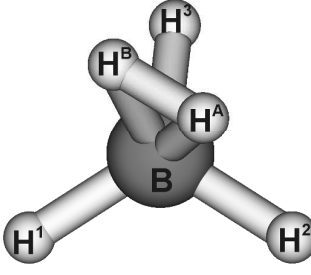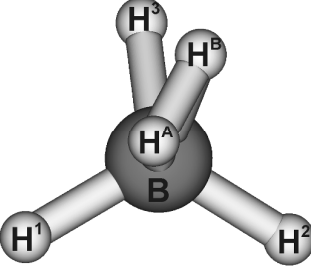
	η^2-H_2/BH_3	TS_{ROT}
$c_A^{\,2}$ (B)	23.6%	23.1%
σ(B$-$H)$\rightarrow\sigma^*$(B$-$H$-$H)	22.4	-
σ(B$-$H)$\rightarrow\sigma^*$(B$-$H$-$H)	3.5	13.5
σ(B$-$H)$\rightarrow\sigma^*$(B$-$H$-$H)	3.5	13.5

Table 2.: Results of the NBO analysis of the BH_3-H_2 side-on complex and transition state of the H_2 rotation, $c_A^{\,2}$ (B) denotes the percentage of the NBO on the boron atom. (energies in kcal/mol).

The results of the NBO analysis are presented in Table 2. The $c_A^{\,2}$ (B) coefficient shows that percentage of the NBO on the boron in the 3c-2e bond is significant, implying a strong interaction between the H_2 unit and the boron atom. The $c_A^{\,2}$ (B) percentage of the NBO on the boron is very similar in the rotational transition sate, indicating a similar bond strength in the TS structure. Besides the 3c-2e bond another significant interaction (22.4 kcal/mol) can be found between the σ(B$-$H^2) orbital and the σ^*(B$-$H$^A-$H^B) orbital of the eclipsing B$-$H^2 bond, similarly to our earlier calculations[21]. In the conventional two electron bond description this interaction corresponds to the σ(B$-$H^2) $\rightarrow \sigma^*$(H$^A-$H^B) interaction. Thus these two notations are used interchangeably throughout this paper, corresponding to the 3c-2e or 2c context. NBO analysis of the rotational transition state (TS$_{ROT}$) shows that

although the magnitude of the interaction with a single B$-$H bond decreases, rotation of the H_2 unit allows backdonation from an other B$-$H bond as well. The geometry of TS$_{ROT}$ also shows that as we rotate the H_2 unit it becomes perpendicular to the B$-$H^2 bond, thus the other two B$-$H bonds can overlap with the B$-$H$^A-$H^B bond better. The sum of these two interactions is comparable to the 22.4 kcal/mol of the rotational minimum. Previous calculations show that the rotational barrier of the H_2 unit in the η^2-H_2-BH_3 complex is very low (0.063 kcal/mol[15]) which means that the H_2 moiety rotates easily, apparently contradicting with a significant interaction between the H_2 unit and one of the B$-$H bonds. Our NBO analysis presented above however shows that the small rotational barrier is the result of significant, but

similarly strong interactions between the two subunits.

Similarly to the case of the transition metals, where the stability of the η^2-H$_2$ complex depends on the balance between two interactions: (i) donation of the σ bond of dihydrogen to an empty d-orbital of the metal, and (ii) backdonation of a d-type occupied orbital of the metal to the σ^*(H$-$H) orbital[25], we can assume that in H$_2$/BR$_3$ complexes the balance between donation to the empty orbital of the boron and backdonation from the B$-$R orbitals plays an equally important role. Both of these interactions $-$ thus the stability of the η^2 complex $-$ can be tuned by changing the R substituents on the boron. Our aim is to explore the possibilities of tuning these stabilising interactions in order to pave the way to η^2-H$_2$ complexes that are stable at room temperature. To identify the effect of the different single substituents on the stability of the complexes and the balance of the component interactions the same bonding

descriptors were used for H$_2$/BH$_2$R as in case of BH$_5$.

