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Repeated Dihydrogen Elimination from Amidine Adducts of Group 13 Element Hydrides: An Evaluation of the Reaction Pathways

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Dinuclear η^2,μ^2-bonded amidinate complexes to group 13 element hydrides are of potential interest for applications in the field of hydrogen storage. In this work repeated dihydrogen elimination starting with amidine-stabilized boron, aluminum, and gallium hydrides is discussed on the basis of quantum chemical calculations which give useful information about the thermodynamic properties of these reactions and the possible reaction pathways in dependence of the chosen amidine derivative. It will be shown that, in agreement to recent experimental work, the thermodynamic properties are greatly influenced by the nature of the substituents bonded to the amidine. The amidine stabilized hydrides first eliminate dihydrogen in an intramolecular process leading to mononuclear amidinate complexes. These complexes could dimerize, if the amidine carries not too bulky organic groups, to give dinuclear complexes featuring two η^2,μ^2-coordinated amidinate ligands. Further dihydrogen elimination leads to the generation of a dinuclear species with two group 13 elements (E) in the formal oxidation state +II and direct E–E bonding. Finally, elimination of another H_2 for E = B possibly gives amidinate complexes featuring a double bond between two boron atoms in the formal oxidation state +I.

Introduction

We recently studied the reaction between $H_3Ga{\cdot}NMe_3$ and the guanidine derivative hppH (1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine). This reaction leads at 0 °C directly to the dinuclear compound $[H_2Ga(hpp)]_2$.[1] According to quantum chemical calculations, the mechanism for this reaction includes (i) formation of the adduct $H_3Ga{\cdot}hppH$, (ii) intramolecular H_2 elimination to give the intermediate $H_2Ga(hpp)$, and (iii) dimerization. $H_2Ga(hpp)]_2$ itself is only stable at temperatures below 25 °C and slowly eliminates another H_2 molecule at 25 °C to presumably afford the dinuclear Ga(II) species $[HGa(hpp)]_2$ featuring a direct Ga–Ga bond. Meanwhile we also repeated the reaction with $H_3B{\cdot}NMe_3$ and obtained crystal structures of the adduct $H_3B{\cdot}hppH$ as well as the dinuclear B(II) compound $[HB(hpp)]_2$.[2] The barrier for H_2 elimination from $[H_2E(hpp)]_2$ (E = B or Ga; see reaction Scheme 1 in Figure 1) is low, and the reaction appears to be reversible under mild conditions. Therefore, guanidinate bridged dinuclear hydrides of boron are in principle interesting for applications in the field of molecular hydrogen storage. Although the hpp ligands carry too much weight, it might be possible to design lighter examples realizing a similar concept.

In this work we seek to extend our analysis to amidinate complexes of some group 13 element hydrides. Thermodynamic data are extremely important to judge on the suitability of these compounds in potential applications. Reactions between $H_3Al{\cdot}NMe_3$ and the bulky amidines ArNC(H)N(H)Ar (HFiso) and ArNC(*t*Bu)N(H)Ar (HPiso), Ar being 2,6-diisopropylphenyl, have recently been studied,[3] and dinuclear hydrides of the formula $H_2Al(Fiso)]_2$ and $[H_2Al(Piso)]_2$ were found to be the products. However, in the case of HFiso, two Fiso $[HC(NAr)_2]$ ligands bridge the two Al atoms, while, with the more sterically encumbered HPiso, the two Piso $[tBuC(NAr)_2]$ ligands prefer a chelating binding mode. With the Fiso ligand, it was even possible to prepare a monomeric stable In hydride, namely $InH(Fiso)_2$.[4] On the other hand,

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(1) It was possible to obtain crystals suitable for X-ray diffraction of the Cl derivative $[HClGa(hpp)]_2$. See: Robinson, G.; Tang, C. Y.; Köppe, R.; Cowley, A. R.; Himmel, H.-J. *Chem.*—Eur. J. **2007**, *13*, 2648–2654.

(2) $[HB(hpp)]_2$ can be prepared by reaction between hppH and $H_3B{\cdot}NMe_3$ at 110 °C.

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10.1021/ic700653z CCC: $37.00

