Inorganic Chemistry
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Can Molecular Cages Be Effective at Small Molecule Activation? A Computational Investigation

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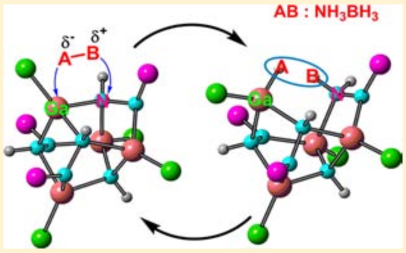
S Supporting Information

ABSTRACT: Several approaches have been investigated in recent years in the area of small molecule activation. The current work introduces a new concept in this field: that of molecular cages, containing only main group elements, serving to activate small molecules. Full quantum mechanical calculations employing DFT/SCS-MP2 methods indicate that recently synthesized Ga−N cage compounds would be excellent candidates for mediating in important reactions such as the catalysis of ammonia borane dehydrogenation. The current work therefore opens up exciting new possibilities in small molecule activation research.



INTRODUCTION

The activation of small molecules has become fertile ground for research in recent years. Various new strategies have been developed in order to activate the C−H, N−H, and O−H bonds in small molecules, using methods as diverse as main-group containing frustrated Lewis pairs (FLPs),[1,2] metal−ligand cooperativity through aromatization/dearomatization of the ancillary ligand,[3] as well as through activation of the metal−nitrogen bond in transition metal complexes.[4,5] Of these approaches, methods that employ systems that move away from transition metal complexes hold special interest because main-group systems have the advantage of being cheaper than their metal counterparts. Therefore, new strategies for small molecule activation that can be based on main-group systems have received considerable attention recently.[6,7]

We have previously shown that solid, zero dimensional (0D) cage structures have the potential to act as catalysts, due to the presence of latent Lewis acidity and basicity in the atoms of the 0D cages.[8] What is discussed in the current work is an approach toward understanding the potential of *molecular cages* toward exhibiting interesting behavior pertaining to small molecule activation. While the 0D cages, containing conjugating phenyl rings, were computationally demonstrated to be capable of functioning more as frustrated Lewis pairs (FLPs),[8] what is discussed in this work is a strategy exploiting the "opening" and "closing" of labile bonds in molecular cages. The idea is illustrated in Figure 1 below, discussing a possibility of homogeneously catalyzing a dissociation process in a small molecule. When approached by the small molecule "CDEF", an existing bond in the cage, "A-B" in Figure 1, can be broken and new bonds formed, thus activating CDEF, and eliminating the new molecule "D−E". The intermediate complex formed in this process would, however, also have the thermodynamic incentive to reconvert back to the original molecular cage, since the cage structure is a stable minima, and it would do so by remaking the broken "A−B" bond, and expelling a new small molecule "C−F". For instance, for the case where "C" and "F" are hydrogen atoms, the process described would be the catalysis of a dehydrogenation reaction. Thus, for appropriate cage structures having labile bonds, and for correspondingly appropriate small molecules that can attack the cage, an energetically feasible catalytic cycle would be set up. This is the working principle that we have employed in order to test the potential for small-molecule activation by molecular cage structures such as the recently synthesized main-group gallium−nitrogen cage compounds.[9]

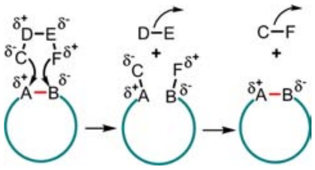


Figure 1. The proposed strategy for exploiting labile bonds in molecular cages: the "opening" and "closing" of the A-B bond in the cage can lead to small molecule activation and catalysis.