The formation energy of the adducts (see Table 3.) shows the overall energetic effect of the R substituents. This overall energy is the result of the following stabilizing components: (i) electron donation from the H^A$-$H^B bond to the empty orbital of the boron, (ii) backdonation from the B$-$R bonds to the H^A$-$H^B antibonding orbital, (iii) backdonation from the R substituents to the H^A$-$H^B antibonding orbital. All of these interactions are influenced by the electronic and geometric properties of the R groups. Electron withdrawing groups are expected to increase the Lewis acidity of the boron centre, while the π-donating groups populate the empty orbital of the boron and decrease the electron accepting ability. The second interaction depends on the energy and the shape of the B$-$R bond, while the third interaction is possible only if the R group possesses a lone electron pair in the proper position.

BH$_2$R+H$_2$	ΔE [kcal/mol]	H$-$H distance [Å]	B$-$H$_2$ distance [Å]
H	-7.2	*0.816*	*1.287*
CH$_3$	-0.2	*0.792*	*1.403*
CF$_3$	-8.9	*0.813*	*1.292*
CCl$_3$	-3.3	*0.804*	*1.331*
SiH$_3$	-11.1	*0.876*	*1.173*
SiF$_3$	-13.9	*0.862*	*1.186*
PH$_2$	2.4	*0.811*	*1.312*
P(O)H$_2$	-10.5	*0.828*	*1.250*

Table 3.: BH$_2$R$-$H$_2$ side-on complex formation energies and characteristic geometry data.

Although electron withdrawing substituents are expected to improve the electron accepting ability of boron, no minima corresponding to an η^2 complex were found on the potential surface in case of R = F, Cl, OH, SH and NH$_2$. In these cases the positive charge of the boron is increased

compared to BH$_3$, however all these substituents also possess lone electron pairs capable of electron donation to the empty orbital of boron. Indeed, NBO analysis shows an additional π-type dative bond between the B and R atoms, hindering the formation of the η^2-H$_2$ complex.

Although two other, weakly π-donating substituent groups, PH_2 and AsH_2 form complexes with H_2, the complexation energies are very low. Comparing the formation energies of the $R = PH_2$ and $R = P(O)H_2$ cases, we can observe the adverse effect of the phosphorous lone pair to the complex formation. In case of CCl_3 the lone pairs of the chlorine atoms can also donate electrons to the empty orbital of the boron. The decreased B−C−Cl angle of the chlorine perpendicular to the H_2BR plane indicates this interaction. The CH_3 substituent also decreases the complex formation energy.

Compared to the formation energy of BH_5 (-7.2 kcal/mol) – the CF_3, $P(O)H_2$, SiH_3 and SiF_3 substituents stabilize the η^2-complex further, the formation energies are -8.9, -10.5, -11.1 and -13.9 kcal/mol respectively.

H^A−H^B and B−H_2 distances (the B−H_2 distance is measured from the boron atom to the H^A−H^B bond critical point) show a similar picture (Table 3.). In the case of substituents when the formation energies are more negative than the BH_5 the H^A−H^B distance increases and the B−H_2 distance decreases.

Since the stability of the complexes could not be explained using solely the electron withdrawing or donating ability of the substituent groups, NBO analysis was also carried out for the H_2BR species. Similarly to the case of BH_5, Lewis structures involving a 3c-2e bond between the boron and the H_2 unit provide the best description of the electron density for all R groups. This construction however does not provide a direct energetic measure of the interaction between the $\sigma(H^A$−$H^B)$ bond and the 2p(B) empty orbital. Restricting the

