

# Insertion of Group 12-16 Hydrides into NHCs: A Theoretical Investigation

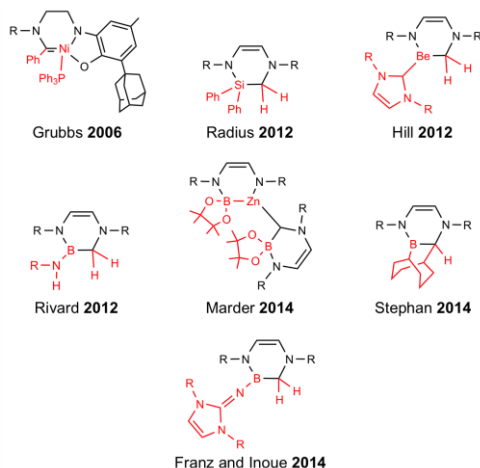
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**Abstract:** The endocyclic ring expansion of N-heterocyclic carbene (NHC) rings by transition metal (Group 12) and main group (Group 13-16) element hydrides has been investigated in a computational study. In addition to previously reported insertion reactivity with Si, B, Be and Zn, similar reactivity is predicted to be feasible for heavier group 13 elements (Al, Ga, In, Tl), with the reaction barriers for Al-Tl calculated to be lower than for boron. Insertion is not expected with group 15-16 element hydrides, as the initial adduct formation is thermodynamically unfavourable. The reaction pathway with group 12 hydrides is calculated to be more favourable with two NHCs rather than a single NHC (analogous to Be), however hydride ring insertion with metal dihydrides is not feasible, but rather a reduced NHC is thermodynamically favoured. For group 14, ring-insertion reactivity is predicted to be feasible with the heavier dihydrides. Trends in reactivity of element hydrides may be related to the protic or hydridic character of the element hydrides.

## Introduction

In recent years N-heterocyclic carbenes (NHCs) have found increasing utility as stabilising ligands in transition metal and main-group chemistry,<sup>[1]</sup> especially in the fields of catalysis<sup>[2]</sup> and novel bonding environments.<sup>[3]</sup> However, in what appears as a contradiction to the stabilization afforded by NHC ligands, NHCs have recently been observed to undergo degradation reactivity when interacting with selected element hydrides.

The first report of NHC degradation was provided by Grubbs in 2006,<sup>[4]</sup> who noticed that the reaction of  $\text{NiClPh}(\text{PPh}_3)_2$  with an NHC resulted in Ni insertion into the C-N bond of the NHC with migration of the Ph group to the carbene carbon. Activation of the C-N bond and ring expansion by non-metals was first observed in 2012 by Hill<sup>[5]</sup> and Radius.<sup>[6]</sup> Radius described the insertion of hydrosilane ( $\text{PhSiH}_3$ ) into  $\text{NHC}^{i\text{Pr}}$  (notation refers to *i*Pr substituent on each N), while Hill reported the insertion of a beryllium hydride into NHC. Around the same time, Rivard<sup>[7]</sup> independently observed similar phenomena of ring insertion using the same  $\text{NHC}^{i\text{Pr}}$  with boron hydrides. The unusual reactivity of NHCs with element-hydrides continues to be explored by Radius,<sup>[8]</sup> with recent observations of deprotonation reactivity and rearrangement to abnormal NHC coordination beyond adduct formation and ring insertion.



**Figure 1.** Examples of hydride insertion into N-heterocyclic carbenes (NHCs).

Following the experimental observation of Radius, our group carried out a theoretical study of the reaction pathway involving silane insertion into an NHC,<sup>[9]</sup> which was extended<sup>[10]</sup> to include both the beryllium and boron hydrides used by Hill<sup>[5]</sup> and Rivard<sup>[7]</sup> in addition to alternative NHC environments.<sup>[11]</sup> Theoretical studies suggest that a similar pathway occurs in each case, with common steps leading to ring expansion and subsequent insertion of the element hydride into the NHC. As initially hypothesised by Radius,<sup>[6]</sup> and supported by theoretical studies,<sup>[9-12]</sup> the ring expansion pathway can be summarised in four key steps:

- (i). The formation of an initial adduct between the elemental hydride species and the NHC.
- (ii). Primary hydrogen migration from the element hydride to the carbene carbon.
- (iii). Activation and expansion of the central carbon–nitrogen bond of the NHC, leading to insertion of the element hydride species into the C–N bond in the ring.
- (iv). Secondary hydrogen migration from the element hydride to the carbene carbon forming a stable six-membered ring.

