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ARTICLE

Can Main Group Systems Act as Superior Catalysts for Dihydrogen Generation Reactions? A Computational Investigation

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The protolytic cleavage of the O-H bond in water and alcohols is a very important reaction, and an important source for producing dihydrogen. Full quantum chemical studies with density functional theory (DFT) reveal that germanium based complexes, such as $\text{HC}\{\text{CMeArB}\}_2\text{GeH}$ ($\text{Ar} = 2,6\text{-iPr}_2\text{C}_6\text{H}_3$), with the assistance of silicon based compounds such as SiF_3H , can perform significantly better than the existing state-of-the-art post-transition metal based system for catalyzing the dihydrogen generation from water and alcohols through the protolysis reaction.

Introduction

The replacement of existing fossil fuels with an efficient alternative energy resource is essential to meet growing energy demands. A promising candidate for this purpose is dihydrogen, a fuel which is known to have the highest energy density per unit of mass compared to the other known fuels. Furthermore, dihydrogen is also non-toxic and green. Therefore, many attempts have been made through important chemical reactions such as the steam reforming processes,¹ the water gas shift reaction²⁻⁴ (WGS), as well as through the biomass conversion of hydrocarbons^{5, 6} and alcohols⁷⁻¹¹ to improve dihydrogen production. However, the handling of hydrogen fuel for practical applications is still difficult, since it requires better storage and transport facilities. Therefore, there is considerable interest in the possibility of the chemical storage of hydrogen. Significant efforts have been made in this area, including the dehydrogenation of ammonia borane,¹²⁻¹⁶ alcohols^{8, 9, 11} and formic acid,¹⁷⁻¹⁹ the protolysis of organosilanes²⁰⁻²⁶ with water or alcohols and the use of organic heterocycles^{27, 28} as storage materials. This approach has traditionally involved the use of transition metal based catalyst systems for the necessary small molecule activation.

However, recent studies have focused on the replacement of transition metal based catalysts with compounds belonging to the main group, which are often observed to be less toxic and cheaper than transition metal complexes. In this regard, some of the important developments include frustrated lewis acid-base pairs,^{29, 30} molecular cages,^{31, 32} carbenes³³ and their higher analogues.³⁴⁻⁴¹ An important class of compounds in this category are the Group 14 compounds. The alkyne and the alkene analogues of Group 14 compounds show reactivity

towards small molecules,^{40, 42} *via* the activation of C-C, C=C, C=N and N=N bonds, and play an important role in various metathesis processes. The synthetic difficulty involved in making these compounds has been resolved either by the use of sterically encumbered ligands,^{43, 44} or by the formation of donor-acceptor complexes with BH_3 or metal carbonyl complexes.⁴⁵⁻⁴⁹ Low-valent Group 14 hydrides, in particular, have been shown to be significant in small molecule activation.^{44, 50-54} The monomeric terminal hydrides LMH [$\text{M} = \text{Ge}$ or Sn , $\text{L} = \text{CH}\{\text{N}(\text{Ar})(\text{CMe})\}_2$, $\text{Ar} = 2, 6\text{-iPr}_2\text{C}_6\text{H}_3$] (**GeH-1**) activate small molecules such as CO_2 , ketones, alkenes, as well as azo and diazo compounds.⁵⁵⁻⁵⁹ Here, the reaction gives the corresponding formate, alkoxide, vinyl and hydrazone derivative of the Ge(II) hydride, denoted as **GeH-1** in Figure 1 below.

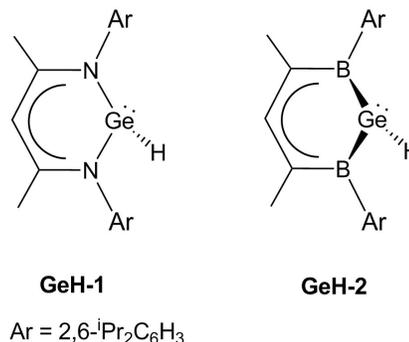


Figure 1. The Ge (II) hydrides, **GeH-1** and **GeH-2**.

It is important to note, though, that computational investigations by Sakaki and co-workers⁵³ have shown that, due to the presence of a strong Ge-O bond in alkoxide and formate intermediates, a complete catalytic cycle is not possible with

GeH-1 through the oxidative addition of the H₂ molecule, as is the case with transition metal complexes. A solution to this problem has been obtained through the use of the hydrosilylation process using silanes,⁵³ a process that regenerates the Ge-H species, thereby completing the catalytic cycle. In place of silanes, HBpin has also been employed⁵⁴ along with germanium (II) and tin (II) hydride compounds to convert carbonyl compounds to their hydroborated analogues, with efficiencies rivalling the most active catalysts presently available for such reactions.

However, a catalytic cycle has not yet been reported for dihydrogen generation by the protolytic cleavage of O-H bond in water or alcohols using Ge (II) hydride compounds. Most of the reported catalytic cycles for this reaction involve transition metal based systems, employing precious metals such as rhodium, rhenium, platinum and gold.^{21-23, 60-65} Recently, Parkin and co-workers have reported a catalytic cycle with the zinc hydride catalyst: [Tris(2-pyridylthio)methyl]zinc hydride ($[\kappa^3\text{-Tptm}]\text{ZnH}$) for the hydrolysis and alcoholysis of phenylsilanes.²⁶ A computational study by Sakaki and co-workers on $[\kappa^3\text{-Tptm}]\text{ZnH}$ has shown that various hydrosilanes can be effective in this reaction, since the reaction requires a small activation energy.⁶⁶ Experimental and theoretical calculations by Shubina and co-workers have shown that the proton-transfer and H₂-elimination reactions in the presence of alcohols can also be performed by main group Group 13 hydrides.^{67, 68} They have also provided a detailed mechanistic investigation on the reaction process.

The focus of the current work is to computationally explore the possibility of main group systems, specifically Ge (II) hydrides, catalyzing the protolytic cleavage of the O-H bond in water and alcohols, followed by the reaction with hydrosilanes, leading to the formation of dihydrogen and completing the catalytic cycle. Employing a full quantum chemical approach with density functional theory (DFT), we have proposed a new Ge (II) hydride compound (**GeH-2**) (shown in Figure 1), which is a modification of **GeH-1**, that can cleave the O-H bond in water, methanol and ethanol efficiently to provide dihydrogen. We have proposed the regeneration of **GeH-2** with the assistance of the hydrosilane, SiF₃H. Our aim is to explore the potential of Ge (II) hydrides in important catalytic processes, by employing a theoretical, predictive approach – showing how modifications to existing Ge (II) hydrides can lead to significant improvement in activity. It is expected that such an approach will provide insight for both experimental and computational groups working in the area of developing new main group catalysts for dihydrogen generation and other reactions, like the work of Sakaki and coworkers.⁵³ As will be demonstrated in the Results and Discussion Section, the proposed Ge (II) hydride compound would not only be considerably more efficient than **GeH-1**, it would rival and, indeed, be an improvement on the state-of-the art zinc based system in catalyzing the important protolytic cleavage reaction, for all the three substrates that have been considered.