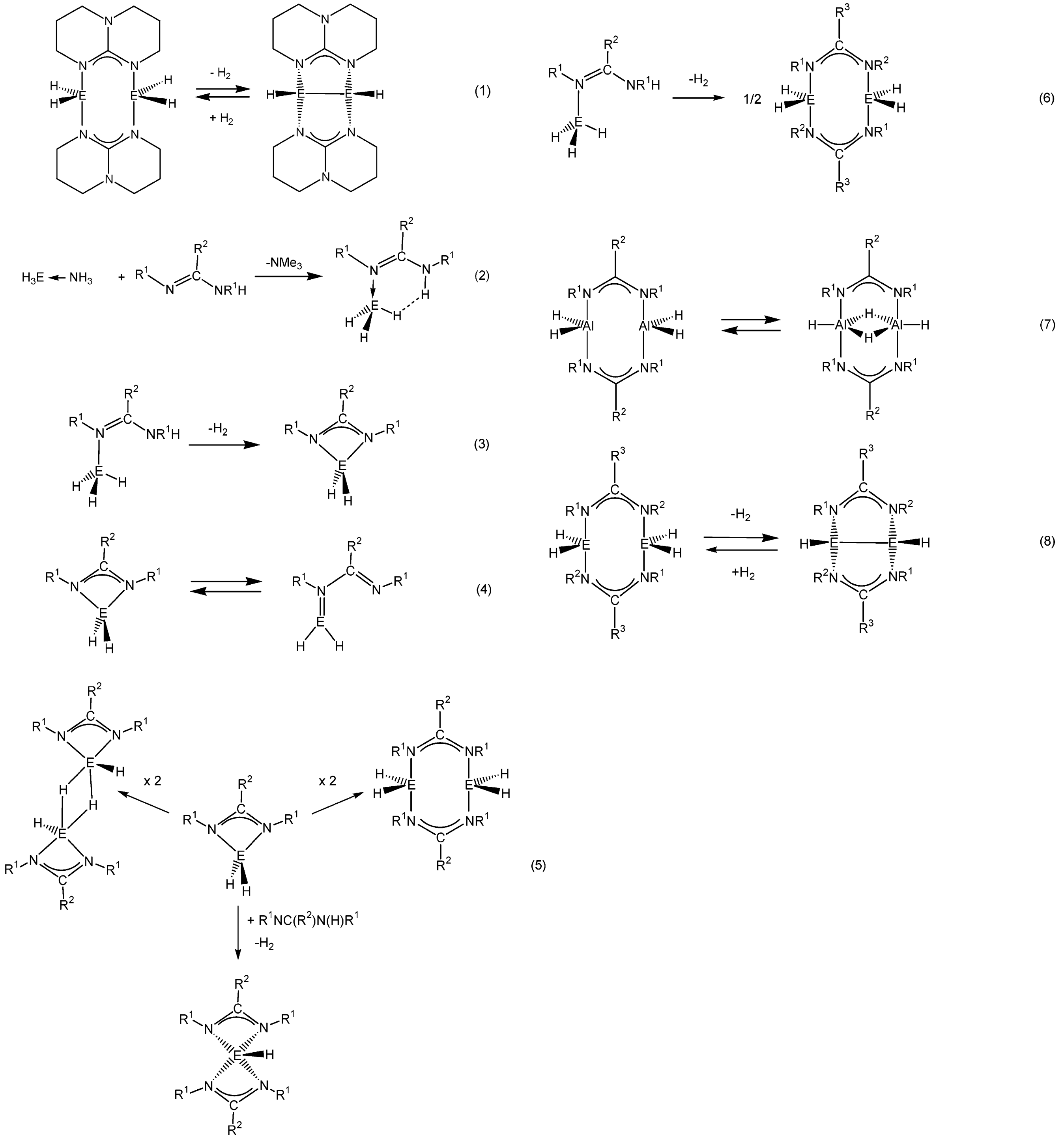

Figure 1. Reaction equations for the reactions discussed in this work.

1:1 adducts of amidines to H_3E, which should represent the first intermediates in these reactions, have not yet been isolated.

Results and Discussion

The discussion should start with the structures of the free amidines. It follows an evaluation of the adduct formation with group 13 element hydrides (step 1), intramolecular dihydrogen elimination followed by cyclization and/or dimerization (step 2), further dihydrogen elimination (step 3) to give dinuclear species featuring two group 13 elements in formal oxidation states of +II which are directly connected to each other in diamagnetic compounds, and finally, only for E = B, dihydrogen elimination to give dinuclear B(I) species featuring a B=B double bond.

Structures of the Free Amidines. Reactions of six different amidines were analyzed. These are the parent compound HNC(H)NH$_2$, the methyl derivatives HNC(Me)-NH$_2$, MeNC(H)N(H)Me, and HNC(H)NMe$_2$, and the bulky amidines PhNC(H)N(H)Ph and PhNC(*t*Bu)N(H)Ph (see Figure 2). The latter two differ from the amidines HFiso and HPiso, which have been used previously in experimental

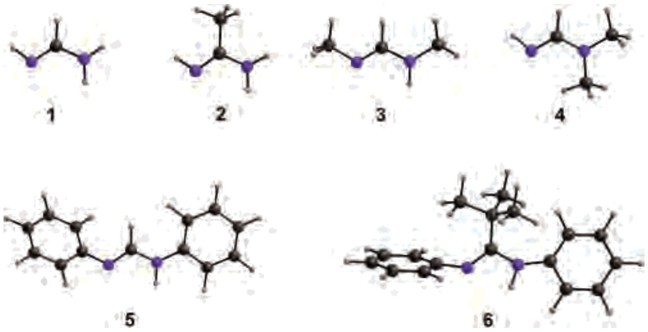

Figure 2. Optimized structures (BP86/TZVPP) for the free amidines $H_3E{\cdot}N(H)C(H)NH_2$ (**1**), $H_3E{\cdot}N(H)C(Me)NH_2$ (**2**), $H_3E{\cdot}N(Me)C(H)N(H)Me$ (**3**), $H_3E{\cdot}N(H)C(H)N(Me)_2$ (**4**), $H_3E{\cdot}N(Ph)C(H)N(H)Ph$ (**5**), and $H_3E{\cdot}N(Ph)C(tBu)N(H)Ph$ (**6**).

Figure 3. Optimized structures (BP86/TZVPP) for the adducts $H_3B{\cdot}N(Ph)C(H)N(H)Ph$, and $H_3B{\cdot}N(Ph)C(tBu)N(H)Ph$.

work,[3] only by substitution of the phenyl rings by two isopropyl groups in positions 2 and 6. Table 1 (in which the amidines are numbered **1**−**6**) summarizes some salient parameters obtained for the free amidines, which will be shown to undergo some changes upon coordination. $HNC(H)NMe_2$ comes out to be slightly more stable than $MeNC(H)N(H)Me$ (by 4 kJ mol^{-1} without and 3 kJ mol^{-1} with ZPE corrections and by a Gibbs energy which is 3 kJ mol^{-1} smaller).

Step 1: Formation of the Amidine Adducts to Group 13 Element Hydrides. Table 2 compares the changes in energy and standard Gibbs energy as calculated for reactions leading from ammonia adducts of EH_3 (E = B, Al, or Ga) to several different adducts of amidines [namely $H_3E{\cdot}N(H)C(H)NH_2$, $H_3E{\cdot}N(H)C(Me)NH_2$, $H_3E{\cdot}N(Me)C(H)N(H)Me$, $H_3E{\cdot}N(H)C(H)NMe_2$, $H_3E{\cdot}N(Ph)C(H)N(H)Ph$, and $H_3E{\cdot}N(Ph)C(tBu)N(H)Ph$; see reaction Scheme 2 in Figure 1, Figure 3, and Table 3). The standard Gibbs energy changes for all these base exchange reactions were calculated to be negative, showing the greater tendency of group 13 element hydrides for adduct formation with an amidine in comparison to an amine. Nevertheless, a quantitative inspection reveals important differences. In all adducts except of $H_3B{\cdot}N(H)C(H)NMe_2$ intramolecular $H\cdots H$ contacts are established between one of the H atoms attached to the group 13 element and an H atom of the amido group (see reaction Scheme 2 in Figure 1). The BP86/TZVPP method was tested by calculations on the interaction between two $H_3B{\cdot}NH_3$ molecules (head-to-tail dimer). We obtained the following bond distances (in pm) and bond angles (in deg): B−N 163.1; B−H 122.3 (pointing toward the second molecule, two B−H) and 121.3 (pointing away, one B−H); N−H 103.8 (pointing toward the second molecule, one N−H) and 102.3 (pointing away, two N−H); shortest $H\cdots H$ 198.3 (4 interactions); $B-H\cdots H$ 87.8; $N-H\cdots H$ 145.5. These values are in good agreement with those calculated previously using other methods.[5] The $H\cdots H$ contacts lower the energy of the adduct, and as a consequence, the reactions leading to $H_3E{\cdot}N(H)C(H)NMe_2$ adducts are less exothermic compared with the other reactions. From a comparison between the reaction energies calculated for formation of $H_3E{\cdot}N(H)C(H)NMe_2$ with those of $H_3E{\cdot}N(H)C(H)NH_2$ and other adducts to methyl derivatives of the parent amidine, the strength of the $H\cdots H$ contacts can be estimated to be ca. 20 kJ mol^{-1}. The distances of the shortest $H\cdots H$ contacts decrease in the order $H_3E{\cdot}N(H)C(H)NH_2 > H_3E{\cdot}N(H)C(Me)NH_2 > H_3E{\cdot}N(Me)C(H)N(H)Me > H_3E{\cdot}N(Ph)C(H)N(H)Ph > H_3E{\cdot}N(Ph)C(tBu)N(H)Ph$. Despite the short $H\cdots H$ contacts, formation of the sterically crowded adducts $H_3E{\cdot}N(Ph)C(H)N(H)Ph$ and $H_3E{\cdot}N(Ph)C(tBu)N(H)Ph$ is energetically less favored. This can be explained by (i) conformational changes of the phenyl groups and the N−C−N angle between the free amidine and the adduct (see Table 3 and Figure 3) and (ii) the relatively large E−N bond distances in the $H_3E{\cdot}N(Ph)C(H)N(H)Ph$ and $H_3E{\cdot}N(Ph)C(tBu)N(H)Ph$ adducts (see Table 3). The E−N bond distances are generally comparable to those found in amine adducts to group 13 element hydrides [e.g., in the quinuclidine adducts $H_3E{\cdot}N(CH_2CH_2)_3CH$, representing examples of relatively strong bonding, E−N bond distances of 160.8(5) (E = B),[6] 199.1(4) (E = Al),[7] and 206.3(4) pm (E = Ga)[8] were measured in the crystalline phase]. We already showed in a previous work that the BP86 method gives relatively accurate values for the Ga−N bond fragmentation and dissociation energies.[9] Thus, the BP86 method in combination with a relatively large basis set should also

