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Repeated Dihydrogen Elimination from Boranes and Gallanes Stabilized by Guanidine-Type Bases: A Quantum Chemical Study Motivated by Recent Experimental Results

Oxana Ciobanu[a] **and Hans-Jörg Himmel***[a]

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Monomeric boranes and gallanes stabilized by guanidine derivatives undergo in certain cases H_2 elimination reactions leading in a first step to dinuclear E(III) hydrides (E = B or Ga) and in the second step upon elimination of further H_2 to dinuclear compounds with the elements in the formal oxidation state +II featuring a direct E–E bond. The thermodynamics for such H_2 elimination reactions were calculated applying several methods and basis sets. In addition the calculations provide information about possible mechanisms. Thus the calculations suggest the first step to be an intramolecular H_2 elimination followed by a cycloaddition reaction. The second H_2 elimination, in which E–E and H–H bonds are formed at the expense of E–H bonds, is almost energy neutral, as anticipated from the small differences in electronegativity between E and H. The reaction barriers are important indicators to answer the question if H_2 elimination can be made reversible. Reversible H_2 elimination and addition would make this class of compounds in principle interesting for hydrogen storage applications, although obviously the weight percentage of stored dihydrogen is in the special systems presented herein not sufficient for mobile applications. The compounds can also be applied for dehydrocoupling and transfer hydrogenation to deliver a stoichiometric amount of H_2 to olefins. Finally, the possibility of elimination of a third H_2 leading to a dinuclear E(I) species with an E–E double bond is discussed.

Introduction

Guanidine derivatives have been widely used as ligands in main group and transition metal complexes.[1] Part of the interest in these compounds stems from their potential applications in catalytic reactions. They either bind as neutral ligands, or after H^+ abstraction as negatively charged guanidinate ligands. Two binding modes have been observed for the guanidinate ligand. Thus it can act as a bisdentate chelating ligand to one metal atom or as a bridging ligand to two metal atoms. $Cl_2Al\{(N\mathit{i}Pr)_2CN(CH_3)_2\}$ is an example in which the chelating binding mode is realized.[2] By the use of the guanidinate hpp⁻ (hppH = 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine) the bridging mode can be realized, the dinuclear compound $[(CH_3)_2Al(hpp)]_2$ being one authenticated representative.[2] The hpp ligand has also been proven to be efficient in bringing two transition metals close to another in dinuclear complexes so that they engage in direct and sometimes multiple metal–metal bonding. Examples include the complexes $Nb_2(hpp)_4$ [3] and $M_2(hpp)_4Cl_2$ (e.g. M = Ru,[4] W, Os and Pt [5]).

Recently we have studied the reaction of $H_3Ga{\cdot}NMe_3$ with hppH[6] leading directly to the dinuclear hydride $[H_2Ga(hpp)]_2$ (see Scheme 1). While we were so far not able to grow crystals of $[H_2Ga(hpp)]_2$ with a quality high enough for X-ray diffraction measurements, we obtained a crystal structure for its derivative $[HClGa(hpp)]_2$. The adduct $H_3Ga{\cdot}hppH$, which is likely to be the first intermediate in this reaction, is unstable under the applied reaction conditions, readily eliminates dihydrogen and dimerises. Our experiments show that $[H_2Ga(hpp)]_2$ is also stable only below room temperature and easily loses another molecule of H_2 at slightly elevated temperatures to give presumably the compound $[HGa(hpp)]_2$, featuring a Ga–Ga single bond and a *cis*-bent arrangement of the H–Ga–Ga–H fragment (see Scheme 2). The two Ga atoms are thus reduced from the formal oxidation state +III to the formal oxidation state +II. Thermodynamic considerations suggest that the combined Ga–Ga and Ga–H bonds established in the product are almost similar in strength than the combined Ga–H bonds of the reactant, in line with the small difference in electronegativity between Ga and H (1.82 and 2.20 on the Allred–Rochow scale, respectively). This dihydrogen elimination and Ga–Ga bond formation has stirred our interest because we previously have studied in matrix isolation experiments the uptake of dihydrogen by the matrix isolated Ga_2 dimer leading to Ga–Ga bond breakage and formation of the hydride $Ga(\mu\text{-}H)_2Ga$ (see Scheme 3).[7] The barrier for this reaction, as estimated experimentally from isotopic (H/D) measurements, amounts to not more than