Computational Details

All the calculations have been done with Turbomole 6.4,⁶⁹ using the TZVP basis set⁷⁰ and the PBE functional.^{71, 72} Dispersion corrections⁷³⁻⁷⁵ using DFT-D3 has been included in all the geometry optimization calculations. Solvent effects have been incorporated through single point calculations with COSMO,⁷⁶ with THF (epsilon = 7.5) as the solvent. The resolution of identity (RI),⁷⁷ along with the multipole accelerated resolution of identity (marij)⁷⁸ approximations have been employed for an accurate and efficient treatment of the electronic Coulomb term in the DFT calculations. 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. The same thermodynamic treatment has been done for the free energy values reported in the Schemes 1-4, 6, S1 and S2. All the obtained transition states were confirmed to have only a single negative frequency corresponding to the correct normal mode. In addition, Intrinsic Reaction Coordinate (IRC)⁷⁹ calculations were done with all the transition states in order to further confirm that they were the correct transition states, yielding the correct reactant and product structures. In order to obtain the frontier molecular orbitals of the Ge (II) hydride complexes shown in Figure S1 of the Supporting Information file, the structures of the complexes were optimized with Gaussian 09.⁸⁰

In order to estimate the level of accuracy of our calculations using PBE/TZVP, we have also performed single point calculations with the B3LYP functional and the QZVP basis set for the case of the Ge (II) hydride reaction with water. The results show that the trend in the potential energy surface obtained at the PBE/TZVP level of theory is also found when the potential energy surface is obtained at the B3LYP/QZVP level of theory (see Scheme S1 of the Supporting Information file). Please note that the reported gas phase free energy values at the B3LYP/QZVP level of theory includes zero point energy, internal energy and entropic contributions taken from frequency calculations on the optimized minima and transition state structures obtained at the PBE/TZVP level of theory. Validation of this approach has been provided through full optimization of selected small molecules at the B3LYP/QZVP level and the subsequent comparison of the thermodynamic parameters with the PBE/TZVP level of calculations (See Table S1). The values in Table S1 suggest that the entropy values vary less than only 0.004 kcal/mol for the considered systems between PBE/TZVP and B3LYP/QZVP//PBE/TZVP level of calculations. The same procedure has been employed for the singlet and triplet state calculations for **GeH-2** (see Figure S2).

It is also to be noted that quantum mechanical (QM) softwares employ the Sackur–Tetrode equation to estimate the translational entropy, which leads to overestimation, sometimes by more than 10.0 kcal/mol, of the calculated free energy. This is because the volume is calculated by assuming an ideal gas approximation for the system, leading to an incorrect evaluation of the volume term in the Sackur–Tetrode equation. Therefore,

the enthalpic potential energy surfaces have also been provided for all the cases in the Supporting Information file (see scheme S2-S4). The results of the enthalpy profiles and the corresponding free energy profiles have been compared and discussed in the Results and Discussion section.

Results and discussion

(A) Dihydrogen production with a reported germanium (II) hydride

As discussed in the Introduction, the Ge (II) hydride compound $\text{HC}\{\text{CMeArN}\}_2\text{GeH}$ ($\text{Ar} = 2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3$) (**GeH-1**) (see Figure 1) has been reported to react with many substrates such as CO_2 , ketone, alkene, azo and diazo compounds.⁵⁵⁻⁵⁹ However, the reaction of **GeH-1** with H_2O and alcohols such as CH_3OH and $\text{C}_2\text{H}_5\text{OH}$ has not yet been reported. Since water and alcohols are an important feedstock to provide dihydrogen through protolysis, it is necessary to consider the dihydrogen generation through the protolytic cleavage of O-H bond in these molecules using the Ge (II) hydride. Therefore, in the current work we have considered the hydrogen generation from water, methanol and ethanol using **GeH-1**. As also mentioned in the Introduction, we will investigate the same protolysis reaction using a modified version of **GeH-1**: **GeH-2** (see Figure 1).

The optimized geometry of **GeH-1** is shown in Figure 2. The calculated geometrical parameters at the PBE/TZVP level were found to be in very good agreement with the experimentally reported values.⁵⁵ The reaction energy profile of **GeH-1** with one molecule of water, methanol and ethanol leading to the corresponding alkoxide compound and H_2 molecule is shown in Scheme 1 (A).

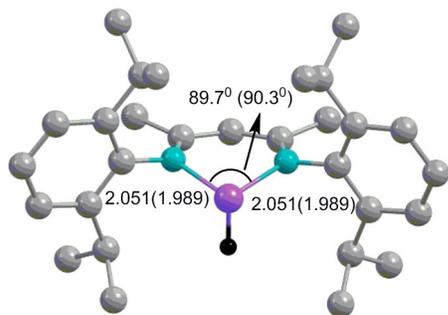
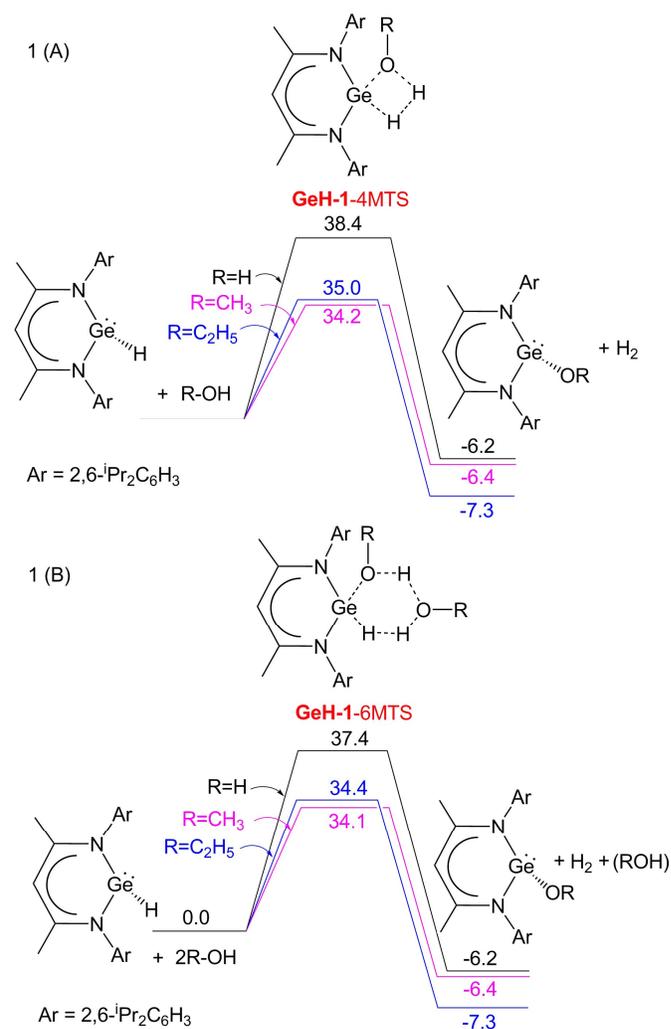


Figure 2. The optimized geometry of the Ge (II) hydride $\text{HC}\{\text{CMeArN}\}_2\text{GeH}$ ($\text{Ar} = 2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3$) (**GeH-1**); the experimental values are given inside the parenthesis.