Following on from the initial theoretical work,<sup>[9-10, 12]</sup> Su<sup>[13]</sup> subsequently investigated the possible insertion by group 14 element hydrides  $\text{EH}_2\text{Ph}_2$  ( $\text{E} = \text{C}, \text{Si}, \text{Ge}, \text{Sn}, \text{Pb}$ ) into  $\text{NHC}^{i\text{Pr}}$ . Each element hydride was predicted to follow the pathway described above, with the free energy of reaction ( $\Delta G$ ) ranging from a moderately unfavourable +35.3 kJ/mol ( $\text{CH}_2\text{Ph}_2$ ) to relatively favourable -114.2 kJ/mol ( $\text{SiH}_2\text{Ph}_2$ ), where favourable product formation followed the trend  $\text{Si} > \text{Ge} > \text{Sn} > \text{Pb} > \text{C}$ .<sup>[13]</sup> Fang and co-workers reported a theoretical study comparing ring insertion of symmetric ( $\text{NHC}^{\text{Me}}$ ) and unsymmetric NHCs ( $\text{NHC}^{\text{Me}/i\text{Pr}}$ ), determining that each N-alkyl NHC system followed the same four-step pathway with phenylsilane compounds, and provided almost identical free energies of reaction.<sup>[14]</sup>

A number of experimental studies have subsequently been reported that expand the number and range of cases of insertion into NHCs. Marder and co-workers<sup>[15]</sup> reported the first example of Zn insertion, which arose from attempts to use a zinc-chloride adduct of  $\text{NHC}^{\text{Mes}}$  to facilitate the borylation of alkyl halides. Rather, reaction of  $\text{NHC-ZnCl}_2$  with bis(pinacolato)-diboron ( $\text{B}_2\text{pin}_2$ ) in the presence of  $\text{KOtBu}$  lead to the simultaneous activation of two NHC rings resulting in a double-ring expanded product with insertion of zinc into one NHC ring while Bpin was inserted into the secondary NHC ring. The extensive rearrangement also resulted in catalyst deactivation.

In 2014 Stephan reported the insertion of 9-borabicyclo[3.3.1]nonane (9-BBN),<sup>[16]</sup> mirroring the four-step insertion pathway.<sup>[6]</sup> Analogous boron reactivity includes bis(catecholato)diboron ( $\text{B}_2\text{cat}_2$ ) and bis(neopentylglycolato)-diboron ( $\text{B}_2\text{neop}_2$ ).<sup>[17]</sup> The reaction of tetramethyl substituted NHC with  $\text{B}_2\text{cat}_2$  produced the  $(\text{NHC})\text{B}_2\text{cat}_2$  adduct, which was reported as thermally stable in solution. Subsequent heating over several hours however lead to ring expansion of the NHC with insertion of one Bcat species followed by migration of the other Bcat to the carbene carbon. It was shown that the expanded product could be synthesised directly by heating (70 °C)  $\text{B}_2\text{cat}_2$  with two equivalents of the NHC for several hours. Interestingly, this degradation pathway was even shown to occur at room temperature when using the more reactive  $\text{B}_2\text{neop}_2$ .<sup>[17]</sup> Franz and Inoue<sup>[18]</sup> explored steric effects on the insertion pathway of iminoborane dihydride ( $\text{NHBH}_3$ ) into  $\text{NHC}^{i\text{Pr}}$  or  $\text{NHC}^{\text{Mes}}$  ( $\text{Mes} = 2,4,6\text{-trimethylphenyl}$ ), finding that insertion followed that of the previously reported pathway. It was concluded that a balance in sterics for both the NHC and hydride species was required for the pathway to occur. Franz and Inoue also noted that this particular borane complex required two equivalents of the NHC for insertion to occur.<sup>[18]</sup>

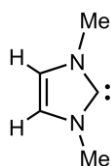
As the use of NHCs rapidly expands to elements across the entire periodic table, it is of interest to examine if the occurrence of NHC ring insertion and degradation by element hydrides is widely applicable. For example, the group 12 elements ( $\text{Zn}, \text{Cd}, \text{Hg}$ ), which are formally defined as late

transition metals, commonly exhibit properties similar to those found in the main group of the periodic table. Group 12-NHC complexes are not unknown: as far back as 1970 Wanzlick reported the isolation of a stable NHC-Hg complex.<sup>[19]</sup> Rivard has recently reported the isolation of NHC-Zn and NHC-Cd complexes,<sup>[20]</sup> although attempts to form element hydrides from the element halides resulted in scission of the E-C bond for Cd; only Zn was found to yield an element hydride species.