Werner Uhl and co-workers have experimentally isolated the oligonuclear gallium−nitrogen cage compounds such as $({}^{\mathrm{i}}\mathrm{PrGa})_4(\mathrm{NH\text{-}NPh})_3\mathrm{NH}$ and $(\mathrm{MeGa})_4(\mathrm{NH\text{-}N}{}^{\mathrm{t}}\mathrm{Bu})_4$ as molecular intermediates during the conversion of gallium hydrazide to gallium nitride by the thermolysis process.[9] The structural features of the Ga−N cage compound $({}^{\mathrm{i}}\mathrm{PrGa})_4(\mathrm{NH\text{-}NPh})_3\mathrm{NH}$ have been reported to be similar to the arrangement of the phosphorus atoms in the $[\mathrm{P}_{11}]^{3-}$ anion. The cage is reported to have six interconnected five-membered rings in an envelope conformation, which accounts for its stability. The optimized geometry of the caged structure is shown in Figure 2 below. The cage moiety contains four different Ga−N bonds, the bonds being distinguished from each other by the chemical environment of the gallium and the nitrogen atoms.

Received: September 12, 2012
Published: March 28, 2013

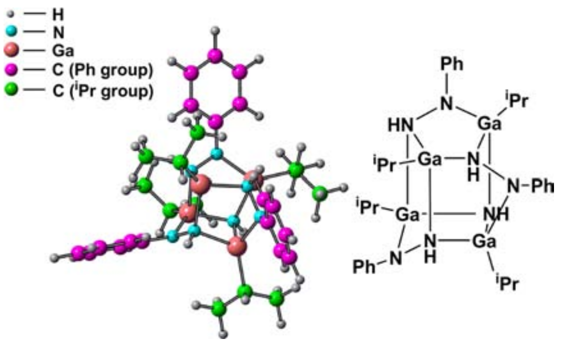


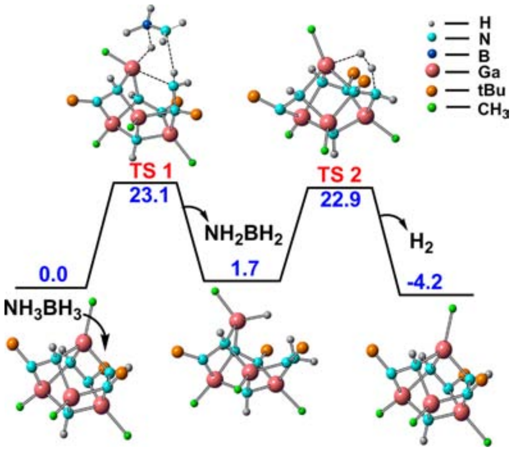
Figure 2. The DFT optimized geometry of the cage $(^iPrGa)_4(NH\text{-}NPh)_3NH$.

Fontaine and co-workers[10] have shown recently that aluminum−phosphorus dimeric compounds display FLP type behavior in the presence of CO_2, upon dissociation of the dimer. Uhl and co-workers have recently also made dimeric aluminum−phosphorus compounds that exhibited frustrated Lewis pair behavior and could activate molecules such as CO_2 and phenyl isocyanate.[11,12] We believe that the gallium−nitrogen containing caged structure shown in Figure 2 could, likewise, also display Lewis acidic and Lewis basic tendencies and thus act to activate small molecules, through the "opening" and "closing" of the Ga−N bonds in the cage, as discussed earlier. For example, for the case of the activation of the small molecule ammonia borane (AB), NH_3BH_3, the Lewis acidic gallium atom in a Ga−N bond of the cage will be susceptible to attack by the hydridic hydrogen attached to the boron of NH_3BH_3, while the Lewis basic nitrogen of the same bond approach and attack the protic hydrogen attached to the AB nitrogen, leading to the type of catalytic cycle illustrated in Figure 1. Our objective in this work is to employ computational methods in order to investigate this possibility, by studying the dissociation and recoordination of the Ga−N bonds in the Ga−N caged compound $(^iPrGa)_4(NH\text{-}NPh)_3NH$, when approached by ammonia borane. That our calculations represent a valid approach is shown by a computational investigation of an experimentally reported system: the dimeric aluminum−phosphorus complex, $(Me_2PCH_2AlMe_2)_2$, which has been experimentally shown to activate the small molecule: CO_2. Since several other molecular cage structures have also recently been synthesized and reported, some with gallium−nitrogen linkages[13,14] and others with aluminum−nitrogen bonds,[15,16] we believe that the current computational study will open up interesting possibilities for exploiting this new class of compounds.