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Table 1. Salient Parameters (Bond Distances in pm, Bond Angles in deg) As Calculated for Uncoordinated Amidines[a]

param	**1**	**2**	**3**	**4**	**5**	**6**
N=C	128.3	128.7	127.8	128.8	128.7	128.8
C−N	137.3	138.4	137.3	136.9	136.9	141.1
N−H	102.2	102.4		102.3		
N−H	101.6/101.1	101.5/101.4	101.8		101.8	101.9
N−C−N	122.0	119.0	123.1	123.1	120.3	110.6

[a] See also Figure 2 for the numbering. Compound key: **1**, $H_3E\cdot N(H)C(H)NH_2$; **2**, $H_3E\cdot N(H)C(Me)NH_2$; **3**, $H_3E\cdot N(Me)C(H)N(H)Me$; **4**, $H_3E\cdot N(H)C(H)N(Me)_2$; **5**, $H_3E\cdot N(Ph)C(H)N(H)Ph$; **6**, $H_3E\cdot N(Ph)C(tBu)N(H)Ph$.

Table 2. Reaction Energies (in kJ mol^{-1}, with and without ZPE Corrections) and ΔG^0 (at 1 bar, 298 K) As Calculated for the Formation of Amidine Adducts to Group 13 Element Hydrides

reacn	ΔE	ΔE_{ZPE}	ΔG^0
$H_3B\cdot NH_3 + HNC(H)NH_2 \rightarrow H_3B\cdot N(H)C(H)NH_2 + NH_3$	−36	−42	−38
$H_3B\cdot NH_3 + HNC(Me)NH_2 \rightarrow H_3B\cdot N(H)C(Me)NH_2 + NH_3$	−42	−49	−45
$H_3B\cdot NH_3 + MeNC(H)N(H)Me \rightarrow H_3B\cdot N(Me)C(H)N(H)Me + NH_3$	−43	−48	−44
$H_3B\cdot NH_3 + HNC(H)NMe_2 \rightarrow H_3B\cdot N(H)C(H)NMe_2 + NH_3$	−12	−16	−12
$H_3B\cdot NH_3 + PhNC(H)N(H)Ph \rightarrow H_3B\cdot N(Ph)C(H)N(H)Ph + NH_3$	−16	−23	−20
$H_3B\cdot NH_3 + PhNC(tBu)N(H)Ph \rightarrow H_3B\cdot N(Ph)C(tBu)N(H)Ph + NH_3$	−16	−23	−20
$H_3Al\cdot NH_3 + HNC(H)NH_2 \rightarrow H_3Al\cdot N(H)C(H)NH_2 + NH_3$	−35	−38	−33
$H_3Al\cdot NH_3 + HNC(Me)NH_2 \rightarrow H_3Al\cdot N(H)C(Me)NH_2 + NH_3$	−41	−46	−43
$H_3Al\cdot NH_3 + MeNC(H)N(H)Me \rightarrow H_3Al\cdot N(Me)C(H)N(H)Me + NH_3$	−38	−41	−34
$H_3Al\cdot NH_3 + HNC(H)NMe_2 \rightarrow H_3Al\cdot N(H)C(H)NMe_2 + NH_3$	−16	−18	−10
$H_3Al\cdot NH_3 + PhNC(H)N(H)Ph \rightarrow H_3Al\cdot N(Ph)C(H)N(H)Ph + NH_3$	−14	−18	−13
$H_3Al\cdot NH_3 + PhNC(tBu)N(H)Ph \rightarrow H_3Al\cdot N(Ph)C(tBu)N(H)Ph + NH_3$	−15	−20	−16
$H_3Ga\cdot NH_3 + HNC(H)NH_2 \rightarrow H_3Ga\cdot N(H)C(H)NH_2 + NH_3$	−26	−29	−25
$H_3Ga\cdot NH_3 + HNC(Me)NH_2 \rightarrow H_3Ga\cdot N(H)C(Me)NH_2 + NH_3$	−31	−36	−32
$H_3Ga\cdot NH_3 + MeNC(H)N(H)Me \rightarrow H_3Ga\cdot N(Me)C(H)N(H)Me + NH_3$	−30	−33	−28
$H_3Ga\cdot NH_3 + HNC(H)NMe_2 \rightarrow H_3Ga\cdot N(H)C(H)NMe_2 + NH_3$	−7	−10	−3
$H_3Ga\cdot NH_3 + PhNC(H)N(H)Ph \rightarrow H_3Ga\cdot N(Ph)C(H)N(H)Ph + NH_3$	−8	−13	−8
$H_3Ga\cdot NH_3 + PhNC(tBu)N(H)Ph \rightarrow H_3Ga\cdot N(Ph)C(tBu)N(H)Ph + NH_3$	−9	−15	−12

be able to reproduce the thermodynamic properties calculated for $H_3B\cdot NH_3$ and $H_3Al\cdot NH_3$.[10]