To investigate how wide-spread this NHC insertion reactivity might be, we have carried out a systematic theoretical study of NHC insertion with group 12 to 16 element hydrides (EH<sub>n</sub>), which encompasses relevant main group hydrides as well as late transition metal hydrides. Results may be expected to provide insight into mechanism and energetic trends within each group, and potentially identify new targets for synthesis that exhibit this new NHC reactivity. If this reaction pathway is applicable for other hydrides it may also impact on future catalysis and stabilisation studies involving these elements at elevated temperatures.

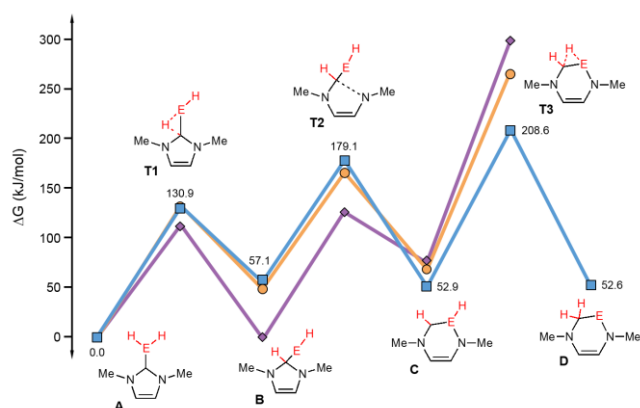
## Results and Discussion

For computational efficiency, a methyl-NHC (NHC<sup>Me</sup>) was used for all calculations. Previous work indicates that a simplified N-H substituent is insufficient whereas N-methyl gives results consistent with larger substituent groups that would be used under experimental conditions.<sup>[10]</sup>



### Group 12

The metal hydrides ZnH<sub>2</sub>, CdH<sub>2</sub> and HgH<sub>2</sub> were utilized to investigate insertion into a single NHC molecule. The complete four-step reaction pathway as outlined above was investigated for each transition metal hydride, with results collated in Table 1 (gas-phase results are included in the Supporting Information) and illustrated in Figure 2. All three group 12 hydrides followed a similar pathway to that previously reported for Si, Be and B hydrides.



**Figure 2.** Insertion pathway for  $\text{NHC}^{\text{Me}}$  involving  $\text{ZnH}_2$  (blue),  $\text{CdH}_2$  (orange) and  $\text{HgH}_2$  (purple). Calculated relative free energies (kJ/mol) for the Zn species are shown for comparison. Due to complete degradation of the ring, the final six-membered compound (**D**) was not located for  $\text{CdH}_2$  or  $\text{HgH}_2$ .

Formation of the initial adduct (**A**) between the group 12 hydrides and  $\text{NHC}^{\text{Me}}$  is thermodynamically unfavoured including solvent effects, varying from +8.2 kJ/mol for Zn to +15.9 and +45.0 kJ/mol for Cd and Hg, respectively. In contrast, gas phase results indicate that adduct formation is thermodynamically favoured for all three hydrides.

**Table 1.** SCS-MP2/def2-TZVP//M06-2X/def2-TZVP calculated relative energies ( $\Delta G$ , kJ/mol) for group 12-16 hydrides. Solvent effects (acetonitrile) included via MP2 electronic energies.