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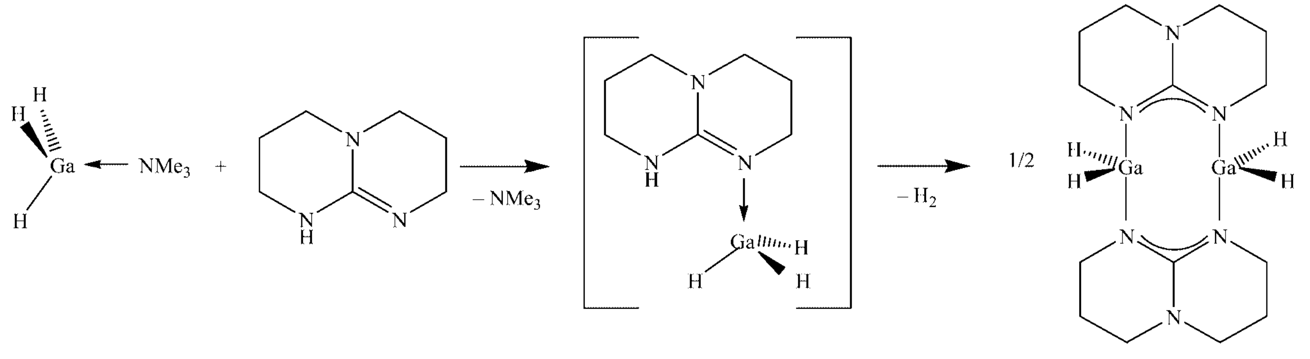
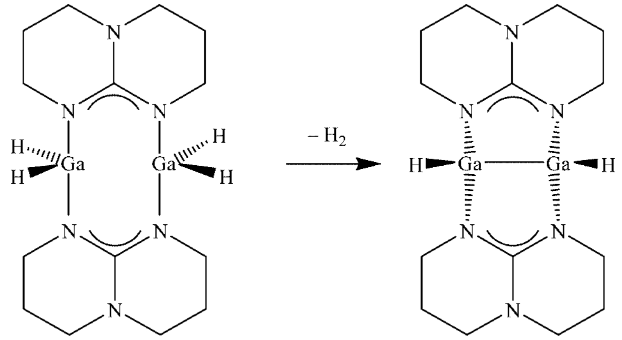
[a] Anorganisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg,
Im Neuenheimer Feld 270, 69120 Heidelberg, Germany
E-mail: hans-jorg.himmel@aci.uni-heidelberg.de

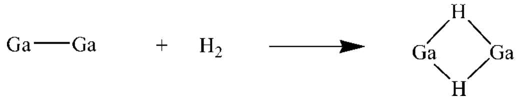


Scheme 1.

40 kJ mol^{-1}. The reaction of Ga_2 with H_2 to give Ga_2H_2 was calculated to be exothermic (–96 kJ mol^{-1}).[8] Thus, here again, like in the case of $[H_2Ga(hpp)]_2$, the combined Ga–Ga and H–H bonds, being now present in the reactants, are only slightly disfavoured over the two Ga–H–Ga three-center-two-electron bonds established in the product. If the barrier for H_2 addition in $[HGa(hpp)]_2$ is comparable with that found for the Ga_2 dimer, this class of dinuclear hydrides of group 13 elements is interesting for facile reversible H_2 activation. The compounds can certainly be applied for dehydrocoupling reactions and function as a transfer hydrogenation to deliver a stoichiometric amount of H_2 to olefins as was recently shown for $H_3B{\cdot}NHMe_2$.[9] Therefore it is highly desirable to get insight into the reaction mechanisms with the aid of quantum chemical calculations. In the following we report our work for B and Ga compounds.



Scheme 2.



Scheme 3.

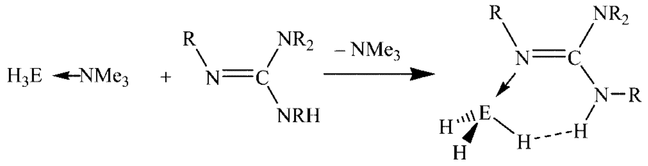
Results and Discussion

The presentation of the results and their discussion are divided into four sections. The first is concerned with the starting reagent, the adducts of guanidine and some of its derivatives to EH_3 (E = B or Ga), and the thermodynamics of their formation. In the second section intramolecular H_2 elimination facilitated by intramolecular H···H contacts in the adducts and subsequent dimerization to give dinuclear species is analysed. We will present a detailed mechanism for this important second step on the basis of our quantum chemical calculations. The third section deals with additional H_2 elimination to give the dinuclear group 13 element compounds featuring four-coordinate group 13 elements in the formal oxidation state +II and a direct E–E bond. Finally, the fourth section briefly discusses the possibility of further H_2 eliminination leading to a compound featuring two directly connected tri-coordinated E atoms in the formal oxidation state +I. Table 1 includes the reaction energies, with and without ZPE (zero-point vibrational energy) corrections, and the changes in the standard Gibbs energy, ΔG^0, for salient reactions discussed herein.

Step 1. Formation and Structural Characterization of the Adducts of EH_3 to Guanidine-Type Bases