Step 2: Intramolecular H_2 Elimination Followed by Cyclization. The short H···H contacts lower the activation barrier for intramolecular H_2 elimination. It has been shown that complexes with chelating (η^2-bonded) amidinate ligands are possible products or intermediates of these reactions (see reaction Scheme 3 in Figure 1, Figure 4, and Table 4). The N−C−N angles in these complexes are significantly smaller than in free amidines, especially for the B compounds, where the angle decreases to not more than 99° in $tBuC(NPh)_2BH_2$. Other calculated bond distances and angles are summarized in Table 5 and can be compared to parameters experimentally measured in some derivatives. Thus, in $\{PhC[N(SiMe_3)]_2\}BBr_2$, the B−N and N−C bond distances measure 155.9(4) and 133.9(8) pm, respectively, and the N−B−N and N−C−N bond angles were determined to be 85.2(3) and 104.0(3)°.[11] This compares with Ga−N and N−C bond distances of 204.7(6)/203.1(6) and 133.6(9)/131.9(9) pm and N−Ga−N and N−C−N bond angles of 64.7(2) and 110.6(7)° as determined for the amidinate complex $[PhC(NPh)_2]GaMe_2$.[12] In $[AlH(\mu\text{-}H)(Piso)]_2$, Al−N and N−C bond distances of 192.0(2)/197.0(2) and 135.5(3)/133.4(3) pm were measured,[3] and the N−C−N and N−Al−N bond angles amount to 107.3(2) and 67.64(8)°. H_2 elimination followed by cyclization is generally an endothermic process for amidine adducts to boron and gallium hydrides. The only exception is the very bulky amidine $PhNC(tBu)N(H)Ph$, for which these processes were calculated to be exothermic. In the case of the amidine adducts to aluminum hydride, all reactions are exothermic.

For E = B, the four-membered ring is in equilibrium with a diene-type structure featuring a B=N and a C=N double bond (see reaction Scheme 4 in Figure 1). $H_2BN(H)C(H)NH$ exhibits an energy 10 kJ mol^{-1} without and 8 kJ mol^{-1} with ZPE corrections lower than the four-membered ring form. ΔG^0 for conversion of the four-membered ring into the diene-type form amounts to −10 kJ mol^{-1}. However, so far there is no experimental evidence for a molecule of this sort in the diene-type structure.

Reaction Scheme 5 (see Figure 1) shows three possible reactions starting with the monomeric amidinate complex. There are experimental indications for all three of them, depending on the nature of the amidinate ligand. Reaction with a second amidine leads to mononuclear bis(amidinate) complexes featuring five-coordinated group 13 element atoms. These reactions were shown to occur with bulky amidinates and E = Al, Ga,[3] and In,[4] leading to stable hydrides even in the case of In. In the case of $R^1 = R^2 = H$, the reactions were calculated to be exothermic for E = B, Al, and Ga. However, the value calculated for E = Al sticks out ($\Delta G^0 = -89$ for Al and −25 and −26 kJ mol^{-1} for E = B and Ga, respectively), which can be explained by the greater tendency of Al in comparison to B and Ga for five-coordination. In Figure 5 the structures as calculated for B and Al are illustrated. It can be seen that, in the case of B, only one of the ligand adopts a chelating η^2-bonding mode,

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Table 3. Bond Distances (in pm) and Angles (in deg) As Calculated for Amidine Adducts to Group 13 Element Hydrides (**1**−**6**)[a]

param	**1**	**2**	**3**	**4**	**5**	**6**
E = B						
H···H	189.8	186.3	181.7	208.5[b]	170.0	169.0
B−H	123.3	123.4	123.1	122.3	123.1	123.7
B−H	122.3	122.4	122.4	122.2	122.0	122.2
B−H	121.3	121.4	121.5	121.7	121.0	120.8
B−N1	158.0	157.7	158.5	159.9	159.7	161.1
N1═C	130.1	130.7	130.3	130.6	131.3	132.8
C−N	134.3	134.9	134.1	134.5	134.2	136.8
N2−H	102.3/100.9	102.4/101.1	102.6		103.1	103.6
B−N1−C	124.8	125.4	122.2	135.5	121.0	120.6
N1−C−N1	121.1	118.5	122.5	128.8	121.3	112.8
E = Al						
H···H	176.2	173.5	173.2	216.2[b]	164.3	157.6
Al−H	164.0	164.0	163.9	162.1	164.1	164.3
Al−H	161.0	161.0	161.1	161.7	160.9	161.1
Al−H	160.9	161.0	161.1	161.4	160.3	160.1
Al−N1	200.7	199.9	200.8	202.3	203.7	204.5
N1═C	130.4	131.1	130.4	130.7	131.4	132.6
C−N	133.7	134.4	133.9	134.2	134.1	136.7
N2−H	103.2/101.0	103.3/101.0	103.4		104.1	104.9
Al−N1−C	127.1	128.2	124.9	139.6	123.8	123.2
N1−C−N2	122.6	119.8	124.0	126.9	122.7	113.9
E = Ga						
H···H	182.3	179.8	177.7	224.9[b]	170.2	166.1
Ga−H	161.0	161.1	161.0	159.1	161.2	161.5
Ga−H	158.1	158.2	158.1	158.9	158.2	158.0
Ga−H	157.9	158.1	158.1	158.5	157.3	157.2
Ga−N1	208.6	207.7	208.8	211.4	212.3	214.2
N1═C	130.0	130.5	129.9	130.3	130.8	131.8
C−N2	134.1	134.8	134.2	134.5	134.5	137.4
N−H	102.7/100.9	102.7/101.0	103.1		103.6	104.0
Ga−N1−C	126.5	127.6	124.1	138.9	122.3	122.4
N1−C−N2	122.7	119.8	124.1	126.7	122.7	114.2

[a] Compound key: **1**, $H_3E\cdot N(H)C(H)NH_2$; **2**, $H_3E\cdot N(H)C(Me)NH_2$; **3**, $H_3E\cdot N(Me)C(H)N(H)Me$; **4**, $H_3E\cdot N(H)C(H)N(Me)_2$; **5**, $H_3E\cdot N(Ph)C(H)N(H)Ph$; **6**, $H_3E\cdot N(Ph)C(tBu)N(H)Ph$. [b] Value refers to the shortest EH···HC distance.