	A	T1	B	T2	C	T3	D
$\text{ZnH}_2$	0 (+8.2) <sup>a</sup>	130.9	57.1	179.1	52.9	208.6	52.6
$\text{CdH}_2$	0 (+15.9)	133.0	48.0	165.7	68.6	268.1	<i>b</i>
$\text{HgH}_2$	0 (+45.0)	114.7	-1.1	126.1	76.0	303.2	<i>b</i>
$\text{BH}_3$	0 (-176.7)	202.7	112.2	124.0	57.9	135.0	-27.9
$\text{AlH}_3$	0 (-117.7)	195.1	131.2	148.8	20.2	139.3	22.3
$\text{GaH}_3$	0 (-86.1)	182.6	139.1	177.2	55.7	176.6	31.1
$\text{InH}_3$	0 (-57.9)	179.2	119.2	188.3	75.3	201.1	41.5
$\text{TlH}_3$	0 (-37.2)	162.2	83.1	190.9	90.0	204.0	14.1
$\text{SiH}_2\text{Ph}_2$	0 (+39.4)	106.8	-13.3	96.2	24.1	70.0	-138.0
$\text{SiH}_4$	0 (-21.1)	115.6	1.8	112.5	38.8	89.4	-108.5
$\text{SiH}_2$	0 (-167.5)	215.7	131.8	166.3	63.4	111.8	11.8
$\text{GeH}_2$	0 (-142.6)	191.2	129.6	175.4	77.9	139.4	25.8
$\text{SnH}_2$	0 (-144.7)	195.3	130.6	176.8	79.8	143.5	25.5
$\text{PbH}_2$	0 (-56.6)	126.3	91.2	162.5	70.8	132.7	-10.3
$\text{NH}_3$	0 (+45.3)	<i>c</i>	11.4	<i>d</i>	325.6	434.5	122.3
$\text{PH}_3$	0 (+36.2)	<i>c</i>	19.9	<i>d</i>	140.0	257.8	-14.4
$\text{AsH}_3$	0 (+45.9)	<i>c</i>	6.7	<i>d</i>	196.3	281.3	-23.8
$\text{BiH}_3$	0 (+32.2)	<i>c</i>	7.4	<i>d</i>	154.8	<i>c</i>	-37.1
$\text{OH}_2$	0 (+31.1)	<i>c</i>	28.0	<i>c</i>	<i>c</i>	<i>c</i>	+201.5
$\text{SH}_2$	0 (+257.0)	-2.9	-205.1	-50.8	-92.4	17.9	-174.8
$\text{SeH}_2$	0 (+228.2)	-6.9	-172.8	-27.3	-73.1	31.2	-146.2
$\text{TeH}_2$	0 (+159.9)	36.2	-223.1	26.7	-20.4	67.5	-121.6

[a] Energies in parentheses are in relation to the free species. [b] The final six-membered compound (**D**) was not located, with ring opening readily occurring. [c] Structure not located. [d] The TS from **B** led to ring opening rather than **C**.

The weak interaction is further demonstrated with the initial adduct **A** exhibiting elongated metal-C bonding interactions of 2.202 Å (Zn), 2.491 Å (Cd) and 2.821 Å (Hg), which are longer than the sum of covalent radii for metal-C single bonds of 1.93 Å (Zn), 2.11 Å (Cd) and 2.08 Å (Hg).<sup>[21]</sup> The Zn-carbene interaction is longer than in the Zn species isolated by Hillmyer and Tolman (2.04 to 2.05 Å depending on the zinc substituents of chloride or benzyl alcohol),<sup>[22]</sup> the zinc dihydride bridged NHC<sup>iPr</sup> compound synthesised by Maron and Okuda (2.05 Å)<sup>[23]</sup> as well the Zn-carbene interaction of 2.07 Å reported by Brown and Rivard.<sup>[24]</sup> The carbene stabilised compounds isolated by Roesler and co-workers<sup>[25]</sup> yielded metal-carbene distances of 2.00 Å (Zn), 2.25 Å (Cd) and 2.18 Å (Zn). The bond distances in these isolated compounds are consistent with the sum of single-bond covalent radii of Pyykkö.<sup>[21]</sup> In adduct **A** the consistent increase in H-M-H bond angle from ~140° (Zn) to ~170° (Hg) and E-C<sub>NHC</sub> distance in moving down the group is consistent with weaker NHC-EH<sub>2</sub> interactions that are progressively dominated by electrostatic and dispersion interactions.