COMPUTATIONAL DETAILS

All the calculations in this study have been performed with the aid of the Turbomole 6.0 suite of programs,[17] using the PBE functional.[18] The TZVPP[19] basis set has been employed for the calculations reported in the manuscript. Only for the calculations shown in Scheme 6, the TZVP basis set[19] was employed, with subsequent single point calculations done at the TZVPP level. The resolution of identity (RI),[20] along with the multipole accelerated resolution of identity (marij)[21] approximations have been employed for an accurate and efficient treatment of the electronic Coulomb term in the DFT calculations. Solvent effects were incorporated with single point calculations using the COSMO model,[22] with toluene ($\varepsilon = 2.38$) as the solvent. It is to be noted that for the comparison to the experimental results of Boudreau et al.,[10] with regard to the activation of CO_2 by the dimeric aluminum−phosphorus complex: $(Me_2PCH_2AlMe_2)_2$, the COSMO calculations were done with dichloromethane, CH_2Cl_2, ($\varepsilon = 9.10$) as the solvent. The values reported are ΔG values, with zero point energy, internal energy and entropic contributions included through frequency calculations on the optimized minima and transition state structures, with the temperature taken to be 298.15 K. Care has been taken to ensure that all the reported transition state structures contained only one negative frequency corresponding to the correct normal mode. In order to account for the fact that all the species are in solution, the translational entropy term in the calculated structures was corrected through a free volume correction introduced by Mammen et al.[23] This free volume correction accounts for the unreasonable enhancement in translational entropy by calculating the volume through the ideal gas law, as done in the Turbomole and other software. Furthermore, for the case of the dehydrogenation of ammonia borane (AB) mediated by "Bond 1" (as specified in the manuscript) of the Ga−N model cage $(CH_3Ga)_4(NH\text{-}NPh)_3NH$, single point SCS-MP2[24,25] calculations have been done with the DFT optimized geometries for the case of all the intermediates and transition states along the potential energy surface, for the purpose of comparison with the DFT results.

Scheme 6. Free Energy Profile for the Dehydrogenation of Ammonia Borane (AB) Mediated by the Ga−N_mod Model Cage $(CH_3Ga)_4(NH\text{-}N^tBu)_3NH$[a]

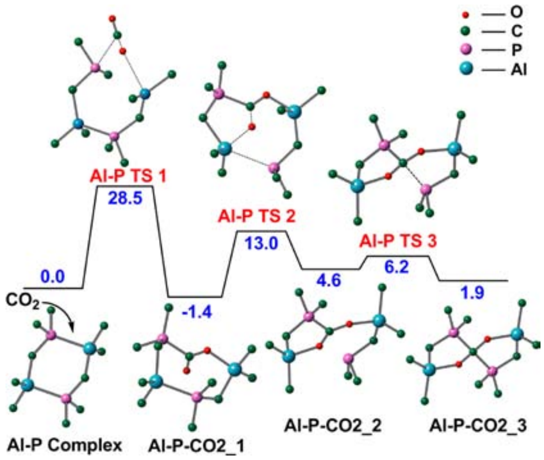


[a] All the structures shown are the fully optimized geometries from the DFT calculations; all the values are in kcal/mol.