The reaction of **GeH-1** with R-OH ($\text{R}=\text{H}, \text{CH}_3, \text{C}_2\text{H}_5$) was found to be thermodynamically favourable by 6.2 kcal/mol, 6.4 kcal/mol and 7.3 kcal/mol respectively. However, as seen in Scheme 1 (A), each of the reactions requires a high barrier: the energy barriers corresponding to the three reactions are 38.4 kcal/mol, 34.2 kcal/mol and 35.0 kcal/mol respectively. However, it is to be noted that, as Scheme 1 (A) illustrates, the reaction involves a four membered transition state, **GeH-1-4MTS**. Since a four membered transition state is more strained, a six membered transition state (**GeH-1-6MTS**) can be

considered for the same reaction by having two participating ROH ($\text{R}=\text{H}, \text{CH}_3, \text{C}_2\text{H}_5$) molecules. A similar six membered transition state has been reported for the Zn based catalyst with the water and methanol substrates by Sakaki and co-workers⁶⁶. The free energy profile for the reaction of **GeH-1** with two R-OH ($\text{R}=\text{H}, \text{CH}_3, \text{C}_2\text{H}_5$) molecules is shown in Scheme 1(B). The results indicate that the energy barrier decreases slightly for the reaction involving the six membered transition state in comparison to the four membered transition state pathway: the corresponding barriers for the reactions are 37.4 kcal/mol, 34.1 kcal/mol, and 34.4 kcal/mol respectively. The high barriers obtained suggest that the reaction is not feasible at room temperature. Furthermore, as will be shown later, the values are significantly higher than those for the zinc-based system.



Scheme 1. The free energy profile for the reaction of **GeH-1** with R-OH ($\text{R}=\text{H}, \text{CH}_3, \text{C}_2\text{H}_5$).

As discussed in the Computational Details section, an error in the activation energy calculations is possible due to the overestimation of entropy, due to the ideal gas approximation made in determining the translational entropy. This will be large in the case of six membered TS which includes three

reacting species, as is the case here, with two ROH molecules and one **GeH-1** molecule. The comparison of the free energy profile with the corresponding enthalpy profile (see Scheme S2 of the Supporting Information file) gives an energy difference of 13.5 kcal/mol, 12.4 kcal/mol and 12.7 kcal/mol for the four membered TS barriers and 23.6 kcal/mol, 25.2 kcal/mol, 25.2 kcal/mol for the six membered TS barriers, respectively, for the H₂O, CH₃OH and C₂H₅OH cases. However, since the entropic contribution is overestimated, roughly by a factor of two, the actual energy differences between the enthalpy and free energy values are likely to be about 6.8 kcal/mol, 6.2 kcal/mol and 6.4 kcal/mol respectively for the four-membered transition state cases, and 11.8 kcal/mol, 12.6 kcal/mol and 12.6 kcal/mol respectively for the six membered transition state cases. Similar reduction in the differences between the enthalpy and free energy values can be expected for all the other profiles that have been calculated and discussed here.

However, since the reaction shows a thermodynamical favourability and since Ge (II) hydride systems are generally known to have very good reactivity towards a variety of small molecules,^{44, 50-54, 55-59} we have considered the modification of **GeH-1** to create a system that can cleave the O-H bond efficiently in water and alcohols. This will be discussed in the next section.

(B) On demand hydrogen generation by the new Ge (II) hydride, **GeH-2**, from water, methanol and ethanol

Recent studies have shown that the boron based ligands are very good in stabilizing main group compounds. Aldridge and co-workers have synthesized acyclic silylene complexes stabilized by boryl ligands.⁸² Also, recently they have shown that boryl ligands can even stabilize Group 13 radical compounds.⁸³ The unusual stability of these compounds has been achieved by the strong σ donating ability of the boryl ligands.⁸⁴ Moreover, such ligands were found to help reduce the HOMO-LUMO gap in some of these compounds, which were observed to activate small molecules even under ambient conditions.^{37, 82, 85} Therefore, in our current study, we have considered the modification of **GeH-1** by replacing the two nitrogen atoms coordinated to the germanium atom in the ring with two boron atoms. The optimized geometry of the predicted Ge (II) hydride compound HC{CMeArB}₂GeH (Ar = 2,6-ⁱPr₂C₆H₃) (**GeH-2**) is shown in Figure 3 below. Compared to **GeH-1**, the germanium atom in **GeH-2** is seen to project out of the ring plane to a greater extent. The frontier molecular orbitals of **GeH-1** and **GeH-2** are shown in Figure S1 of the Supporting Information File and the natural charges obtained from the NBO analysis are given in Table 1. The calculations show that, for **GeH-2**, the singlet is more stable, with the singlet-triplet energy gap being 1.3 kcal/mol, which is considerably smaller than that of **GeH-1**, where the value obtained was 39.2 kcal/mol. However, subsequent single point calculations with B3LYP/QZVP shows the triplet ground state for the **GeH-2** system: the gas phase free energy value obtained at B3LYP/QZVP//PBE/TZVP as shown in Figure S2 (a) of the

Supporting Information file indicates that the triplet state is stable by 3.8 kcal/mol over the singlet. However, as will be discussed below when the free energy profiles of the reaction of **GeH-2** system with water are described, it is likely that the reactions with the **GeH-2** system will occur through the singlet pathway.

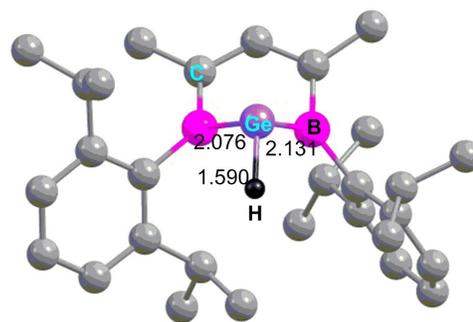


Figure 3. The optimized geometry of the Ge (II) hydride, HC{CMeArB}₂GeH (Ar = 2,6-ⁱPr₂C₆H₃) (**GeH-2**).