Consistent with previous studies, the initial H-migration from the metal to the carbene carbon (**T1**) provides sizable barriers of 130.9 (Zn), 133.0 (Cd) and 114.7 (Hg) kJ/mol.<sup>[10]</sup> Transition state **T1** is followed by formation of minimum **B**, in which the transition metal hydride is stabilised. The second transition state (**T2**) is associated with C-N expansion in the NHC ring, with the metal hydride pivoting towards to the newly expanded C-N bond. The energy barrier for **T2** ranges from 117.7 (Cd) to 127.1 (Hg) kJ/mol, and is smaller than the **T1** barrier for Zn and Cd. For Hg the **T2** barrier is 12.4 kJ/mol greater than for **T1**. Following expansion of the C-N bond, the element hydride is inserted into the C-N bond forming a six-membered ring (**C**). Stable structure **C** provides a planar cyclical ring with the hydrogen comfortably positioned outwards thus stabilising the ring in the case of Zn, Cd and Hg.

For each group 12 element, the pathway from **C** to **T3** provides the rate-determining step, with large barriers of 155.7 (Zn), 199.5 (Cd) and 227.2 (Hg) kJ/mol. This is due to the inability of the second hydrogen to migrate from the transition metal hydride to the carbene carbon leaving a two-coordinate metal. Group 12 metals are coordinately unsaturated in the two-coordinate N-E-C motif (E = metal) found in **D**, and would be expected to be very reactive and unstable. The large atomic radii and electron deficiency of the metal would require electron-donating ligands to stabilize the metal, for which it is apparent that the NHC is insufficiently electron donating to stabilize the N-E-C motif.

The final product (**D**) was only able to be located for Zn; for both Cd and Hg the transition metal separated itself from the ring with subsequent ring-opening of the NHC. For ZnH<sub>2</sub>, the overall reaction to produce **D** is endergonic by 53 kJ/mol from adduct **A**, and endergonic by 61 kJ/mol from the initial reactants ZnH<sub>2</sub> and NHC<sup>Me</sup>.

The distinction between Zn and the heavier elements is reflected in the structure and character of **T3**. The E-C bond distances in **T3** are 1.975 Å (Zn), 2.768 Å (Cd) and 2.809 Å (Hg), which for both Cd and Hg represents a significant increase compared to the E-C bonds in **C**. In fact, for Cd the E-C bond distance in **T3** is actually greater than in the initial adduct **A**. Similar trends are noted in calculated Wiberg bond indices (WBI), where with Zn the WBI for E-C only varies by 4% between **C** (WBI 0.518) and **T3** (WBI 0.497), indicative of similar E-C bonding environments in **C** and **T3**. With Cd the WBI in **T3** (0.313) is reduced by 37% compared to **C** (0.493), and with Hg the reduction is 52% from **C** to **T3** (WBI from 0.587 to 0.280). For both Cd and Hg, the elongated E-C bond in **T3** is 0.6-0.7 Å greater than the sum of single-bond covalent radii,<sup>[21]</sup> and is indicative of the E-C weak interaction that results in ring-opening and dissociation of the metal rather than formation of **D**.

The large barriers calculated for the final transition (involving a secondary hydrogen transfer) and endergonic reactions to form **D** indicate that formation of **D** with a single NHC is unfavourable and will not occur under standard experimental conditions. It is noted that ZnH<sub>2</sub> behaves differently (e.g. lower barriers) to that of its heavier analogues CdH<sub>2</sub> and HgH<sub>2</sub>, and so Zn offers the greatest potential reactivity with NHCs from the group 12 elements.

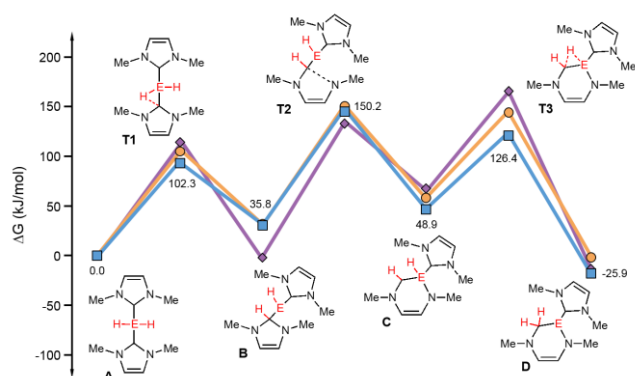
The weak affinity displayed by the group 12 elements for a single NHC is no surprise, as the experimentally viable products required either multiple carbenes to induce coupling or bulkier ligands

to stabilise these species.<sup>[22, 25]</sup> In this regard we investigated the reaction of ZnH<sub>2</sub>, CdH<sub>2</sub> and HgH<sub>2</sub> with two NHC molecules, which is analogous to the reactivity observed for Be<sup>[5, 10]</sup> with a similar closed-shell electronic configuration. Results for the calculated pathway are presented in Table 2, with the relative energies plotted in Figure 3.