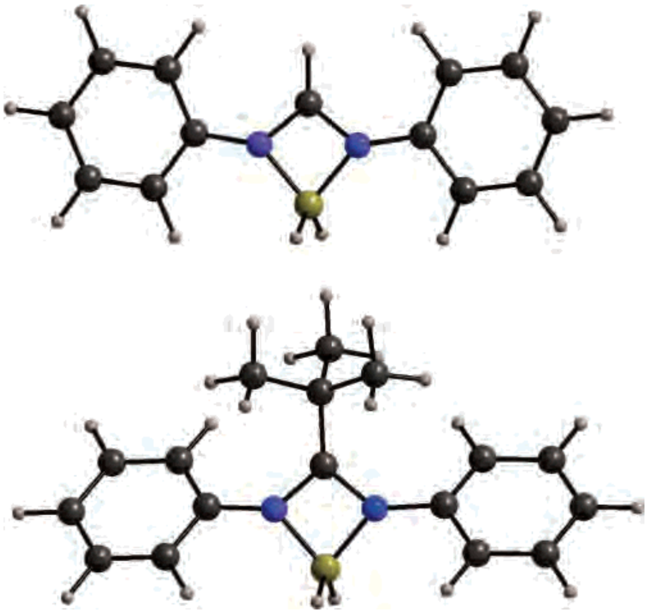

Figure 4. Optimized structures (BP86/TZVPP) for the η^2-coordinated amidinate complexes $HC(NPh)_2BH_2$ and $tBuC(NPh)_2BH_2$.

while the other prefers to be η^1-bonded. The Al as well as the Ga compounds adopt structures with two η^2-coordinated amidinate ligands. In agreement with the calculated structures, the N−E bond distances measured in $(Fiso)_2EH$ compounds (E = Al, Ga, and In) come out to be unequal. Thus, e.g., in $(Fiso)_2AlH$ each of the Fiso ligands establishes a short N−Al bond distance of 191.0(3) pm together with a longer one of 207.1(3) pm. The N−C bond distances adopt values in the range 129.5(4)−134.0(4) pm. The smallest N−Al−N bond angles are 66.49(12) and 66.88(12)°, and the N−C−N bond angles come out to be 112.1(3) and 114.3(3)°. Dimerization to give a dinuclear compound with two η^2,μ^1-chelating amidinate ligands and two bridging H atoms was observed for E = Al and the bulky amidinate Piso.[3] According to the calculations presented herein, bulky amidinates give the most stable η^2-coordinated amidinate complexes, and therefore, it is not surprising that in these cases the coordination mode remains unchanged upon dimerization. Quantum chemical calculations for the route to dimers with η^2,μ^1-coordination of the two amidinate moieties were not carried out in this work.

Step 3: Dimerization to Species with Two η^2,μ^2-Coordinated Amidinates. Depending on the amidinate and the group 13 element, the cyclic or the diene-type amidinate complexes could be intermediates on the way to dinuclear species featuring two η^2,μ^2-coordinated amidinates according to reaction Scheme 6 (see Figure 1). There is already experimental evidence for formation of such dimeric compounds. Thus, as early as 1978, the two derivatives $[MeC(NMe)_2AlMe_2]_2$ and $[MeC(NMe)_2GaMe_2]_2$ were structurally characterized by X-ray diffraction.[13] In $[MeC(NMe)_2AlMe_2]_2$,

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Table 4. Reaction Energies (in kJ mol^{-1}, with and without ZPE Corrections) and ΔG^0 (at 1 bar, 298 K) As Calculated for Intramolecular H_2 Elimination and Cyclization of Amidine Adducts to Group 13 Element Hydrides[a]

reacn	ΔE	ΔE_{ZPE}	ΔG^0
$H_3B{\cdot}N(H)C(H)NH_2 \rightarrow HC(NH)_2BH_2 + H_2$	+74	+46	+21
$H_3B{\cdot}N(H)C(Me)NH_2 \rightarrow MeC(NH)_2BH_2 + H_2$	+69	+41	+14
$H_3B{\cdot}N(Ph)C(H)N(H)Ph \rightarrow HC(NPh)_2BH_2 + H_2$	+36	+8	−18
$H_3B{\cdot}N(Ph)C(tBu)N(H)Ph \rightarrow tBuC(NPh)_2BH_2 + H_2$	−10	−37	−66
$H_3Al{\cdot}N(H)C(H)NH_2 \rightarrow HC(NH)_2AlH_2 + H_2$	−5	−27	−52
$H_3Al{\cdot}N(H)C(Me)NH_2 \rightarrow MeC(NH)_2AlH_2 + H_2$	−8	−30	−53
$H_3Al{\cdot}N(Ph)C(H)N(H)Ph \rightarrow HC(NPh)_2AlH_2 + H_2$	−23	−47	−64
$H_3Al{\cdot}N(Ph)C(tBu)N(H)Ph \rightarrow tBuC(NPh)_2AlH_2 + H_2$	−50	−73	−101
$H_3Ga{\cdot}N(H)C(H)NH_2 \rightarrow HC(NH)_2GaH_2 + H_2$	+28	+5	−19
$H_3Ga{\cdot}N(H)C(Me)NH_2 \rightarrow MeC(NH)_2GaH_2 + H_2$	+27	+4	−20
$H_3Ga{\cdot}N(Ph)C(H)N(H)Ph \rightarrow HC(NPh)_2GaH_2 + H_2$	+7	−17	−33
$H_3Ga{\cdot}N(Ph)C(tBu)N(H)Ph \rightarrow tBuC(NPh)_2GaH_2 + H_2$	−18	−41	−67
$HC(NH)_2BH_2 + HNC(H)NH_2 \rightarrow [HC(NH)_2]_2BH + H_2$	−24	−42	−25
$HC(NH)_2AlH_2 + HNC(H)NH_2 \rightarrow [HC(NH)_2]_2AlH + H_2$	−93	−108	−89
$HC(NH)_2GaH_2 + HNC(H)NH_2 \rightarrow [HC(NH)_2]_2GaH + H_2$	−27	−45	−26

[a] Further reactions of $HC(NH)_2EH_2$ with $HNC(H)NH_2$ are also considered.

Table 5. Bond Distances (in pm) and Angles (in deg) As Calculated for Several Amidinates of the General Formula $R^1C(NR^2)_2EH_2$ (R^1 = H, Me, *t*Bu; R^2 = H, Ph) and $[HC(NH)_2]_2EH$

param	$HC(NH)_2EH_2$	$MeC(NH)_2EH_2$	$HC(NPh)_2EH_2$	$tBuC(NPh)_2EH_2$	$[HC(NH)_2]_2EH$
			E = B		
B−H	120.9	121.0	120.8	121.3/120.9	120.3
B−N	160.5	160.1	160.5	158.8	161.3/165.0, 148.7
N−C	132.8	133.3	133.5	135.4	131.7/133.6, 128.7/137.2
H−B−H	116.0	115.7	116.5	115.9	
N−B−N	80.2	80.0	80.4	80.9	79.2
N−C−N	102.3	101.1	101.8	99.0	103.3, 123.3
			E = Al		
Al−H	159.7	159.9	159.5	159.7/160.2	159.8
Al−N	197.2	196.2	198.3	196.0	195.4/208.0
N−C	132.9	133.6	133.5	135.1	131.8/133.5
H−Al−H	121.4	120.6	122.2	121.5	
N−Al−N	68.0	68.0	67.8	67.7	63.2
N−C−N	112.1	110.5	111.9	107.8	113.4
			E = Ga		
Ga−H	156.8	156.9	156.5	156.9	156.2
Ga−N	204.6	203.6	206.2	203.8	198.9/221.4
N−C	132.5	133.2	133.1	134.9	131.3/133.4
H−Ga−H	126.1	125.4	127.2	126.0	
N−Ga−N	65.2	65.2	64.8	64.8	63.2
N−C−N	112.6	110.8	112.1	108.2	113.4