Recent experimental work by us has shown that these adducts are either the end-products or reactive intermediates formed in the course of the reaction between $H_3E{\cdot}NMe_3$ and guanidine-type bases (see Scheme 4), depending on the possibilities for intramolecular HH bonding and subsequent H_2 elimination.[10] The adducts could generally also be synthesized from $LiGaH_4$ and guanidine·HCl. However, herein only the base-exchange route is discussed which is more straightforward to calculate and was used in most of the experimental work carried out in our group. Table 1 compares the changes in energy and Gibbs energy accompanied by reaction between the model compounds $H_3E{\cdot}NH_3$ (E = B, Ga) and guanidine or its derivatives 1,1,3,3-tetramethylguanidine and hppH. To test the accuracy of our calculational method, we have compared the crystallographically obtained dimensions of the adduct $H_3Ga{\cdot}N(H)C(NMe_2)_2$ [10] with those calculated (see Table 2 and Figure 1). It can be seen that the general level of agreement is pleasing. According to our calculations, the B–N distances in $H_3B{\cdot}NH_3$, $H_3B{\cdot}N(H)C(NH_2)_2$, $H_3B{\cdot}N(H)C(NMe_2)_2$ and $H_3B{\cdot}hppH$ measure 165.4, 158.6, 159.2, and 159.0 pm. The Ga–N distances in the corresponding Ga hydrides were calculated to be 218.0, 207.8, 209.1 and 206.8 pm, respectively. The experimentally determined Ga–N bond length for $H_3Ga{\cdot}N(H)C(NH_2)_2$ measures 198.81(19) pm. For comparison, Ga–N distances of

206.3(4), 208.1(4), 207.9(3), and 204.24(18) pm were measured in H_3Ga·quinuclidine,[11] $H_3Ga·NMe_3$,[12] $H_3Ga·NHMe_2$,[13] and $H_3Ga·NH_2Me$.[14] Thus the guanidine-type bases lead to relatively short E–N bonds, in agreement to our recent experimental X-ray diffraction results for $H_3Ga·N(H)C(NMe_2)_2$ and in line with the stronger basicity of guanidines in comparison to amines.[10] An important structural detail concerning the reactivity of adducts such as $H_3E·N(H)C(NH_2)_2$ and H_3E·hppH is the short H···H contacts established between one or two of the negatively polarised H atoms attached to E and a positively polarised H atom attached to one of the amido groups. Thus in $H_3B·N(H)C(NH_2)_2$ and H_3B·hppH, H···H separations of 175.5 and 162.5 pm are adopted. In the corresponding Ga species, the H···H separations measure 177.1 and 173.7 pm, respectively. These contacts are significantly shorter than the range of 200–240 pm normally prescribed for unconventional dihydrogen bonding of this sort.[15] For comparison, in $[H_2GaNH_2]_3$ [16] and $[H_3AlN(H)Me_2]_2$ [13] intermolecular H···H contacts of 197(2) and 192.5(1.9) pm, respectively, were measured. Particular attention was given to the intermolecular H···H contacts in crystalline $H_3B·NH_3$, which were determined in neutron diffraction experiments to be 202 pm.[17] Work on these H···H contacts has been spurred by the search for hydrogen storage materials.[18] The contacts are the reason for the generally lower thermal stability of these compounds in the solid state in comparison to the solution. In adducts such as $H_3E·N(H)C(NMe_2)_2$, there is no possibility for intramolecular HH bonding. The analysis of the crystal structure shows, however, that intermolecular HH contacts are established [with shortest H···H contacts of 210(5) pm].[10] Due to the absence of intramolecular H···H interactions, this experimentally verified molecule can be used as reference system to roughly estimate the strength of the H···H contacts in other adducts. As expected, formation of 1,1,3,3-tetramethylguanidine borane and gallane is slightly exothermic [energies of –19 and –18 kJ mol^{-1}, respectively, were calculated (see Table 1)]. Formation of $H_3E·N(H)C(NH_2)_2$ is significantly more exothermic (reaction energies of –35 and –30 kJ mol^{-1}, respectively). The difference in the energy change for reactions to give the adducts of guanidine and 1,1,3,3-tetramethylguanidine should at least partially be caused by the HH bonds which can only be established in the guanidine complex. Thus, as a first estimate, the H···H contacts in $H_3B·N(H)C(NH_2)_2$ should be ca. 12–16 kJ mol^{-1} strong. For comparison, the intermolecular H···H bonds in crystalline $H_3B·NH_3$ (with a larger bond length of 202 pm [17]) were calculated to be in average ca. 13 kJ mol^{-1} strong.[19] These results demonstrate the importance of intramolecular H···H interactions in the adducts.



Scheme 4.

Table 1. Energy changes (in kJ mol^{-1}) without (ΔE) and with (ΔE_{ZPE}) zero-point vibrational energy corrections, and changes in the standard Gibbs energy ΔG^0 (also in kJ mol^{-1}) as calculated for important reactions discussed in this work (fmr = four-membered ring).