RESULTS AND DISCUSSION

Reactivity of a Dimeric Aluminum−Phosphorus Lewis Pair toward CO_2 Activation. The focus of the current work is to understand the catalytic possibilities present in the activation of NH_3BH_3 by Ga−N containing molecular cages that have been synthesized by Uhl et al.[9] However, as mentioned in the Introduction, calculations have also been done to investigate the potential of other Lewis pair containing structures that have been experimentally shown to activate small molecules. Specifically, we have investigated the behavior of the dimeric aluminum−phosphorus complex: $(Me_2PCH_2AlMe_2)_2$ (henceforth referred to as the "Al−P" complex), which has been shown by Boudreau et al. to activate CO_2.[10] As shown in Scheme 1 below, one of the Al−P bonds of the dimeric Al−P complex can be activated in the presence of CO_2. This leads to

Scheme 1. Free Energy Profile for the Activation of CO_2 with the Al−P Lewis Pair $(Me_2PCH_2AlMe_2)_2$[a]

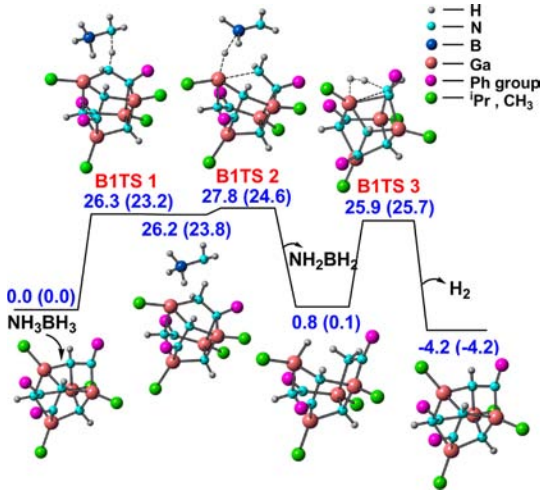


[a] All the structures shown are the fully optimized geometries from the DFT calculations; all values are in kcal/mol.

a structure where the CO_2 is inserted in the Al−P bond, with the carbon coordinating to the phosphorus and the oxygen coordinating to the aluminum. This is referred to as **Al−P−CO_2_1** in Scheme 1 below and is more stable by 1.4 kcal/mol than the Al−P complex. The barrier for this process is calculated to be 28.5 kcal/mol. Subsequent to this, a facile internal reorganization can occur, leading to the activation of the other Al−P bond, leading to the eventual formation of the structure "**Al−P−CO_2_3**" (see Scheme 1). The structure **Al−P−CO_2_3** has been experimentally obtained,[10] thus indicating the feasibility of the reactivity of the dimeric ring structure, Al−P complex, toward CO_2. As the free energy surface shown in Scheme 1 indicates, the slowest step of the reaction has a barrier of 28.5 kcal/mol, which provides the explanation as to why the reaction between CO_2 and Al−P complex is found to proceed very slowly: it takes more than 18 h to get the species **Al−P−CO_2_3** when Al−P and CO_2 are reacted at ambient temperature. Another competing pathway, where the CO_2 inserts between the two aluminiums of the Al−P dimer, was calculated and found to have a prohibitively high barrier of 38.3 kcal/mol (see Scheme S1 in the Supporting Information), thereby indicating that the pathway shown in Scheme 1 is more feasible. It is also to be noted that in the presence of 2 equiv of CO_2, the dimeric Al−P species (Al−P Complex) has been experimentally found to split into two $Me_2PCH_2AlMe_2$ molecules that form adduct complexes with CO_2. Calculations show that this process is facile by 14.2 kcal/mol (see Scheme S2 in the Supporting Information), which provides an explanation as to why the CO_2 bound monomeric structure (**Al−P−CO_2_4** in Scheme S2) is observed experimentally to form within 15 min under ambient conditions. Lastly, some intermediates that had been computationally investigated by Boudreau et al.[10] have also been optimized and found to match well in energy (gas phase values) with the values reported by Boudreau et al.[10]

Overall, the calculations provide some insight into how the activation of small molecules can be done by Lewis pairs containing ring structures that have been experimentally studied. However, the experimental work shows a stoichiometric reaction between the small molecule and the studied ring structure. The real utilization of such Lewis pairs containing ring or cage structures would occur if they can be made to *catalyze* transformations involving small molecule activation. That is the focus of the rest of the work, taking the example of the catalysis of ammonia borane (AB) dehydrogenation by the Ga−N cage structure, which is discussed below.