Lewis structures to 2 center bonds results in a description of lower quality (on the average 97% of the electron density is accounted for in the Lewis structure versus the 99% of the 3c-2e bonded cases), however the interaction energy between $\sigma(H^A$−$H^B)$ and the 2p(B) empty orbital is readily available*. The magnitude of donation from the $\sigma(H^A$−$H^B)$ orbital to the 2p(B) empty orbital -as obtained from the 2c restricted calculations- shows good correlation with the contribution of boron in the 3c-2e orbitals (R^2=0.99), confirming that these descriptors can be used interchangeably (see Table 4). The correlation shown with the complexation energies however is poor (R^2=0.66), indicating that in addition to the $\sigma(H$−$H)\rightarrow$2p(B) electron transfer, an other interaction also contributes to the stabilization of the complex. Orbital interaction energies collected in Table 4 illustrate that backdonation from the B−R and B−H σ orbitals indeed plays a significant role in the formation of the BH_2R−H_2 complexes. Although the notation of the backdonation interaction is different in the two used Lewis structures (in case of 2c $\sigma(B$−$R) \rightarrow \sigma*(H$−$H)$ and in case of 3c2e $\sigma(B$−$R) \rightarrow \sigma*(B$−H−$H))$, they describe the same effect as evidenced by the similar values in the corresponding columns of Table 4.

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*The second order perturbative analysis of the orbital interactions provide stabilization energies relative to an idealized (high energy) Lewis structure, therefore these values are not directly comparable to complexation energies. Especially in case of lower quality Lewis structures these energies can be exaggerated, nevertheless their relative magnitude is expected to indicate trends in stabilization effects.

R	c_A^2 (B)	3c2e		2c		
		σ(B−R)→ σ*(B−H−H)	σ(B−H)→ σ*(B−H−H)	σ(H−H)→ 2p(B)	σ(B−R)→ σ*(B−H−H)	σ(B−H)→ σ*(B−H−H)
H	23.6%	22.4	3.5 3.5	389.4	22.4	3.5 3.5
CH₃	19.3%	0.0	10.1 10.1	265.2	0.0	10.1 10.1
CF₃	24.2%	0.0	12.2 12.2	426.0	0.0	12.2 12.2
CCl₃	22.9%	3.5	10.2 10.3	380.5	0.0	10.2 10.3
SiH₃	29.4%	36.9	5.1 5.1	625.5	37.3	5.1 5.1
SiF₃	29.4%	34.9	3.9 5.8	628.8	34.9	3.9 5.8
PH₂	23.6%	2.1	4.0 20.7	391.0	2.0	3.9 21.0
P(O)H₂	26.7%	3.6	2.7 23.6	501.5	3.6	2.7 23.6

Table 4.: Results of the NBO analysis of the $BH_2R−H_2$ side on complex. Data on the left side is obtained allowing the construction of 3c-2e bonds in the reference Lewis structure, while the right side is obtained allowing only 2c bonds. c_A^2 (B) denotes the percentage of the NBO on the boron atom. Interaction energies are given in kcal/mol

The σ(B−R) → σ*(B−H−H) interaction also influences the relative position of the H_2 unit over the H_2BR molecule. In Table 5. the position of the H−H bond was shown in case of different R substituents. In case of R = CH_3, CF_3, CCl_3 and P(O)H_2 the H−H bond was perpendicular to the B−R bond, while in case of SiH₃ and SiF₃ the two bonds were in an eclipsed position. An explanation to this behaviour is provided by the frontier molecular orbitals of the H_2BR molecules (Table 5). In all cases the LUMO orbital is the empty p-type orbital of the boron, facilitating the σ(H−H) → 2p(B) interaction in the complexes. The shape of the HOMO and HOMO-1 orbitals however depends on the R group, showing significant differences in the perpendicular and eclipsed cases. The symmetry of the HOMO of $H_2B−SiH_3$ and $H_2B−SiF_3$ provides m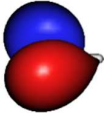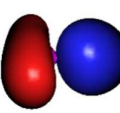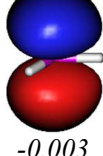aximal interaction with a σ*(H−H) orbital if the H−H bond is parallel with the B−Si bond, while the HOMO of $H_2B−CH_3$ prefers a perpendicular orientation. In case of R = CF_3 the proximity of the fluorine lone pairs hinders the interaction with the HOMO, forcing the H−H bond to interact instead of the HOMO-1, resulting again in a perpendicular orientation. In $H_2B−PH_2$ the position of the phosphorus lone pair deactivates the interaction with the HOMO. The degeneracy of the HOMO and HOMO-1 in the BH_5 molecule enables the efficient interaction in both orientations, manifesting in the extremely low rotational barrier of the H_2 unit[15].
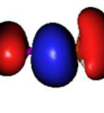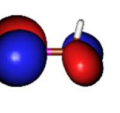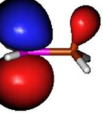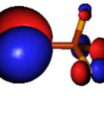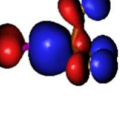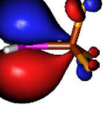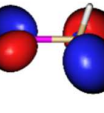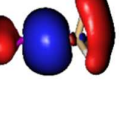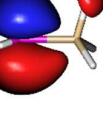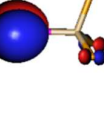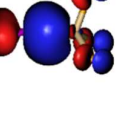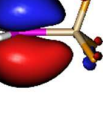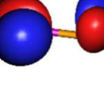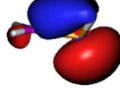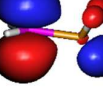
R substituents stabilizing the H_2/BH_2R complexes can be found with both perpendicular (CF_3) and eclipsed (SiH₃, SiF₃) orientations, however the CF_3 group shows only marginal stabilization compared to the BH_5 molecule. Based on the strong