Reaction	ΔE	ΔE_{ZPE}	ΔG^0
$HNC(NH_2)_2 + H_3B·NH_3 \rightarrow H_3B·N(H)C(NH_2)_2 + NH_3$	–35	–42	–38
$HNC(NMe_2)_2 + H_3B·NH_3 \rightarrow H_3B·N(H)C(NMe_2)_2 + NH_3$	–19	–25	–19
hppH + $H_3B·NH_3 \rightarrow H_3B$·hppH + NH_3	–48	–55	–47
$HNC(NH_2)_2 + H_3Ga·NH_3 \rightarrow H_3Ga·N(H)C(NH_2)_2 + NH_3$	–30	–35	–29
$HNC(NMe_2)_2 + H_3Ga·NH_3 \rightarrow H_3Ga·N(H)C(NMe_2)_2 + NH_3$	–18	–21	–14
hppH + $H_3Ga·NH_3 \rightarrow H_3Ga$·hppH + NH_3	–42	–46	–39
$H_3B·N(H)C(NH_2)_2 \rightarrow H_2B(\mu\text{-}NH)_2CNH_2$ (fmr) + H_2	+62	+34	+8
$H_3B·N(H)C(NH_2)_2 \rightarrow H_2B{=}N(H)(CNH_2)NH$ (diene) + H_2	+63	+36	+9
H_3B·hppH $\rightarrow H_2B$(hpp) (fmr) + H_2	+70	+46	+14
H_3B·hppH $\rightarrow H_2B$(hpp) (diene) + H_2	+74	+46	+17
$H_3Ga·N(H)C(NH_2)_2 \rightarrow H_2Ga(\mu\text{-}NH)_2CNH_2$ (fmr) + H_2	+25	+4	–5
H_3Ga·hppH $\rightarrow H_2Ga$(hpp) (fmr) + H_2	+22	+1	–25
$2\ H_3BN(H)C(NH_2)_2 \rightarrow \{H_2B[HNC(NH_2)NH]\}_2 + 2\ H_2$	–76	–113	–113
$2\ H_3B(\text{hppH}) \rightarrow [H_2B(\text{hpp})]_2 + 2\ H_2$	–35	–72	–70
$2\ H_3GaN(H)C(NH_2)_2 \rightarrow \{H_2Ga[HNC(NH_2)NH]\}_2 + 2\ H_2$	–74	–110	–109
$2\ H_3Ga(\text{hppH}) \rightarrow [H_2Ga(\text{hpp})]_2 + 2\ H_2$	–38	–75	–65
$\{H_2B[HNC(NH_2)NH]\}_2 \rightarrow \{HB[HNC(NH_2)NH]\}_2$ (planar) + H_2	+171	+148	+119
$\{H_2B[HNC(NH_2)NH]\}_2 \rightarrow \{HB[HNC(NH_2)NH]\}_2 + H_2$	+74	+46	+19
$[H_2B(\text{hpp})]_2 \rightarrow [HB(\text{hpp})]_2 + H_2$	+32	+1	–30
$\{H_2Ga[HNC(NH_2)NH]\}_2 \rightarrow \{HGa[HNC(NH_2)NH]\}_2 + H_2$	+7	–7	–33
$[H_2Ga(\text{hpp})]_2 \rightarrow [HGa(\text{hpp})]_2 + H_2$	+5	–18	–49
$\{HB[HNC(NH_2)NH]\}_2 \rightarrow \{B[HNC(NH_2)NH]\}_2 + H_2$	+254	+231	+202
$[HB(\text{hpp})]_2 \rightarrow [B(\text{hpp})]_2 + H_2$	+90	+68	+39

Table 2. Comparison between calculated and observed bond lengths (in pm) for 1,1,3,3-tetramethylguanidine-gallane (see Figure 1 for the atomic numbering).

Bond length	Exp.[a]	BP/TZVPP	MP2/TZVPP
Ga–N1	198.81(19)	209.1	206.1
Ga–H	161(4)	159.4	157.7
	149(4)	158.9	156.8
	157(4)	159.0	157.0
N1–C1	131.6(3)	131.6	130.7
N1–H	78(3)	101.9	101.0
C1–N2,3	134.7(3)	137.0	135.5
	136.0(3)	138.2	136.7
N2,3–C2,5	145.5(3)	145.5	144.6
	145.7(3)	146.0	145.0
	145.8(3)	145.9	144.9
	144.8(3)	146.0	145.0

[a] From ref.[10]

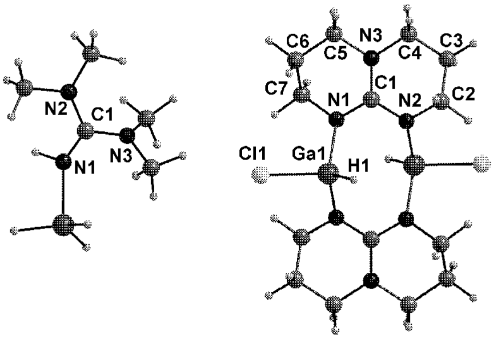


Figure 1. Molecular structures of 1,1,3,3-tetramethylguanidine gallane (left side) and $[HClGa(hpp)]_2$ (right side) as determined by X-ray diffraction.

Step 2. Intramolecular H_2 Elimination Followed by Dimerization to Give Dinuclear Hydrides