the Al−N and N−C (of the central NCN unit) bond distances amount to 192.8(1)/192.3(1) and 133.1(1)/132.9(1) pm, respectively. For $[MeC(NMe)_2GaMe_2]_2$, Ga−N and N−C (of the central NCN unit) bond distances of 198.1(4)/197.7(4) and 133.4(5)/133.7(6) pm were measured. More recently, the Al hydride $[AlH(\mu\text{-}H)(Fiso)]_2$ was synthesized and structurally characterized.[3] This molecule features two bridging H atoms to give five-coordination of the two Al atoms. The calculations in this work have to answer the questions if this structure is preferred for all amidinate complexes to group 13 element hydrides or if the isomer with four terminal E−H bonds is favored for some choice of R^1 and R^2 (see reaction Scheme 7 in Figure 1). For $[HC(NH)_2AlH_2]_2$, the structure with four terminal Al−H bonds indeed represents the global energy minimum. However, the structure in which two hydrogen atoms adopt bridging positions between the two Al atoms is energetically close by (see Table 6). The structure with four terminal Al−H bonds is slightly favored by 24 kJ mol^{-1} without and 29 kJ mol^{-1} with ZPE corrections, and the standard Gibbs energy comes out to be smaller by 34 kJ mol^{-1}. However, substitution of the two H atoms attached to the N atoms by phenyl groups changes the energetic order. Thus, the complex $[HC(NPh)_2AlH(\mu\text{-}H)]_2$ (see Figure 6) is by 11 kJ mol^{-1} without and 5 kJ mol^{-1} with ZPE corrections more stable than the $[[HC(NPh)_2AlH_2]_2$ form. The Gibbs energy is 2 kJ mol^{-1} smaller. This shows once again the effect substitution can have on the structure in these compounds.

In the case of the B and Ga compounds, our calculations found no minimum featuring bridging H atoms, in line with the lower tendency of B and Ga for five-coordination. Nevertheless, also for E = B two minima were found (the vibrational analysis returned no imaginary frequency), in which the B atoms are either on the same side (resembling a boat conformation) or opposite sides (resembling a chair conformation) (see Figure 6). Surprisingly, the boat-type structure is energetically favored by 26 kJ mol^{-1} (without) and 25 kJ mol^{-1} with ZPE corrections and exhibits a standard Gibbs energy which is 26 kJ mol^{-1} lower. The values quoted in Tables 6 and 8 refer to the boat-type structure.

Table 6. Reaction Energies (in kJ mol^{-1}, with and without ZPE Corrections) and ΔG^0 (at 1 bar, 298 K) As Calculated for H_2 Elimination Followed by Dimerization of Amidine Adducts to Group 13 Element Hydrides[a]

reacn	ΔE	ΔE_{ZPE}	ΔG^0
$2H_3B{\cdot}N(H)C(H)NH_2 \rightarrow [HC(NH)_2BH_2]_2 + 2H_2$	−84	−115	−117
$2H_3B{\cdot}N(H)C(Me)NH_2 \rightarrow [MeC(NH)_2BH_2]_2 + 2H_2$	−67	−100	−104
$2H_3B{\cdot}N(Ph)C(H)N(H)Ph \rightarrow [HC(NPh)_2BH_2]_2 + 2H_2$	−14	−78	−36
$2H_3Al{\cdot}N(H)C(H)NH_2 \rightarrow [HC(NH)_2AlH_2]_2 + 2H_2$	−156	−186	−188
$2H_3Al{\cdot}N(H)C(Me)NH_2 \rightarrow [MeC(NH)_2AlH_2]_2 + 2H_2$	−143	−174	−173
$2H_3Al{\cdot}N(Ph)C(H)N(H)Ph \rightarrow [HC(NPh)_2AlH(\mu\text{-}H)]_2 + 2H_2$	−92	−123	−120
$2H_3Ga{\cdot}N(H)C(H)NH_2 \rightarrow [HC(NH)_2GaH_2]_2 + 2H_2$	−84	−115	−114
$2H_3Ga{\cdot}N(H)C(Me)NH_2 \rightarrow [MeC(NH)_2GaH_2]_2 + 2H_2$	−69	−101	−101
$2H_3Ga{\cdot}N(Ph)C(H)N(H)Ph \rightarrow [HC(NPh)_2GaH_2]_2 + 2H_2$	−16	−54	−50
$[HC(NH)_2AlH_2]_2 \rightarrow [HC(NH)_2AlH(\mu\text{-}H)]_2$	+24	+29	+34
$[HC(NPh)_2AlH_2]_2 \rightarrow [HC(NPh)_2AlH(\mu\text{-}H)]_2$	−11	−5	−2

[a] Note that $[HC(NPh)_2AlH(\mu\text{-}H)]_2$, featuring two bridging H atoms, is by −11 kJ mol^{-1} without and −5 kJ mol^{-1} with ZPE corrections more stable than $[HC(NPh)_2AlH_2]_2$, featuring four terminal Al−H bonds. All other products prefer the structure with four terminal E−H bonds.

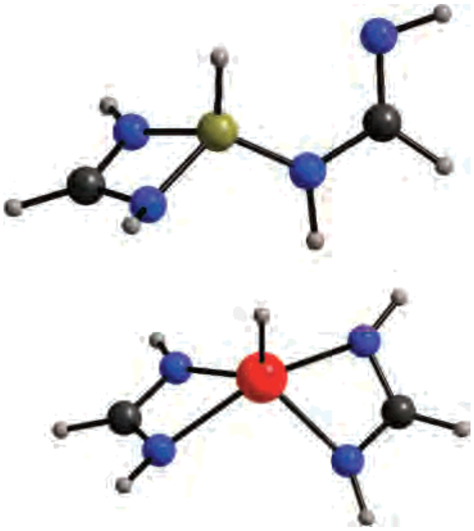

Figure 5. Optimized structures (BP86/TZVPP) for the bis(amidinate) complexes $[HC(NH)_2]_2BH$ with one η^2- and one η^1-coordinated amidinate and $[HC(NH)_2]_2AlH$ with two η^2-coordinated amidinates.