Scheme 2. Free Energy Profile for the Dehydrogenation of Ammonia Borane (AB) Mediated by the Ga−N cage[a]



[a] All the structures shown are the fully optimized geometries from the DFT calculations; the values outside the parentheses are the values for the real system, $(^{i}PrGa)_4(NH\text{-}NPh)_3NH$; the values for the model system $(CH_3Ga)_4(NH\text{-}NPh)_3NH$ are given inside the perentheses; all values are in kcal/mol.

Catalysis of Ammonia Borane (AB) Dehydrogenation by the Ga−N Cage. As mentioned in the Introduction, computational studies have been done to investigate the potential of recently synthesized cage structures containing gallium and nitrogen (the "Ga−N" cage) toward small molecule activation, such as the catalysis of ammonia borane (AB) dehydrogenation. Shown in Scheme 2 is the free energy profile for the dehydrogenation catalysis of AB mediated by the dissociation and recoordination of one of the bonds of the Ga−N cage. Ammonia borane, it bears mention, is one of the most promising compounds for the chemical storage of hydrogen,[26] and its catalytic dehydrogenation is an important area of research.[27] It is also to be noted that, while complexes such as $B(C_6F_5)_3$ have been employed to initiate AB dehydrogenation,[28] no main-group systems have been developed to date that can catalytically dehydrogenate AB, which indicates the significance of the current studies with main-group containing cage systems. It was found that AB dehydrogenation with the Ga−N cage would follow a three-step pathway: (i) the transfer of the protic hydrogen from the nitrogen of AB to the nitrogen of the Ga−N bond of the cage, (ii) the subsequent transfer of the hydridic hydrogen from the boron of AB to the gallium of the Ga−N bond leading to the complete rupture of the Ga−N bond and the elimination of NH_2BH_2, and (iii) the reformation of the Ga−N bond by elimination of the protic and hydridic hydrogens to yield H_2, to complete the catalytic cycle. As Scheme 2 indicates, step (i) leads to an intermediate that is higher in energy by 26.2 kcal/mol than the separated reactant species: the cage and AB. This is because the cage rearranges during the protic hydrogen transfer, in order to make new four- and six-membered rings, leading to greater ring strain and, therefore, to the unstable intermediate. Indeed, the barrier for the first reaction is almost at the same level (26.3 kcal/mol) as the intermediate. The optimized structure of the intermediate, which shows the four- and six-membered rings formed more clearly, is shown in Figure 3 below. It is to be noted that catalytic reaction cycles having unstable intermediates have been reported in the past.[29] The barrier for the subsequent reaction of this first intermediate species requires only 1.6 kcal/mol and will yield the second intermediate (see Scheme 2). This species has only five-membered rings, with the Ga−N bond completely ruptured. The final step, eliminating hydrogen, requires a barrier of 25.9 kcal/mol with respect to the separated reactant species and will regenerate the Ga−N bond. The overall process is exothermic by 4.2 kcal/mol. The three barriers obtained {26.3 kcal/mol, 1.6 kcal/mol (from the intermediate) and 25.9 kcal/mol} are in the range of AB dehydrogenation barriers obtained in transition metal catalyst systems,[4,30] and the overall exothermicity of the reaction indicates that the process would be thermodynamically favorable.