Table 1. NBO charges for **GeH-1** and **GeH-2**.

GeH-1		GeH-2	
Ge	0.686	Ge	0.519
H	-0.247	H	-0.163
N ₁	-0.603	B ₁	0.428
N ₂	-0.604	B ₂	0.287

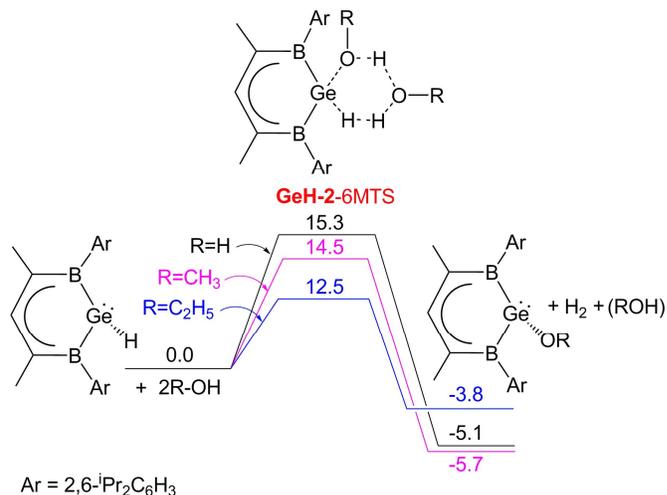
We have investigated the generation of the dihydrogen molecule from water, methanol and ethanol through the protolysis reaction by singlet **GeH-2**. The free energy profile for the reaction pathway involving a six membered transition state (**GeH-2-6MTS**) is shown below in Scheme 2. The formation of the corresponding alkoxide and the H₂ molecule was found to be thermodynamically favourable by 5.1 kcal/mol, 5.7 kcal/mol and 3.8 kcal/mol respectively. The corresponding barriers were calculated to be 15.3 kcal/mol, 14.5 kcal/mol and 12.5 kcal/mol respectively for water, CH₃OH and C₂H₅OH. The activation barrier was found to be decreased considerably with respect to the pathway involving a four membered transition state (**GeH-2-4MTS**), where the corresponding barriers are 25.3 kcal/mol, 22.5 kcal/mol and 22.1 kcal/mol respectively (see Scheme S5 in the Supporting Information file). This suggests the feasibility of employing **GeH-2** over **GeH-1** in the cleavage of the O-H bond and subsequent dihydrogen generation from substrates of the type R-OH. As mentioned in the previous section, here, too, the free energy profile shows a large energy variation with respect to the corresponding enthalpy profile in the case of 4MTS and 6MTS (see Scheme S3). The energy differences are 8.6 kcal/mol, 9.3 kcal/mol, 9.3 kcal/mol for the four membered transition state case and 20.7 kcal/mol, 22.8 kcal/mol, 21.1 kcal/mol for the six membered transition state case. As done earlier, the differences are likely to be roughly the half of the calculated values, due to the overestimation of the translational entropy in the calculations. It is also to be

noted that the enthalpy values for the 6MTS is negative with respect to the free reactant species (see Scheme S3). This suggests the possibility of an adduct reactant complex, which we have not considered in the present calculations. However, after the inclusion of the entropy (correctly to roughly half, as mentioned earlier), the barriers are eventually found to be positive, even when compared to the starting reactant species.

It is to be noted that all the results reported in the previous paragraph consider the singlet pathway, even though, as mentioned earlier, the ground state of the **GeH-2** system at the B3LYP/QZVP//PBE/TZVP level is a triplet. The reason for this is that the barriers for the process are significantly higher if it goes through a triplet pathway. We have considered the triplet state calculations of the barrier for both the four and six membered transition states, **GeH-2-4MTS** and **GeH-2-6MTS**, for the case of the reaction with water. As shown is Figure S2(b) and S2(c) of the Supporting Information file, the calculations at PBE/TZVP, as well as B3LYP/QZVP//PBE/TZVP show a higher barrier for the triplet transition state. The difference in the gas phase singlet and triplet free energy barriers for the 4M and 6M transition states in the case of water is 9.9 kcal/mol and 12.9 kcal/mol respectively at the PBE/TZVP level; and 10.2 kcal/mol and 14.8 kcal/mol at the B3LYP/QZVP//PBE/TZVP level, thereby eliminating the possibility of a triplet pathway. Similar observations have been reported by Apeloig and co-workers for the intramolecular C–H bond insertion reaction involving the triplet silylene.⁸⁶ Based on these observations, we have considered the reaction of singlet **GeH-2** in further calculations.

In order to understand the difference in reactivity of **GeH-2** in comparison with **GeH-1**, we have analyzed the HOMO-LUMO gap of these two systems. The HOMO-LUMO gap corresponding to **GeH-1** and **GeH-2** are 54.5 kcal/mol and 34.5 kcal/mol respectively for the singlet state and 27.5 kcal/mol and 15.5 kcal/mol respectively for the triplet case. As pointed out by Sakaki and co-workers, donation and back-donation between the frontier orbitals of a germanium hydride and the incoming substrate both play a role in bond cleavage reactions.⁵³ Hence, having a small HOMO-LUMO gap (analogous to transition metal systems) would be particularly advantageous in such systems, and explains the significant improvement in the barrier heights when going from **GeH-1** to **GeH-2**. It is also reported that lower HOMO-LUMO gap is essential for many small molecule activation processes, such as the activation of dihydrogen by silylenes.^{37,82,85}

It is notable that while the HOMO-LUMO gap is 34.5 kcal/mol in singlet **GeH-2**, the singlet is more stable than the triplet by only 1.3 kcal/mol. This is because the nature of the orbitals is altered considerably for **GeH-2** upon going singlet to triplet. As shown in Figure S3 in the Supporting Information file, the HOMO and the LUMO in singlet **GeH-2** is considerably different in shape in comparison to the HOMO and the LUMO in triplet **GeH-2** (see Figure S3).

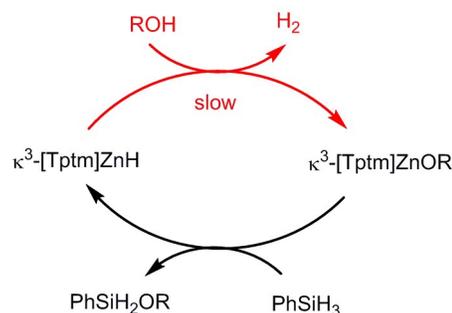


Ar = 2,6-*i*-Pr₂C₆H₃

Scheme 2. The free energy profile for the reaction of **GeH-2** with R-OH (R=H, CH₃, C₂H₅).