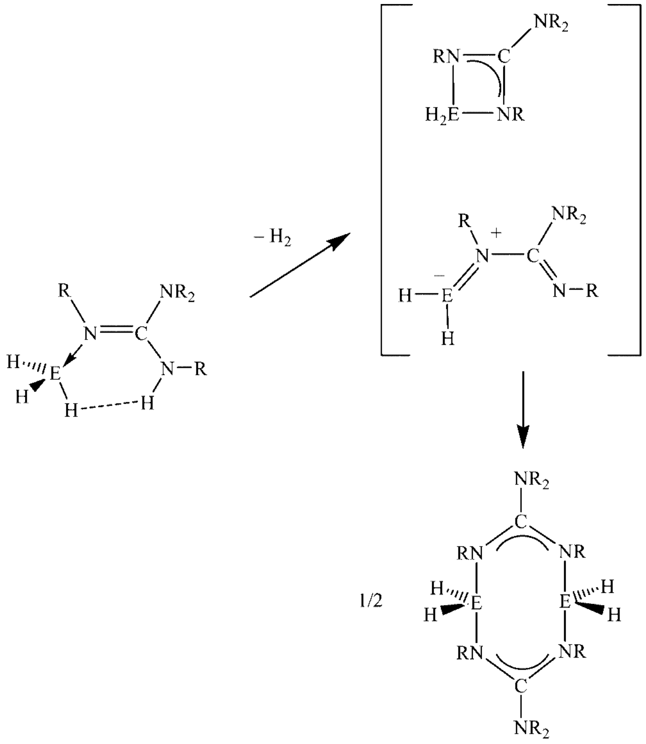
The relatively strong intramolecular H···H interactions in the adducts of hppH and $HNC(NH_2)_2$ to EH_3 argue for facile H_2 elimination, in full agreement to the body of experimental results accumulated for this class of compounds in our laboratory. The final products of these first H_2 elimination reactions are dinuclear species featuring an eight-membered ring in which all four E–N bond lengths are almost equally long (156.9–157.2 and 199.1–199.5 pm in $\{H_2E[HNC(NH_2)NH]\}_2$, 157.8 and 200.3 pm in $[H_2E(hppH)]_2$ (E = B and Ga, respectively). They have also in common an approximately tetrahedral coordination of the group 13 element atoms. E.g. in $[H_2Ga(hpp)]_2$, the H–Ga–H, N–Ga–H and N–Ga–N angles are 123.4°, 101.4°/109.5° and 111.0°, respectively. To test the accuracy of the calculations, the calculated structure for the dimer $[HClGa(hpp)]_2$ was compared to the one determined from X-ray diffraction analysis (see Table 3). From Table 3 comparing the bond lengths it can be seen that the general level of agreement is satisfying. In agreement to our experimental findings, the overall reactions were in all cases calculated to be exothermic (see Table 1). E.g. in the case of $\{H_2B[HNC(NH_2)NH]\}_2$, a reaction energy of –76 without and –113 kJ mol^{-1} with ZPE corrections was calculated. ΔG^0 for this reaction amounts to –113 kJ mol^{-1}. The experiments indicate that the barrier for this second step is not very high. What can be said about the exact mechanism for this process?

Table 3. Comparison between calculated and observed bond lengths (in pm) for $[HClGa(hpp)]_2$ (see Figure 1 for the atomic numbering).

Bond length	Exp.[a]	BP/TZVPP	MP2/TZVPP
Ga1–Cl1	220.15(15)	225.0	225.2
Ga1–N1	194.2(4)	198.5	199.0
Ga1–N4	192.8(4)	198.4	198.9
Ga1–H1	147(5)	156.3	156.8
N1–C1	135.3(6)	135.0	135.4
N1–C7	146.8(6)	146.6	146.5
C1–N2	134.7(6)	135.0	135.3
C1–N3	133.5(6)	136.8	137.6
N2–C2	147.8(7)	146.5	146.5
C2–C3	151.1(10)	152.6	153.0
C3–C4	150.7(8)	152.4	152.7
C4–N3	148.3(6)	146.8	146.9
N3–C5	147.3(6)	146.8	146.9
C5–C6	152.0(7)	152.3	152.7
C6–C7	151.2(7)	152.6	153.0

[a] From ref.[6] Note that the molecule has a center of inversion.

At least two intermediates have to be considered (see Scheme 5).[20] The first one features a four-membered EN_2C ring and can be described as a guanidinate complex to EH_2 in which the guanidinate unit adopts a bidentate chelating coordination mode [e.g. $H_2E(\mu\text{-}NH)_2CNH_2$ for reaction with guanidine]. These intramolecular H_2 eliminations represent endothermic processes (see Table 1). However, for the B compounds they are more endothermic than for the Ga homologues. Thus formation of $H_2B(\mu\text{-}NH)_2CNH_2$ is ac-



Scheme 5.

companied by an energy change of +62 without and +34 kJ mol^{-1} with ZPE corrections. However, with +8 kJ mol^{-1} the ΔG^0 value is very small. In the case of formation of the four-membered ring species $H_2B(hpp)$, the energies without and with ZPE are +70 and +46 kJ mol^{-1}, and ΔG^0 amounts to not more than +14 kJ mol^{-1}. For Ga compounds, formation of the four-membered ring compounds is even associated with a negative ΔG^0 value [–5 kJ mol^{-1} for $H_2Ga(\mu\text{-}NH)_2CNH_2$ and –25 kJ mol^{-1} for $H_2Ga(hpp)$].