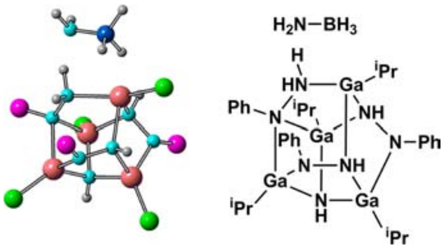
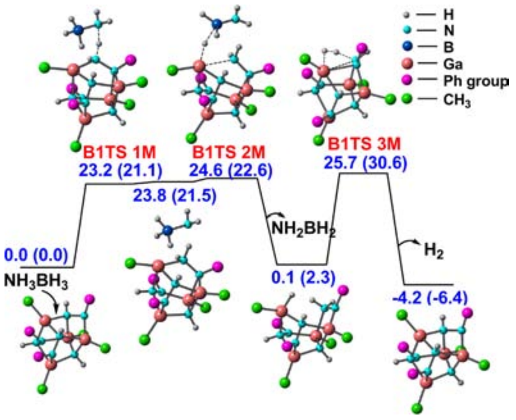


Figure 3. The DFT optimized geometry of the first intermediate formed by the reaction of ammonia borane with the $(^{i}PrGa)_4(NH\text{-}NPh)_3NH$ cage.

As Scheme 2 indicates, a further set of calculations have been done with a model system: $(CH_3Ga)_4(NH\text{-}NPh)_3NH$, made by replacing the isopropyl groups attached to the gallium atoms in $(^{i}PrGa)_4(NH\text{-}NPh)_3NH$ with methyl groups. The corresponding values for the intermediates and transition states for the AB dehydrogenation with the model cage are shown in parentheses in Scheme 2. A comparison of the corresponding values indicates that the model system provides results that are both qualitatively and quantitatively comparable to the real cage system. Hence, for the purposes of computational expediency, the validated model cage will be employed for subsequent investigations of Ga−N bond activation, as well as for other reactions.

A further study has been done in order to test the efficacy of the PBE/TZVPP DFT approach adopted here. For the model system, single point SCS-MP2 calculations (also with the RI approximation) have been done with the DFT optimized structures, obtained along the free energy surface. Previous investigations have also considered this approach of single point MP2 calculations done on DFT optimized structures.[25,31] The ΔG values (with the internal energy and entropy contributions taken from the DFT calculations) are shown in Scheme 3. The values are seen to match quite well with those obtained with the DFT calculations. Therefore, the results indicate that the prediction of the nature of the catalytic process remains the same when considering the DFT/MP2 level of theory, thus validating the PBE/TZVPP DFT approach adopted here.

Scheme 3. Free Energy Profiles Comparing the DFT/SCS-MP2 Approach to the DFT Approach for the Dehydrogenation of Ammonia Borane (AB) Mediated by the Ga−N Model Cage $(CH_3Ga)_4(NH\text{-}NPh)_3NH$ for "Bond 1"[a]



[a] The free energies obtained at PBE/TZVPP level are given outside the parentheses, and the SCS-MP2 corrected free energies are given inside the parentheses; all the structures shown are the fully optimized geometries from the DFT calculations; all the values are in kcal/mol.

It is be noted that the previous studies were done with a specific Ga−N bond in the cage structure. This is the bond corresponding to the gallium atom that is bound to three N−H groups (denoted as "**Bond_1**" in Figure 4 below). It is also possible that the AB dehydrogenation catalysis can be mediated by other Ga−N bonds in the cage. Two other possibilities have been considered, shown as "**Bond_2**" and "**Bond_3**" in Figure 4. The gallium of the two Ga−N bonds, **Bond_2** and **Bond_3**, is connected to two NH and an N-Ph group, with the nitrogen of the Ga−N bond in **Bond_2** being the N−H group and the nitrogen of the Ga−N bond in **Bond_3** being the N-Ph group (see Figure 4 below). The results of the AB dehydrogenation catalysis calculations with **Bond_2** and **Bond_3** are shown in Schemes 4 and 5. For the case of **Bond_2**, the removal of the hydridic and protic hydrogens was found to occur in a concerted fashion — only one barrier of 22.8 kcal/mol was obtained. The Ga−N bond regeneration step was found to have a barrier of 25.0 kcal/mol. This result suggests that there are multiple sites (that is, different Ga−N bonds) in the Ga−N cage that can mediate the dehydrogenation of AB, thereby increasing the catalytic potential of the molecular cage. For the case of **Bond_3**, however, the barriers were found to be higher, with the second transition state being 44.3 kcal/mol higher than the separated reactants (see Scheme 5). Calculations determining the energy required to displace the nitrogen from the gallium in each of the bonds: **Bond_1**, **Bond_2** and **Bond_3** show nearly the same energy profile (see Figure S1 in the Supporting Information). Also, a charge analysis done with