electron withdrawing property of this group we would expect an increased $\sigma(H-H) \rightarrow 2p(B)$ donation, however NBO interaction energies of the corresponding orbitals show only a slight increase (Table 4). The inductive effect of the CF_3 group however is only effective in the σ system, as evidenced by the orbital energies (Table 5). The increased stability of the $R = SiH_3$ and $R = SiF_3$ complexes can be contributed to the backdonation from the $Si-R$ bonds, supported by the augmented $\sigma(B-R) \rightarrow \sigma^*(B-H-H)$ interaction energies. The $\sigma(H-H) \rightarrow 2p(B)$ interaction also shows a significant increase. The synergistic behaviour can be explained by the destabilizing effect of the backdonation on the $H-H$ bond: the weaker bond corresponds to a higher HOMO, making the donation to the empty $2p(B)$ orbital more effective. Furthermore an electron density relay similar to that described in ref. [21] can also increase the density on H_2 available for the σ donation. It is interesting to note that although the magnitude of the backdonation is much smaller, it regulates the larger $\sigma(H-H) \rightarrow 2p(B)$ interaction.

R	H_2 position	HOMO-1	HOMO	LUMO
		BH_2R		
H		*-0.438*	*-0.438*	*-0.003*
CH_3		*-0.419*	*-0.404*	*0.021*
CF_3		*-0.471*	*-0.444*	*-0.029*
SiH_3		*-0.415*	*-0.380*	*-0.020*
SiF_3		*-0.471*	*-0.424*	*-0.049*
PH_2				

|		HOMO-1	HOMO	LUMO
		-0.429	-0.345	-0.001
BHR₂				
SiH$_3$		-0.395	-0.361	-0.034
SiF$_3$		-0.464	-0.429	-0.085
BR₃				
SiH$_3$	-	-0.361	-0.360	-0.047
SiF$_3$		-0.442	-0.441	-0.114

Table 5.: HOMO-1, HOMO and LUMO orbitals of the starting materials.

Further stabilization of the complex can be attempted by replacing the remaining H atoms on boron. The obtained complex formation and Gibbs-free energies were calculated in the cases of BHR_2 and BR_3 ($R = SiH_3$ and SiF_3), and are shown in Table 6.

	SiH$_3$		SiF3	
	complex	penta valent	complex	penta valent
BH$_2$R	**-11.1/** *2.5*	-/-	**-13.9/** *-1.9*	-/-
BHR$_2$	**-14.3/** *-1.9*	**-25.2/** *-12.0*	**-19.7/** *-6.6*	**-31.5/** *-17.2*
BR$_3$	-/-	**-28.4/** *-13.0*	**-23.6/** *-11.2*	**-34.3/** *-21.1*

Table 6.: mono-, di- and trisubstituted adducts formation energies (**bold**) and Gibbs-free energies (*italics*) (energies in kcal/mol).