For E = B, the four-membered ring is in equilibrium with a diene structure featuring a B=N double bond, e.g. $H_2E{=}N(H)C(NH_2){=}NH$ (E = B or Ga, see reaction Scheme 5). For E = Ga, the diene represents no minimum on the potential energy surface, in line with the lower tendency of Ga to form multiple bonds. The energy of the four-membered ring structure is by not more than 1 kJ mol^{-1} favored over the diene-type intermediate in the case of $H_2B{=}N(H)C(NH_2){=}NH$, and 4 kJ mol^{-1} in the case of $H_2B(hpp)$. Figure 2 shows the barrier separating the model diene $H_2B{=}N(H)C(NH_2){=}NH$ from the four-membered ring $H_2B(\mu\text{-}NH)_2CNH_2$. The energy barrier amounts to +56 kJ mol^{-1}, and the difference in Gibbs energy between diene and transition state is +57 kJ mol^{-1} under standard conditions. The diene is characterized by B–H and B–N bond lengths of 119.3/120.0 and 141.0 pm; the N–C single bond and the C–N double bond measure 141.8 and 128.0 pm, respectively. The B atom is by 295.9 pm separated from the next N atom. At the transition state, the two shortest B–N distances measure 149.4 and 222.3 pm, and the B–H and B–N bond lengths were calculated to be 119.8/120.3 and 149.4 pm, respectively. With 130.7 and 137.3 pm, the two shortest C–N distances are much closer together. Finally, in the four-membered ring, B–H, B–N, and N–C bond lengths of 121.1, 161.1, and 134.0/133.5 pm are adopted.

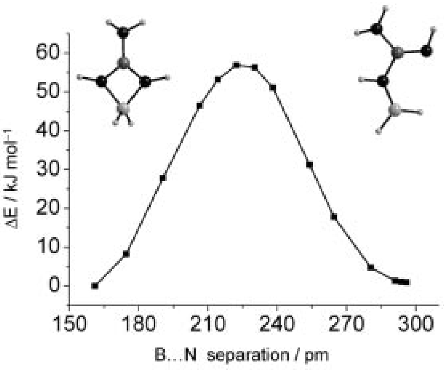


Figure 2. Energy (in kJ mol^{-1}) for conversion of the diene structure into the four-membered ring structure relative to that of the diene $H_2BN(H)C(NH_2)NH$ in dependence of the B···N separation.

Figure 3 illustrates the mechanism for intramolecular H_2 abstraction starting from the precursor $H_3B{\cdot}N(H){=}C(NH_2)_2$ and leading first to the diene structure. The transition state is reached at an H–H distance between the two eliminated H atoms of 82.0 pm. The B–N distances at this point measure 151.3 and 268.0 pm. The reaction barrier is calculated to be 97 kJ mol^{-1} high. There is an abrupt change in the H–H distance after the transition state has been passed. Abrupt energy changes at the point of formation of a significant H···H interaction are typical for H_2 elimination reactions. We observed these abrupt changes also in the case of H_2 elimination from the monomeric hydrides H_2ECl (E = Al, Ga or In), which can be generated in matrix isolation experiments from photolytically induced reaction between ECl and H_2.[21] The diene afterwards undergoes a [4+4] cycloaddition to give the dinuclear hydride.

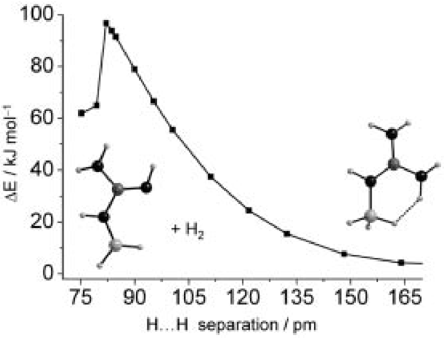
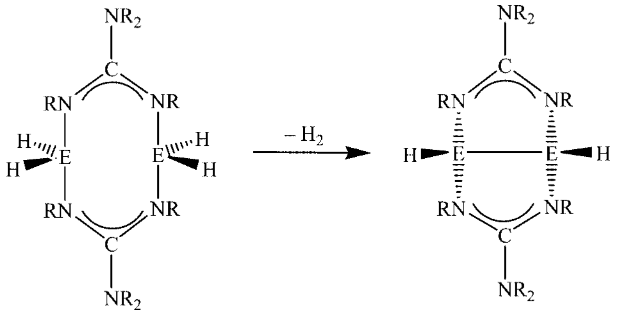


Figure 3. Relative energy (in kJ mol^{-1}) for intramolecular H_2 elimination from the adduct $H_3B{\cdot}N(H)NC(NH_2)_2$ leading to the diene structure in dependence of the H···H separation.

Step 3. Further H_2 Elimination to Give Dinuclear Compounds with the Group 13 Elements in the Formal Oxidation State +II

The body of experimental results accumulated in our group shows that yet another H_2 molecule can be eliminated (see Scheme 6). The products of this H_2 elimination, $\{HE[HNC(NH_2)(NH)]\}_2$ and $[HE(hpp)]_2$, are dinuclear compounds with group 13 elements in the formal oxidation state +II and a direct E–E bond. The H–E–E–H fragment adopts a *cis*-bent arrangement. The E–E distances were calculated to be 178.1 (E = B) and 242.1 pm (E = Ga) in $HE[HNC(NH_2)NH]\}_2$. In $[HE(hpp)]_2$, E–E distances of 175.3 (E = B) and 237.6 pm (E = Ga) are adopted.