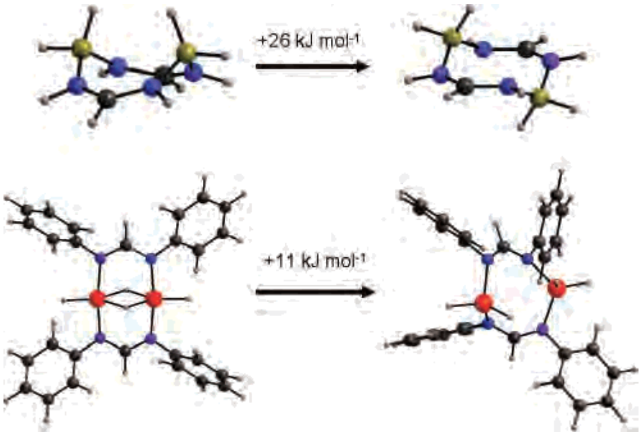

Figure 6. Optimized structures (with BP86/TZVPP) for the two conformers of $[HC(NH)_2BH_2]_2$ and $[HC(NPh)_2AlH_2]_2$.

Step 4: Further Dihydrogen Elimination. Elimination of a further molecule of H_2 represents a redox reaction in the course of which the two group 13 element atoms are reduced from the formal oxidation state +III to the formal oxidation state +II and a direct E−E bond is established (see reaction Scheme 8 in Figure 1 and Tables 7 and 9). Figure 7 illustrates the structure obtained for $[HC(NH)_2BH_2]_2$.

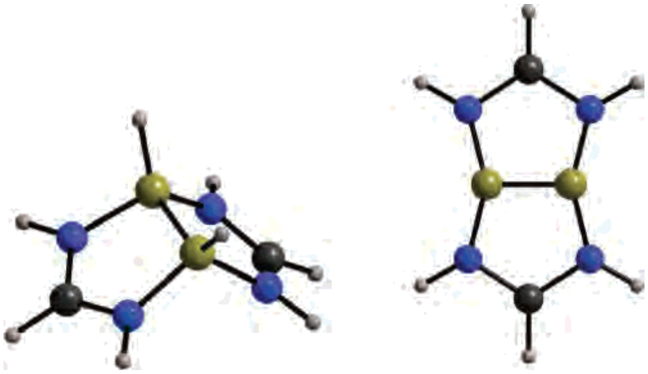

Figure 7. Optimized structures (BP86/TZVPP) for the dimeric compounds $[HC(NH)_2BH]_2$ and $[HC(NH)_2B]_2$.

This is a very interesting step which might be relevant for hydrogen storage. There are indications that the reaction is reversible in the case of the corresponding guanidinato complexes. H_2 elimination from $[HC(NH)_2BH_2]_2$ and $[HC(NH)_2AlH_2]_2$ comes out to be endothermic, and ΔG^0 at standard conditions is also positive. On the other hand, H_2 elimination from $[HC(NH)_2GaH_2]_2$ turns out to be exothermic. For comparison, ΔE for dihydrogen elimination in the guanidinates $[H_2NC(NH)_2BH_2]_2$ and $[H_2NC(NH)_2GaH_2]_2$ was calculated to be +74 and +7 kJ mol^{-1} without and +46 and −7 kJ mol^{-1} with ZPE corrections, and ΔG^0 at standard conditions amounts to +19 and −33 kJ mol^{-1}, respectively. These values are similar to those calculated for amidinate complexes, and therefore, it is highly likely that amidinate complexes can also be used as hydrogen storage materials. Calculations on the barrier for H_2 addition/elimination reactions are generally difficult since a dramatic energy change at the transition state is generally observed.[14] To obtain reliable energies, one therefore has to scan large areas of the potential energy surface. Nevertheless, we calculated the barrier for reaction 8 for E = B, Al, and Ga. The addition of H_2 to $\{[HC(NH)_2]EH\}_2$ comes out to be associated with energy barriers of 130, 122, and 137 kJ mol^{-1} for E = B, Al, and Ga, respectively.

In the case of the guanidinate complexes, H_2 elimination occurred in toluene solutions. To judge on the influence of solvation on reaction 8, additional calculations were carried

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(14) See, for example: Himmel, H.-J. *Dalton Trans.* **2002**, 2678. Himmel, H. J.; Klaus, C. *Z. Anorg. Allg. Chem.* **2003**, *629*, 1477−1483.

Table 7. Bond Distances (in pm) and Angles (in deg) As Calculated for Amidinates of the General Formula $[HC(NR)_2EH_2]_2$ (R = H, Ph; E = B, Al, Ga) and $[HC(NR)_2AlH(\mu\text{-}H)]_2$[a]

param	$[HC(NH)_2EH_2]_2$	$[HC(NH)_2AlH(\mu\text{-}H)]_2$	$[HC(NPh)_2EH_2]_2$	$[HC(NPh)_2AlH(\mu\text{-}H)]_2$
		E = B		
B−H	120.6−121.6		120.1−120.6	
B−N	157.6		158.1−159.8	
N−C	132.1		132.4−133.9	
N−B−N	111.0		108.3/112.3	
N−C−N	127.6		126.8/127.1	
		E = Al		
Al−H_t	159.2−160.9	161.0	159.1−159.8	159.0/159.1
Al−H_b		177.5−177.8		175.2−178.8
Al−N	194.8	197.3	197.5−198.3	201.4−202.1
N−C	132.3	132.5	132.6−133.2	133.0
N−Al−N	106.5	170.2	103.3/106.5	169.8/171.7
N−C−N	126.0	121.2	125.9/126.2	123.8
		E = Ga		
Ga−H	156.1−158.1		156.1−157.0	
Ga−N	200.7		203.6−204.7	
N−C	132.2		132.5−133.5	
N−Ga−N	104.0		101.3/104.0	
N−C−N	126.7		126.5/126.8	

[a] H_t and H_b denote terminal and bridging H, respectively.

Table 8. Reaction Energies (in kJ mol^{-1}, with and without ZPE Corrections) and ΔG^0 (at 1 bar, 298 K) As Calculated for H_2 Elimination of Dimeric Amidinates of the Formula $[HC(NH)_2EH_2]_2$ (E = B, Al, Ga)

reacn	ΔE	ΔE_{ZPE}	ΔG^0
$[HC(NH)_2BH_2]_2 \rightarrow [HC(NH)_2BH]_2 + H_2$	+81	+52	+28
$[HC(NH)_2AlH_2]_2 \rightarrow [HC(NH)_2AlH]_2 + H_2$	+59	+46	+23
$[HC(NH)_2GaH_2]_2 \rightarrow [HC(NH)_2GaH]_2 + H_2$	−6	−20	−44

Table 9. Bond Distances (in pm) and Angles (in deg) As Calculated for Amidinates of the General Formula $[HC(NH)_2EH]_2$ (E = B, Al, Ga)

param	$[HC(NH)_2BH]_2$	$[HC(NH)_2AlH]_2$	$[HC(NH)_2GaH]_2$
E−H	121.7	160.4	157.2
E−E	178.8	254.4	243.0
E−N	158.6	197.5	203.8
C−N	132.3	132.9	132.5
H−E−E	128.1	156.3	154.8
N−E−N	110.8	103.1	100.7
N−C−N	117.0	123.1	123.1

out for E = B with the COSMO program and using $\epsilon_r = 2.38$ for toluene. From these calculations, the energy change upon H_2 elimination from $[HC(NH)_2BH_2]_2$ in toluene at standard conditions was estimated to be +80 kJ mol^{-1}. $\Delta G_S{}^0$, the Gibbs energy change, is +28 kJ mol^{-1}, showing thus no difference with the gas-phase value, in line with the relative nonpolarity of the species involved.