(C) Protolysis in ROH (R=H, CH₃, C₂H₅) molecules: a comparative study of **GeH-2** with an experimentally reported system

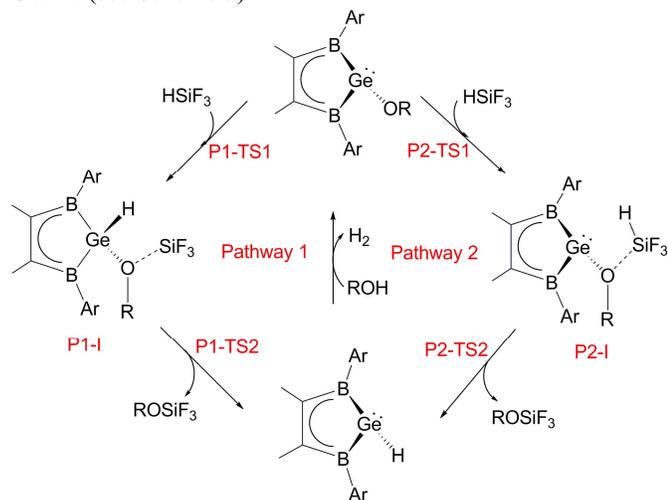
Parkin and coworkers have experimentally shown that the zinc based catalyst, [Tris(2-pyridylthio)methyl]zinc hydride ($[\kappa^3\text{-Tptm}]\text{ZnH}$), is an efficient, multifunctional post-transition metal catalyst capable of catalyzing the rapid release of dihydrogen from water and methanol with the aid of the protolytic cleavage of phenyl silane under ambient conditions.²⁶ In order to understand the efficiency of the newly proposed compound, **GeH-2**, we have determined the free energy profile for the first step of the reaction: the protolytic cleavage of O-H bond in ROH molecules to yield H₂ (see Scheme 3 below), by employing this existing, state-of-the-art post-transition metal based catalyst system. The reason we have focused on the first step is because Sakaki and coworkers have shown that the first step leading to the generation of H₂ is the rate-determining step and the subsequent reaction with various silylenes to complete the catalytic cycle required a smaller barrier.⁶⁶



Scheme 3. The reported catalytic cycle for the reaction of $[\kappa^3\text{-Tptm}]\text{ZnH}$ with R-OH (R=H, CH₃) and phenyl silane.

Shown in Scheme 4 is the free energy profile for the protolysis of ROH (R=H, CH₃, C₂H₅) with the zinc catalyst $[\kappa^3\text{-Tptm}]\text{ZnH}$. Here, the first step involves a metathesis reaction

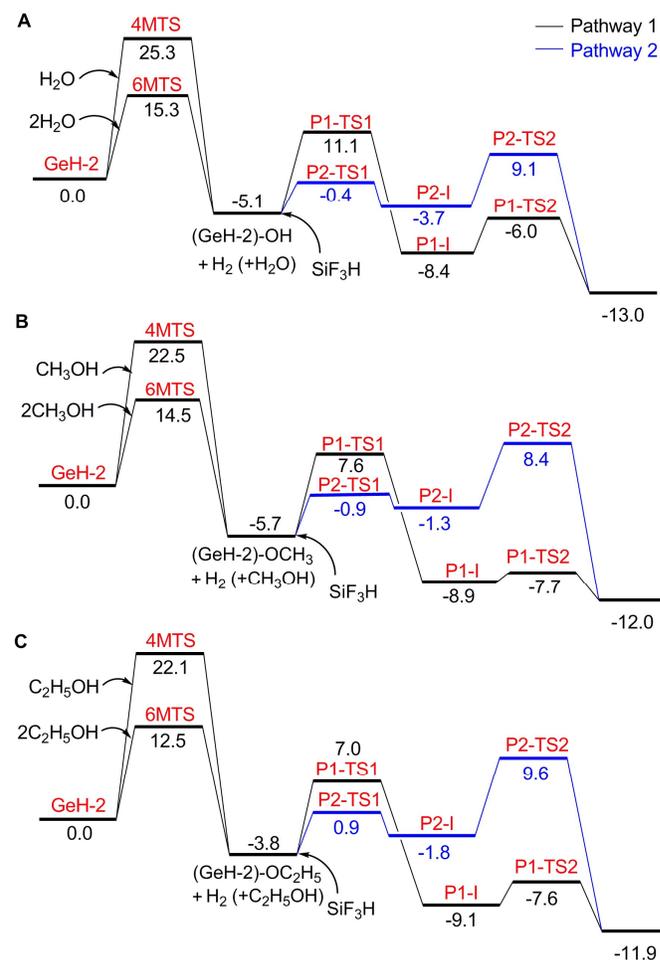
P2-I, as the intermediate with the corresponding transition state **P2-TS1**. The subsequent step involves a metathesis reaction between the Si-H bond and the Ge-O bond in the adduct **P2-I** through the transition state **P2-TS2**, regenerating the catalyst **GeH-2** (see Scheme 5).



Scheme 5. The reaction pathways for the catalytic activation of ROH molecules with **GeH-2** in presence of the silane, SiF_3H .

The free energy profile for the complete catalytic cycle for **GeH-2**, employing SiF_3H to complete the cycle and ROH ($\text{R} = \text{H}$, CH_3 and C_2H_5) as the substrate, is shown in Scheme 6. For the first step, as also observed and noted in the previous sections, the six membered transition state (**6MTS**) is lower in energy in comparison to the four membered transition state (**4MTS**). Furthermore, the energy profile shows that, similar to the zinc catalyst, $[\kappa^3\text{-Tptm}]\text{ZnH}$, case,⁶⁶ the rate determining step is the formation of alkoxide intermediate through the protolytic cleavage in ROH molecules, for $\text{R} = \text{H}$ and $\text{R} = \text{CH}_3$. The further reaction of the alkoxide intermediate with the silane, SiF_3H , requires a small barrier. In all ROH substrates, the formation of the tetra coordinated germanium intermediate in Pathway 1 (**P1-I**) is found to be lower in energy in comparison to the germanium alkoxide-silane adduct obtained in Pathway 2 (**P2-I**). **P1-I** is more stable by 8.4 kcal/mol, 8.9 kcal/mol and 9.1 kcal/mol (ΔG values) in comparison to the reactant species and **P2-I** is more stable by 3.7 kcal/mol, 1.3 kcal/mol and 1.8 kcal/mol (ΔG values), respectively for water, methanol and ethanol. However, in all systems, the energy barrier for the formation of **P1-I** is higher than the barrier for **P2-I** formation. The barrier corresponding to the transition state **P1-TS1** is 16.2 kcal/mol, 13.3 kcal/mol and 10.8 kcal/mol respectively, and 4.7 kcal/mol, 4.8 kcal/mol and 4.7 kcal/mol, respectively for **P2-TS1**. As mentioned earlier, in Pathway 1, the third step is the dissociation of the Ge-O bond in **P1-I**, which requires a very small barrier and the corresponding values for the transition state **P1-TS2** from the intermediate **P1-I** are 2.4 kcal/mol, 1.2 kcal/mol and 1.5 kcal/mol respectively. In Pathway 2, the third step is a metathesis process involving the transition state **P2-TS2**, having a higher energy barrier

compared to **P1-TS2**, and the obtained values are 12.8 kcal/mol, 9.7 kcal/mol and 11.4 kcal/mol.