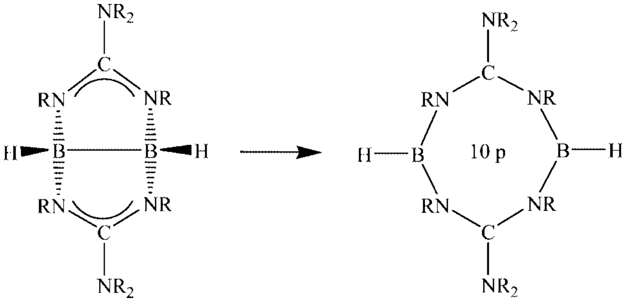


Scheme 6.

Thus the E–E distances lie in a region typical for E–E single bonds (e.g. 172 pm (B_2F_4),[22] 170.2 pm (B_2Cl_2),[23] 168.9 pm (B_2Br_4),[24] and 240.6 pm (Ga_2Cl_4·2 dioxane),[25] 252.5 pm $Ga_2(tmp)_4$ (tmp = 2,2,6,6-tetramethylpiperidino).[26] For the E–H distances the calculations returned 121.9 and 157.5 pm in the case of $\{HE[HNC(NH_2)NH]\}_2$, and 122.4–122.8 and 158.0 pm for $[HE(hpp)]_2$. Finally, the E–N distances are 158.0–158.2 (E = B) and 202.7 pm (E = Ga) for $\{HE[HNC(NH_2)NH]\}_2$, and 158.2–158.4 (E = B) and 203.4 pm (E = Ga) for $[HE(hpp)]_2$. Thus the E–N distances are in all cases almost identical to those established in the molecules prior to H_2 elimination, although there are some major structural changes.

H_2 elimination in all cases comes out to be endothermic, but only very weakly. The small reaction energies are in line with the small differences in electronegativity between B, Ga and H (electronegativity values of 2.01, 1.82 and 2.20, respectively, following the Allred-Rochow scale). As a consequence, ΔG^0 is negative for the formation of $\{HGa[HNC(NH_2)(NH)]\}_2$ and $[HE(hpp)]_2$ (E = B or Ga). Thus for $[H_2Ga(hpp)]_2$, BP/TZVPP calculations predict H_2 elimination to be accompanied by an energy change of not more than +5 kJ mol^{-1}. With –49 kJ mol^{-1}, the ΔG^0 value is significantly negative.

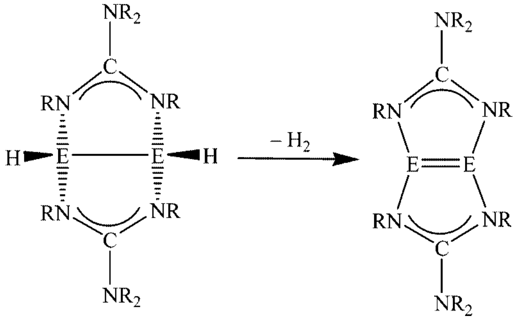
Finally, it is worth mentioning that for $\{HB[HNC(NH_2)NH]\}_2$, the calculations found another energy minimum (exhibiting C_{2h} symmetry) on the potential energy surface. This minimum, with an energy exceeding that of the global minimum by almost 100 kJ mol^{-1} (see Table 1), features a planar, eight-membered ring consisting of four N, two B and two C atoms (see Scheme 7). There are 10 π electrons in the ring, a situation comparable to that in the aromatic $[C_8H_8]^{2-}$ dianion. The planarity indeed argues for at least partial delocalization of the π electrons. The distances within the ring vary (from ca. 136/137 pm for the NC bonds to ca. 144 pm for the BN bonds). In ongoing work we seek to stabilize this energetically disfavoured structure by coordination to a metal fragment.



Scheme 7.

Step 4. Final H_2 Elimination to Give Dinuclear E(I) Molecules

Although so far we have observed no signs of further H_2 elimination in our experiments, calculations were carried out for E = B to answer the question if these reactions might be possible. It has been shown previously by other groups that tetra(amino)diboranes(4) such as bis(dimethylamino)bis(pyrrolyl)diborane(4) or bis(dimethylamino)bis(indolyl)diborane(4) can be reduced with lithium powder to give the corresponding dilithium tetra(amino)diborates.[27] These diborates feature short B–B bond lengths [e.g. 158.4(4) pm for dilithium bis(dimethylamino)bis(indolyl)diborate] which can be described as double bonds.[28] The B_2N_4 moiety is planar, in line with the double bond description (Scheme 8). The B–B distances in $\{B[HNC(NH_2)NH]\}_2$ and $[B(hpp)]_2$ were calculated to be 159.3 and 158.7 pm, respectively and are thus also significantly shorter than those in $\{HB[HNC(NH_2)NH]\}_2$ and $[HB(hpp)]_2$ (see Figure 4). The angle sum at each of the B atoms is 343°, and the B–N distances measure 148.5 pm. With energy changes of +254 and +90 kJ mol^{-1} for formation of $\{B[HNC(NH_2)NH]\}_2$ and $[B(hpp)]_2$, respectively, the reactions are endothermic, and the ΔG^0 values are positive (see Table 1).



Scheme 8.