Step 5: Final Dihydrogen Elimination. For E = B. the possibility of a last H_2 elimination should briefly be discussed. The product is a very interesting species, because it features a B═B double bond between two B atoms in the formal oxidation state +I. The reaction leading to $[HC(NH)_2B]_2$ is calculated to be endothermic (ΔE with and without ZPE corrections is +197 and +173 kJ mol^{-1}, respectively), and ΔG^0 is also positive (+144 kJ mol^{-1}). In our laboratory, we are currently studying the possibility of reducing the corresponding guanidinato complexes with Li powder and other reducing reagents.[15] Figure 7 illustrates the structure of the parent compound $[HC(NH)_2B]_2$. The B═B double bond comes out to be 158.6 pm long, a value which is in agreement to experimentally measured B═B double bonds[15,16] [e.g., 158.4(4) pm in dilithium bis(dimethylamino)bis(indolyl)diborate].[15] The B−N and N−C bond distances are 146.3 and 137.2 pm, and the N−B−N and N−C−N angles were calculated to be 147.8 and 113.4°. With 355.8°, the angle sum at each B atoms indicates an almost planar B_2N_4 skeleton, in line with the double-bond description. Very recently, the synthesis of $As_2\{\mu\text{-}(NAr)_2CR\}_2$ (Ar = 2,6-$iPr_2C_6H_3$ and R = $N(C_6H_{11})_2$ has been reported featuring an As═As double bond of 225.60(5) pm.[17] This molecule can be prepared by reduction of $RC(NAr)_2ECl_2$ with KC_8.

Conclusions

Dinuclear group 13 element hydrides in which the two group 13 elements are bridged by η^2,μ^2-amidinates represent a class of compounds which is of interest for applications in the fields of olefin hydrogenation and hydrogen storage. In this work the thermodynamic properties are analyzed for several relevant reactions starting with amidine stabilized group 13 element (B, Al, and Ga) hydrides. The quantum chemical calculations agree with previous experimental results that the reaction pathways strongly depend on the properties of the substituents on the amidine. Six different

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(15) Li powder has been used successfully for the synthesis of $Li_2[B_2(NR_2)_4$, where at least one of the R groups is or contains an aryl group. See: Nöth, H.; Knizek, J.; Ponikwar, W. *Eur. J. Inorg. Chem.* **1999**, 1931−1937.

(16) Earlier examples of molecules with boron−boron double bonds include tris(mesityl)phenyldiborate and 1,2-bis-(dimethylamino)-1,2-diphenyldiborate. See: Moezzi, A.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1992**, *114*, 2715−2717. Moezzi, A.; Bartlett, R. A.; Power, P. P. *Angew. Chem.* **1992**, *104*, 1075−1076; *Angew. Chem., Int. Ed.* **1992**, *31*, 1082−1083.

(17) Green, S. P.; Jones, C.; Jin, G.; Stasch, A. *Inorg. Chem.* **2007**, *46*, 8−10.

amidines were considered, namely the parent compound HNC(H)NH_2, the methyl derivatives HNC(Me)NH_2, MeNC(H)N(H)Me, and HNC(H)NMe_2, and the bulky amidines PhNC(H)N(H)Ph and PhNC(*t*Bu)N(H)Ph. Relatively strong intramolecular EH···HN contacts (measuring approximately 20 kJ mol^{-1}) are established in these adducts [except of $H_3E\cdot N(H)C(H)NMe_2$], lowering the energy of the adducts and at the same time facilitating H_2 elimination. Mononuclear amidinate complexes were found to be the first products of an intramolecular H_2 elimination. In the case of bulky amidinate ligands, the η^2,μ^1-coordination mode is conserved also in subsequent reactions. Sterically less encumbered amidinates dimerize to give dinuclear hydrides featuring η^2,μ^2-bonded amidinate ligands. These hydrides exhibit four terminal E−H bonds or, in the case of E = Al and certain amidinates, two terminal Al−H bonds and in addition two Al−H−Al bridges. Further H_2 elimination represents a redox reaction in which the E atoms are reduced to the formal oxidation state +II and a direct E−E bond is established. These reactions represent the key step in any possible applications in the field of hydrogen storage. For the $[HC(NH)_2EH_2]_2$ model compounds they are mildly endothermic for E = B and Al but already exothermic for E = Ga. The thermodynamic properties were also calculated for the reactions taking place in (toluene) solutions using the COSMO program. As expected, the effect of solvation is very small for these relatively unpolar molecules. Finally, the possibility of a last H_2 elimination is briefly discussed for E = B. The product is a species with the group 13 element in the formal oxidation state +I and an E = E double bond. In summary, the results presented herein give useful information about the thermodynamic properties of some H_2 elimination reactions which might be of relevance for applications in the field of molecular hydrogen storage and/or olefine hydrogenation.

Computational Details

All calculations were carried out with the TURBOMOLE program.[18] The BP86 method (BP is the short notation for Becke−Perdew and is a gradient-corrected DFT method employing the Becke exchange and Perdew correlation functionals) in combination with a TZVPP (triple-ζ valence, doubly polarized) basis set was applied.[19] The vibrational properties of all compounds were calculated, and the nonexistence of any imaginary frequency confirms that the structures represent minima on the potential energy surface. The solvation effect on the Gibbs energy change for hydrogen elimination from the dinuclear η^2,μ^2-bonded bis(amide) model complex $[HC(NH)_2BH_2]_2$ was estimated with the aid of the COSMO program[20] and using $\epsilon_r = 2.379$ for toluene as well as an estimated COSMO radius of 200 pm for B. The Cartesian coordinates in Å and total energies in hartrees, as well as vibrational properties of all compounds, are provided in the Supporting Information.

Acknowledgment. Continuous financial support from the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

Supporting Information Available: Cartesian coordinates in Å and total energies in hartrees, as well as vibrational properties of all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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