Scheme 6. The free energy profile for the catalytic reaction of **GeH-2** with R-OH ($\text{R} = \text{H}$, CH_3 , C_2H_5), with SiF_3H employed to complete the cycle.

Essentially, the free energy profiles suggest that Pathway 1 is the thermodynamically favoured pathway, and would be operational if the reaction was to take place over a long period of time. On the other hand, Pathway 2 is the kinetically controlled route, with the barriers corresponding to **P2-TS1** being lower for all the three cases studied, in comparison to the competing barrier for Pathway 1, corresponding to **P1-TS1**. Hence, Pathway 2 would be likely to be operational if the reaction were to occur over a shorter length of time. Since catalysis processes generally occur over a short period of time, the results indicate that Pathway 2 would be predominant during the catalysis process. All the optimized transition state geometries are shown in Figure 4 below.

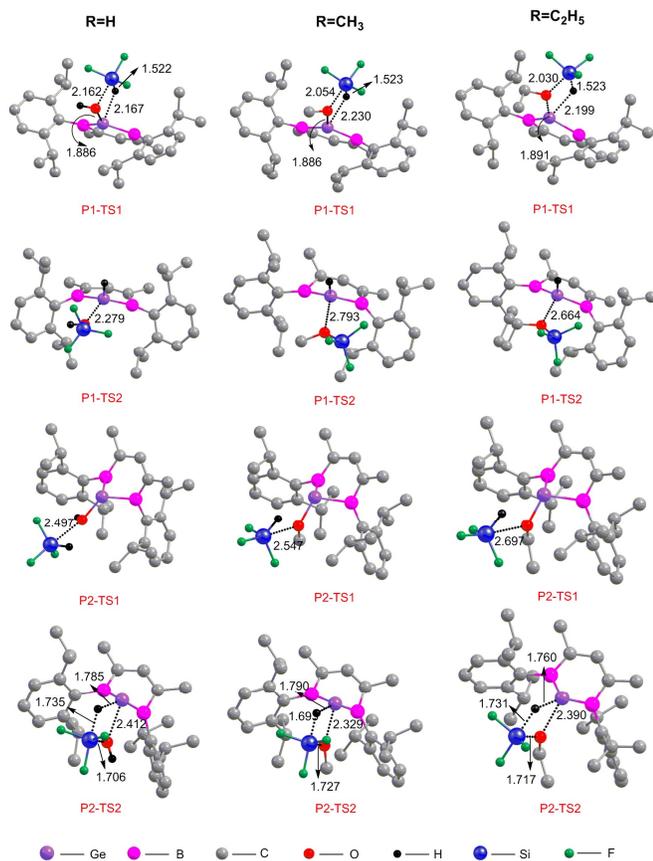


Figure 4. Optimized geometries of all the transition states discussed in the manuscript.

What is heartening to note is that the barrier for the slowest step over the entire cycle, employing **GeH-2**, is lower than the barrier for the slowest step for the state-of-the-art zinc based catalyst system, discussed earlier. This shows the potential of main group complexes to rival or be better than existing transition metal based systems in doing important chemical transformations such as the catalytic generation of dihydrogen molecule from water and alcohols.

Conclusions

There is a need to investigate new catalytic systems that can do important chemical transformations, such as the catalytic generation of the dihydrogen molecule from water and alcohols. While the post-transition metal based system, $[\kappa^3\text{-Tp}^{\text{tm}}]\text{ZnH}$, has been shown to be an effective catalyst for this process under ambient conditions,⁶⁶ what the current study demonstrates, with full quantum chemical calculations with density functional theory (DFT), is that main group systems can be designed that would be significantly more effective at catalyzing the same reaction. Specifically, a new germanium complex has been proposed in the current work, with a coordinating bidentate diboryl ring system: $\text{HC}\{\text{CMeArB}\}_2\text{GeH}$ ($\text{Ar} = 2,6\text{-iPr}_2\text{C}_6\text{H}_3$), denoted as **GeH-2**. For three different substrate cases: water, methanol and ethanol,

it has been shown that the complete catalytic cycle employing **GeH-2** leads to barriers that are significantly lower than the barrier for the slowest step in the catalytic cycle involving the zinc based catalyst system. This has added significance, considering the need to substitute transition metal based systems with main group based alternatives.

As such, the current work reveals the potential of main group systems to catalyze important chemical transformations, and should, therefore, serve as a guide to researchers in this important area of research.

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Notes and references

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Electronic Supplementary Information (ESI) available: [Figure for the frontier molecular orbitals of **GeH-1** and **GeH-2**, Table comparing the thermodynamic parameters at PBE/TZVP and B3LYP/QZVP level; seven Schemes showing free energy and enthalpy profiles as well as Cartesian coordinates of all the intermediates and transition states referred to in the manuscript, have been made available as supplementary information]. See DOI: 10.1039/b000000x/

1. G. Collodi and F. Wheeler, *Chem. Eng. Trans.*, 2010, **19**.
2. P. C. Ford, *Acc. Chem. Res.*, 1981, **14**, 31-37.
3. R. M. Laine, R. G. Rinker and P. C. Ford, *J. Am. Chem. Soc.*, 1977, **99**, 252-253.
4. N. Kuriakose, S. Kadam and K. Vanka, *Inorg. Chem.*, 2012, **51**, 377-385.
5. E. L. Kunkes, D. A. Simonetti, R. M. West, J. C. Serrano-Ruiz, C. A. Gärtner and J. A. Dumesic, *Science*, 2008, **322**, 417-421.
6. G. W. Huber, J. W. Shabaker and J. A. Dumesic, *Science*, 2003, **300**, 2075-2077.
7. R. M. Navarro, M. A. Peñã and J. L. G. Fierro, *Chem. Rev.*, 2007, **107**, 3952-3991.
8. D. R. Palo, R. A. Dagle and J. D. Holladay, *Chem. Rev.*, 2007, **107**, 3992-4021.
9. L. V. Mattos, G. Jacobs, B. H. Davis and F. B. Noronha, *Chem. Rev.*, 2012, **112**, 4094-4123.
10. P. R. d. l. Piscina and N. Homs, *Chem. Soc. Rev.*, 2008, **37**, 2459-2467.