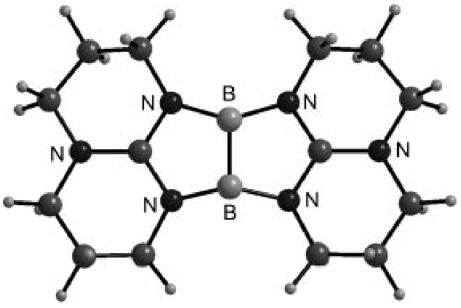
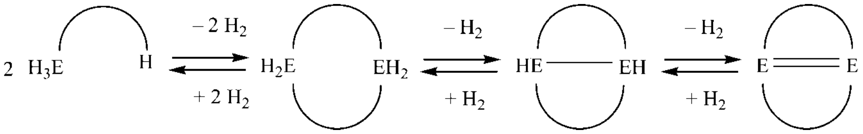


Figure 4. Molecular structure of $[B(hpp)]_2$.

Conclusions

Quantum chemical calculations were carried out to shed light on the mechanisms of repeated H_2 elimination reactions of guanidine-stabilized group 13 element hydrides as recently observed in our laboratory. These repeated H_2 eliminations and the possibility of reversibility under mild conditions make this class of compounds attractive for applications in the fields of (i) catalysed dehydrocoupling reactions and transfer hydrogenation for olefins, and (ii) possibly also molecular hydrogen storage materials. The reactions found for this special class of compounds (hydrides



Scheme 9.

stabilized with guanidine-type bases) are examples for more general systems as illustrated in reaction Scheme 9, in the central step of which E–E and H–H bonds are formed at the expense of E–H bonds. If E has an electronegativity close to that of H, the reaction should be thermodynamically favoured. In Figure 5 the reaction sequence starting with $H_3Ga{\cdot}hppH$ is shown.[29] The standard Gibbs energy changes for almost all H_2 elimination steps are slightly negative. The bulk of our experimental results accumulated for this class of compounds and to some extent also the quantum chemical calculations presented herein show that the reaction barriers are relatively low (H_2 elimination is already observed at temperatures between 25 and 100 °C, depending on the starting adduct).

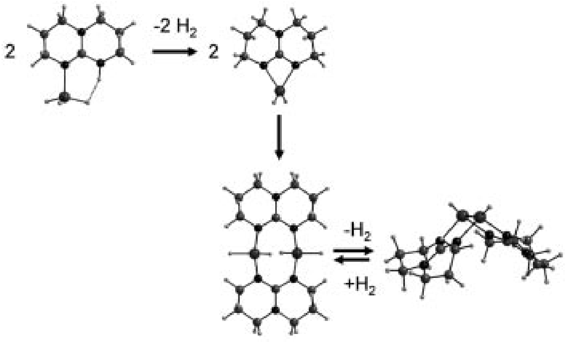


Figure 5. Repeated H_2 eliminations starting with the adduct $H_3Ga{\cdot}hppH$.

The calculations provide important details about each of the elimination steps. Relatively strong intramolecular H···H contacts are present in the starting compounds, adducts of the general formula $H_3E{\cdot}N(R)C(NR'R'')(NR'''H)$ (R–R''' being organic groups). These interactions facilitate elimination of a first H_2 molecule. Our experimental results agree with the quantum chemical calculations that the product of this H_2 elimination is a dinuclear hydride featuring an eight-membered ring. Two possible intermediates were discussed. In the case of boron compounds, a diene intermediate is preferred, which subsequently undergoes a [4+4] cycloaddition. The diene is in equilibrium to a second intermediate, which can be described as a H_2E fragment to which a chelating guanidinate is coordinated, leading to a four-membered ENCN ring. For Ga compounds, the diene structure does not represent an energy minimum on the potential energy surface, but could nevertheless play an important role in the mechanism. The eight-membered ring compounds can eliminate another H_2 molecule in a redox-reaction leading to molecules with two fused five-membered rings and direct E–E bonds between E atoms in the formal oxidation state +II. This process is slightly endothermic. However, the negative sign of ΔG^0 calculated for most of these reactions means that these reactions are generally spontaneous. The experimental results accumulated for this class of compounds indicate that the barrier for these H_2 elimination reactions is not very high so that the chances for reversibility under mild conditions are high. In a final H_2 elimination dinuclear B(I) species with a B–B double bond could be formed. However, ΔG^0 for this process is already positive. We are currently exploring the potential applications of this class of hydrides and similar classes of compounds for dehydrocoupling reactions and hydrogen storage. They certainly can be used highly efficiently for hydrogenation of olefins in the presence of a catalyst.

Computational Details

Quantum chemical calculations were carried out with the TURBOMOLE program package.[30] The structures and corresponding energies of all molecules were optimized using the DFT functional BP86 (BP is the short notation for Becke–Perdew and is a non-local DFT method employing the Becke exchange and Perdew correlation functionals) in combination with a TZVPP (triple-zeta valence, doubly-polarized) basis set.[31] Table 1 includes the reaction energies with and without zero point vibrational corrections (ZPE, calculated with BP86/SVP) together with the standard Gibbs energy changes, ΔG^0, for all relevant reactions.

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