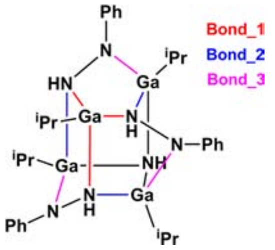
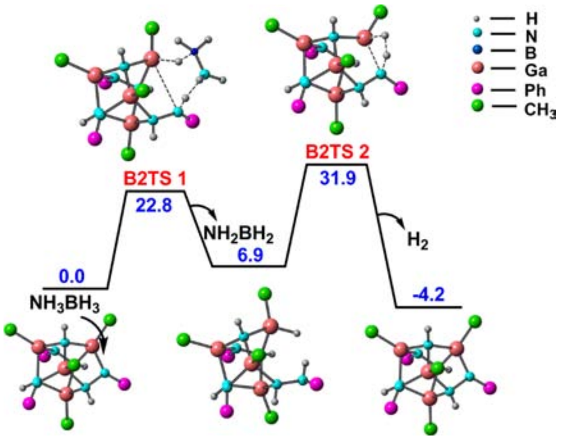


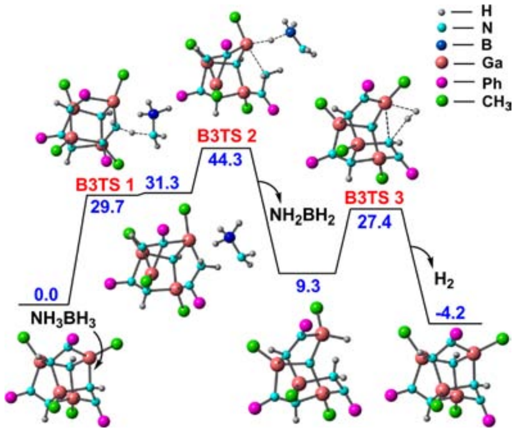
Figure 4. Different Ga−N bonds studied for the reaction of ammoniaborane with the $(^{i}PrGa)_4(NH\text{-}NPh)_3NH$ cage.

Scheme 4. Free Energy Profile for the Dehydrogenation of Ammoniaborane (AB) Mediated by the Ga−N Cage[a]



[a]A second, different Ga−N bond (**Bond_2**) for the model system $(CH_3Ga)_4(NH\text{-}NPh)_3NH$ has been considered in this case; all the structures shown are the fully optimized geometries from the DFT calculations; all the values are in kcal/mol.

Scheme 5. Free Energy Profile for the Dehydrogenation of Ammoniaborane (AB) Mediated by the Ga−N Cage[a]



[a]A third, different Ga−N bond (**Bond_3**) for the model system $(CH_3Ga)_4(NH\text{-}NPh)_3NH$ has been considered in this case; all the structures shown are the fully optimized geometries from the DFT calculations; all the values are in kcal/mol.