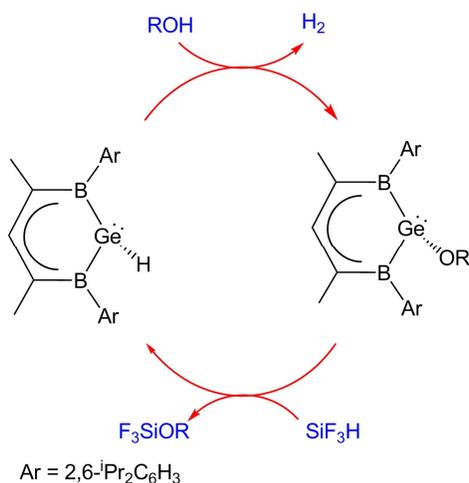
11. J. Sun and Y. Wang, *ACS Catal.*, 2014, **4**, 1078-1090.
12. J. A. Buss, G. A. Edouard, C. Cheng, J. Shi and T. Agapie, *J. Am. Chem. Soc.*, 2014, **136**, 11272-11275.
13. A. Rossin, A. Rossi, M. Peruzzini and F. Zanobini, *ChemPlusChem*, 2014, **79**, 1316-1325.
14. R. T. Baker, J. C. Gordon, C. W. Hamilton, N. J. Henson, P.-H. Lin, S. Maguire, M. Murugesu, B. L. Scott and N. C. Smythe, *J. Am. Chem. Soc.*, 2012, **134**, 5598-5609.
15. A. Paul and C. B. Musgrave, *Angew. Chem.*, 2007, **119**, 8301-8304.
16. M. C. Denney, V. Pons, T. J. Hebden, D. M. Heinekey and K. I. Goldberg, *J. Am. Chem. Soc.*, 2006, **128**, 12048-12049.
17. T. C. Johnson, D. J. Morris and M. Wills, *Chem. Soc. Rev.*, 2010, **39**, 81-88.
18. S. Enthaler, J. von Langermann and T. Schmidt, *Energy Environ. Sci.*, 2010, **3**, 1207-1217.
19. M. Grasemann and G. Laurenczy, *Energy Environ. Sci.*, 2012, **5**, 8171-8181.
20. X. L. Luo and R. H. Crabtree, *J. Am. Chem. Soc.*, 1989, **111**, 2527-2535.
21. E. Mataraso-Tchiroukhine, *J. Chem. Soc., Chem. Commun.*, 1990, 681-682.
22. U. Schubert and C. Lorenz, *Inorg. Chem.*, 1997, **36**, 1258-1259.
23. S. Chang, E. Scharrer and M. Brookhart, *J. Mol. Catal. A: Chem.*, 1998, **130**, 107-119.
24. J. M. Blackwell, K. L. Foster, V. H. Beck and W. E. Piers, *J. Org. Chem.*, 1999, **64**, 4887-4892.
25. J. M. Brunel, *Int. J. Hydrogen Energy*, 2010, **35**, 3401-3405.
26. W. Sattler and G. Parkin, *J. Am. Chem. Soc.*, 2012, **134**, 17462-17465.
27. R. H. Crabtree, *Energy Environ. Sci.*, 2008, **1**, 134-138.
28. D. Teichmann, W. Arlt, P. Wasserscheid and R. Freymann, *Energy Environ. Sci.*, 2011, **4**, 2767-2773.
29. D. W. Stephan and G. Erker, *Angew. Chem., Int. Ed.*, 2010, **49**, 46-76.
30. A. M. Chapman, M. F. Haddow and D. F. Wass, *J. Am. Chem. Soc.*, 2011, **133**, 18463-18478.
31. A. Pal and K. Vanka, *Chem. Commun.*, 2011, **47**, 11417-11419.
32. N. Kuriakose and K. Vanka, *Inorg. Chem.*, 2013, **52**, 4238-4243.
33. U. Siemeling, *Aust. J. Chem.*, 2011, **64**, 1109-1112.
34. N. Tokitoh and R. Okazaki, *Coord. Chem. Rev.*, 2000, **210**, 251-277.
35. R. Becerra, J. P. Cannady and R. Walsh, *J. Phys. Chem. A*, 2002, **106**, 4922-4927.
36. Y. Wang and J. Ma, *J. Organomet. Chem.*, 2009, **694**, 2567-2575.
37. M. Driess, *Nat. Chem.*, 2012, **4**, 525-526.
38. N. Kuriakose and K. Vanka, *Dalton Trans.*, 2014, **43**, 2194-2201.
39. S. Yao, Y. Xiong and M. Driess, *Organometallics*, 2011, **30**, 1748-1767.
40. Z. D. Brown and P. P. Power, *Inorg. Chem.*, 2013, **52**, 6248-6259.
41. M. E. Alberto, N. Russo and E. Sicilia, *Chem. -Eur. J.*, 2013, **19**, 7835-7846.
42. P. P. Power, *Chem. Rec.*, 2012, **12**, 238-255.
43. B. E. Eichler and P. P. Power, *J. Am. Chem. Soc.*, 2000, **122**, 8785-8786.
44. E. Rivard and P. P. Power, *Dalton Trans.*, 2008, 4336-4343.
45. S. M. I. Al-Rafia, A. C. Malcolm, S. K. Liew, M. J. Ferguson and E. Rivard, *J. Am. Chem. Soc.*, 2011, **133**, 777-779.
46. K. C. Thimer, S. M. I. Al-Rafia, M. J. Ferguson, R. McDonald and E. Rivard, *Chem. Commun.*, 2009, 7119-7121.
47. S. Inoue and M. Driess, *Angew. Chem., Int. Ed.*, 2011, **50**, 5614-5615.
48. M. Y. Abraham, Y. Wang, Y. Xie, P. Wei, H. F. Schaefer, P. v. R. Schleyer and G. H. Robinson, *J. Am. Chem. Soc.*, 2011, **133**, 8874-8876.
49. A. K. Swarnakar, S. M. McDonald, K. C. Deutsch, P. Choi, M. J. Ferguson, R. McDonald and E. Rivard, *Inorg. Chem.*, 2014, **53**, 8662-8671.
50. R. Rodriguez, D. Gau, Y. Contie, T. Kato, N. Saffon-Merceron and A. Baceiredo, *Angew. Chem., Int. Ed.*, 2011, **50**, 11492-11495.
51. H. Fang, Z. Ling, P. J. Brothers and X. Fu, *Chem. Commun.*, 2011, **47**, 11677-11679.
52. S. L. Choong, W. D. Woodul, C. Schenk, A. Stasch, A. F. Richards and C. Jones, *Organometallics*, 2011, **30**, 5543-5550.
53. N. Takagi and S. Sakaki, *J. Am. Chem. Soc.*, 2013, **135**, 8955-8965.
54. T. J. Hadlington, M. Hermann, G. Frenking and C. Jones, *J. Am. Chem. Soc.*, 2014, **136**, 3028-3031.
55. L. W. Pineda, V. Jancik, K. Starke, R. B. Oswald and H. W. Roesky, *Angew. Chem., Int. Ed.*, 2006, **45**, 2602-2605.
56. A. Jana, D. Ghoshal, H. W. Roesky, I. Objartel, G. Schwab and D. Stalke, *J. Am. Chem. Soc.*, 2009, **131**, 1288-1293.
57. A. Jana, H. W. Roesky and C. Schulzke, *Dalton Trans.*, 2010, **39**, 132-138.
58. A. Jana, G. Tavcar, H. W. Roesky and M. John, *Dalton Trans.*, 2010, **39**, 9487-9489.
59. S. K. Mandal and H. W. Roesky, *Acc. Chem. Res.*, 2012, **45**, 298-307.
60. S. T. Tan, J. W. Kee and W. Y. Fan, *Organometallics*, 2011, **30**, 4008-4013.
61. E. A. Ison, R. A. Corbin and M. M. Abu-Omar, *J. Am. Chem. Soc.*, 2005, **127**, 11938-11939.
62. R. A. Corbin, E. A. Ison and M. M. Abu-Omar, *Dalton Trans.*, 2009, 2850-2855.
63. E. Choi, C. Lee, Y. Na and S. Chang, *Org. Lett.*, 2002, **4**, 2369-2371.
64. B. P. S. Chauhan, A. Sarkar, M. Chauhan and A. Roka, *Appl. Organomet. Chem.*, 2009, **23**, 385-390.
65. J. John, E. Gravel, A. Hagège, H. Li, T. Gacoin and E. Doris, *Angew. Chem., Int. Ed.*, 2011, **50**, 7533-7536.
66. M. M. Deshmukh and S. Sakaki, *Inorg. Chem.*, 2014, **53**, 8485-8493.
67. O. A. Filippov, A. M. Filin, V. N. Tsupreva, N. V. Belkova, A. Lledós, G. Ujaque, L. M. Epstein and E. S. Shubina, *Inorg. Chem.*, 2006, **45**, 3086-3096.
68. O. A. Filippov, V. N. Tsupreva, L. M. Golubinskaya, A. I. Krylova, V. I. Bregadze, A. Lledos, L. M. Epstein and E. S. Shubina, *Inorg. Chem.*, 2009, **48**, 3667-3678.
69. R. Ahlrichs, M. Bär, M. Häser, H. Horn and C. Kölmel, *Chem. Phys. Lett.*, 1989, **162**, 165-169.
70. S. Ansgar, H. Christian and A. Reinhart, *Chem. Phys. Lett.*, 1994, **100**, 5829-5835.
71. J. P. Perdew and Y. Wang, *Phys. Rev. B*, 1992, **45**, 13244-13249.
72. J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865-3868.
73. S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *Chem. Phys. Lett.*, 2010, **132**, 154104-154119.