Compared to the monosubstituted complexes the di- and trisubstituted adducts have a deeper minimum on the potential energy surface, furthermore a new and energetically more stable minimum appears. In all cases the η^2-H_2 complex is transformed to a more stable pentavalent borane molecule where the hydrogen subunit completely decomposes, the hydrogens are located in the equatorial positions while the R groups prefer the axial positions (Scheme 2.).
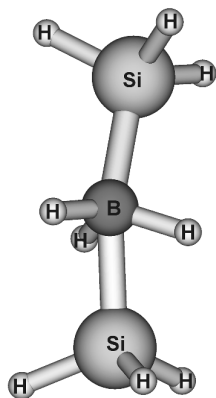
Scheme 2.: Disubstituted silylborane.

There are only a few examples of pentavalent borane compounds in the literature so far[26], however in these cases the boron atom is forced into the hypervalent structure by geometric constraints.

The stability of the pentavalent $H_2B(SiH_3)_3$ and $H_2B(SiF_3)_3$ compounds is remarkable (both possess negative Gibbs-free energies at room temperature, -13.0 and -21.1 kcal/mol respectively), however both substituent groups are highly reactive. In order to provide a feasible synthetic target the applicability of the less reactive $SiMe_3$ substituent was also investigated. (see Scheme 3.).
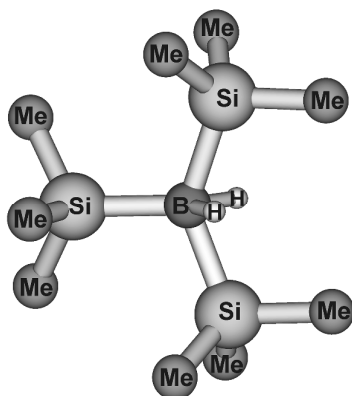
Scheme 3.: BTMS₃−H₂ side on coordinated complex.

In the case of tris(trimethylsilyl)borane the geometry of the molecule is trigonal bipyramid as in case of previously mentioned pentavalent derivatives. Furthermore the formation and Gibbs-free energy are -32.8 and -19.0 kcal/mol respectively.

Conclusion

NBO analysis shows that the stability of the η^2-H_2/BR_3 borane complexes - besides the well-known sigma donation from the hydrogen bond to the empty orbital of the boron also depends on another weaker but significant novel interaction, namely the electron donation from the B−R bond to the H−H σ^* orbital. These two complementary interactions can be influenced by different substituents on the boron. SiR_3 groups were found to stabilize the monosubstituted borane-H_2 adducts. Instead of the side-on coordinated structure the di- and trisubstituted silylborane adducts have trigonal bipyramidal shape and form a natural pentavalent molecule that is unusual among boranes.

Acknowledgements

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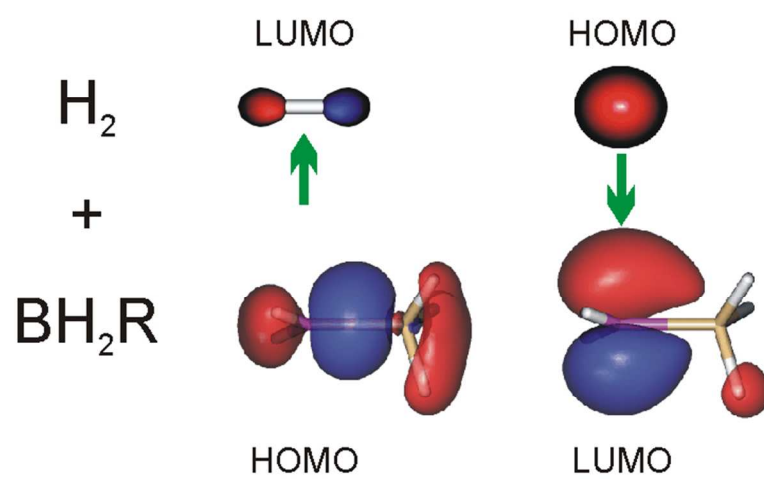
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