NBO[32] shows nearly the same charges present in the case of the gallium and nitrogen atoms in **Bond_1** (Ga: +1.709 and N: −0.978) and **Bond_3** (Ga: +1.721 and N: −0.978). (The values for **Bond_2** are Ga: +1.721 and N: −0.603). These results suggest that the reason for the higher barrier in the case of **Bond_3** lies in the nature of the transition state structure: it is seen that the cage rearrangement during the reaction in the **Bond_3** case involves the formation of a three-membered ring, which is a strained structure. This result indicates that not all the Ga−N bonds in the cage are susceptible to attack by AB.

Finally, in order to analyze the influence of the phenyl group in the considered Ga−N cage, we have done some calculations with a modified Ga−N cage having tertiary butyl groups in place of the phenyl groups in the cage structure. Such a cage structure (referred to henceforth as "Ga−N_mod") have also been synthesized.[9] For these investigations, in order to avoid the computational expense of the TZVPP basis set, we have optimized the geometries with the TZVP[19] basis set and then calculated the single point energies with the TZVPP basis set. The zero point energy, internal energy, and entropy calculations have also been done at the TZVP level and then added to the single point TZVPP energies in order to obtain the free energies for the reaction pathway. Solvent corrections have been included as before, with COSMO,[22] using toluene (ε = 2.38) as the solvent. That this approach will yield reliable results has been verified by repeating the AB dehydrogenation cycle calculations shown in Scheme 2 by following this same procedure. The results are shown in Scheme S3 of the Supporting Information and show that the ΔG values match almost exactly with the values obtained with the full TZVPP calculations, thus validating this approach.

Shown in Scheme 6 is the energy profile of AB dehydrogenation employing Ga−N_mod, with the corresponding **Bond_1** case considered here. What has been found is that the barriers are lower for this particular case in comparison to the corresponding **Bond_1** case in the Ga_N cage. This suggests that the phenyl ring does not play an important electronic role in stabilizing the transition state and that the tertiary butyl group would be better at influencing the AB dehydrogenation kinetics. Thus, the calculations indicate that Ga_N_mod would be a better catalyst for dehydrogenating AB in comparison to the Ga−N cage.

It is also to be noted that we have only considered the first step in the AB dehydrogenation process. This would lead to the formation of the amino borane species, NH_2BH_2, along with the released dihydrogen. As has been experimentally[33] and computationally[34] shown, amino borane can then subsequently react in solution with AB, independent of the catalyst, to yield a soluble polymeric species known as polyborazylene, producing another equivalent of dihydrogen in the process. Apart from this, computational investigations of Zimmerman[34] et al. and Yang et al.[35] have also shown that amino borane can dimerize in an exothermic reaction to yield $(NH_2BH_2)_2$, which can then take part in further reactions.[33] Since these subsequent reactions are considered to take place independent of the catalyst, they have not been further considered in the current investigation. One last point is with regard to the possibility of NH_2BH_2 interacting with the Ga−N bonds of the cage structures to yield new expanded cage structures. Such interesting possibilities, and their implications with regard to the possible formation of new catalytic species, will be considered in future investigations.

■ CONCLUSIONS

Full quantum mechanical calculations have been done to investigate the potential of recently synthesized molecular Ga−N cage compounds to catalyze important reactions such as ammonia borane dehydrogenation. The computational investigations have shown that the Ga−N cages contain multiple favorable sites for the activation of small molecules. The calculations therefore open up interesting new possibilities in the field of small molecule activation and homogeneous catalysis by molecular cages containing main group elements, a potentially important area that has remained unexplored to date.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Four schemes showing free energy profiles, a figure showing the bond length vs energy relation, energy data for all the geometries described in the manuscript as well as Cartesian coordinates of all the intermediates and transition states referred to in the manuscript. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors acknowledge the Centre of Excellence in Scientific Computing, NCL, Pune (COESC) for providing computational resources. Funding from the Department of Science and Technology (DST), India, is also gratefully acknowledged. N.K. wishes to acknowledge University Grants Commission (UGC) for providing a research fellowship. The authors also acknowledge the Multi-Scale simulation and Modeling project – MSM – for financial assistance.

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