74. S. Grimme, *J. Comput. Chem.*, 2004, **25**, 1463-1473.
75. S. Grimme, *J. Comput. Chem.*, 2006, **27**, 1787-1799.
76. A. Klamt and G. Schuurmann, *J. Chem. Soc., Perkin Trans. 2*, 1993, 799-805.
77. K. Eichkorn, O. Treutler, H. Ohm, M. Häser and R. Ahlrichs, *Chem. Phys. Lett.*, 1995, **240**, 283-290.
78. S. Marek, H. Annika and A. Reinhart, *Chem. Phys. Lett.*, 2003, **118**, 9136-9148.
79. K. Fukui, *Acc. Chem. Res.*, 1981, **14**, 363-368.
80. M. J. T. Frisch, G. W.; Schlegel, H. B.; Scuseria, G. E.; M. A. C. Robb, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; G. A. N. Petersson, H.; Caricato, M.; Li, X.; Hratchian, H. P.; A. F. B. Izmaylov, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; M. T. Ehara, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, Y. K. T.; Honda, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; J. E. O. Peralta, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, V. N. K. K. N.; Staroverov, R.; Normand, J.; Raghavachari, K.; A. B. Rendell, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, J. M. K. N.; Millam, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; C. J. Adamo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; A. J. C. Austin, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; K. Z. Morokuma, V. G.; Voth, G. A.; Salvador, P.; J. J. D. Dannenberg, S.; Daniels, A. D.; Farkas, O.; and J. B. O. Foresman, J. V.; Cioslowski, J.; Fox, D. J., Gaussian, Inc., Wallingford CT, Gaussian 09, Revision B.01 **2009**.
81. M. Mammen, E. I. Shakhnovich, J. M. Deutch and G. M. Whitesides, *J. Org. Chem.*, 1998, **63**, 3821-3830.
82. A. V. Protchenko, K. H. Birjkumar, D. Dange, A. D. Schwarz, D. Vidovic, C. Jones, N. Kaltsoyannis, P. Mountford and S. Aldridge, *J. Am. Chem. Soc.*, **2012**, **134**, 6500-6503.
83. A. V. Protchenko, D. Dange, J. R. Harmer, C. Y. Tang, A. D. Schwarz, M. J. Kelly, N. Phillips, R. Tirfoin, K. H. Birjkumar, C. Jones, N. Kaltsoyannis, P. Mountford and S. Aldridge, *Nat. Chem.*, 2014, **6**, 315-319.
84. Y. Segawa, M. Yamashita and K. Nozaki, *Science*, 2006, **314**, 113-115.
85. A. V. Protchenko, A. D. Schwarz, M. P. Blake, C. Jones, N. Kaltsoyannis, P. Mountford and S. Aldridge, *Angew. Chem., Int. Ed.*, 2013, **52**, 568-571.
86. M. Kosa, M. Karni and Y. Apeloig, *J. Am. Chem. Soc.*, 2013, **135**, 9032-9040.

Table of Contents

Title: Can Main Group Systems Act as Superior Catalysts for Dihydrogen Generation Reactions? A Computational Investigation

*Nishamol Kuriakose and Kumar Vanka**



Full quantum chemical calculations with density functional theory (DFT) reveal the potential of newly proposed main group germanium hydride systems to effect important chemical transformations, such as the catalytic cleavage of the O-H bond in water and alcohols, with significantly greater efficiency than existing, state-of-the-art post-transition metal based systems.