**Table 2.** SCS-MP2/def2-TZVP//M06-2X/def2-TZVP calculated relative free energies ( $\Delta G$ , kJ/mol) for group 12 hydrides with two NHCs. Solvent effects (acetonitrile) included via MP2 electronic energies.

	A	T1	B	T2	C	T3	D
ZnH <sub>2</sub>	0 (+40.9) <sup>a</sup>	102.3	35.8	150.2	48.9	126.4	-25.9
CdH <sub>2</sub>	0 (+53.2)	111.1	35.9	155.6	61.0	149.8	-11.6
HgH <sub>2</sub>	0 (+105.0)	118.3	1.2	140.0	67.9	167.3	-28.1

[a] Energies in parentheses are in relation to the free species.



**Figure 3.** Insertion pathway with two NHC<sup>Me</sup> involving ZnH<sub>2</sub> (blue), CdH<sub>2</sub> (orange) and HgH<sub>2</sub> (purple). Calculated relative free energies (kJ/mol) for the Zn species are shown for comparison.

Formation of the initial adduct (**A**) between the group 12 hydrides and two NHC<sup>Me</sup> molecules is increasingly thermodynamically unfavoured for Zn (+40.9 kJ/mol), Cd (+53.2 kJ/mol) and Hg (+105.0 kJ/mol). The trend in energetics is consistent with metal-carbon bonding, with the E-C bond distance increasing and WBI decreasing from 2.243 Å (Zn, WBI 0.41), to 2.532 Å (Cd, WBI 0.33) and 2.863 Å (Hg, WBI 0.21). The progressively weaker metal-carbon bonding in **A** for the heavier analogues is further evidenced by the increasing deviation (0.31, 0.42, 0.78 Å) above the sum of single-bond E-C covalent radii.<sup>[21]</sup>

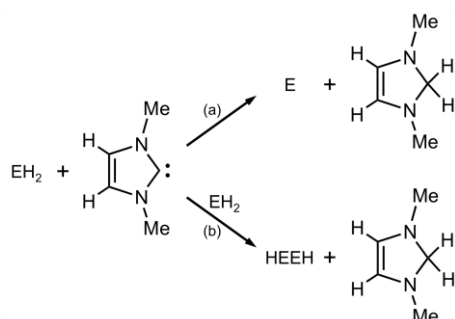
Importantly, inclusion of the second NHC lowers the first barrier (**T1**) for all element hydrides to less than 120 kJ/mol, which is consistent with the **T1** barrier calculated for the experimentally observed silane insertion. Indeed, for the entire pathway after **T1**, inclusion of the second NHC increases the stability of reactants and transition state intermediates. In particular, the final rate-determining barrier (**T3**) that was 156-227 kJ/mol with a single NHC, is lowered to 78-99 kJ/mol. However, the second step (**T2**) of EH insertion remains the rate-determining step. The significant lowering of reaction barriers arises from the second NHC allowing the metal to avoid an unfavourable 2-coordinate configuration, which is analogous to the case with Be hydride insertion.

In each case, the final product (**D**) with two NHCs is thermodynamically favoured compared to (**A**). However, in each case the final product (**D**) is thermodynamically unfavoured compared to the initial free reactants ( $\text{EH}_2$  and  $\text{NHC}^{\text{Me}}$ ).

Comparing the reactions with a single NHC (Figure 2) and two NHCs (Figure 3), it is noted for adduct **A** the metal-C bond distances with two NHCs are slightly greater than for the reaction with a single NHC. In each case the second NHC reduces the stability of **A** relative to the free reactants. The reaction with two NHCs reduces the energetic barriers to insertion compared to a single NHC.

The only experimental report of Zn insertion<sup>[15]</sup> produced a double-ring insertion of Zn and Bpin, for which the mechanism is evidently different from the general four-step process that is followed by Be, B and Si hydride insertion. It is suggested that the ‘simple’ four-step insertion is unlikely to be observed with Zn hydride, although with carefully selected conditions and appropriately substituted NHCs one cannot entirely rule out the possibility of  $\text{ZnH}_2$  insertion.

Two other possible outcomes of the reaction of  $\text{EH}_2$  and NHCs are outlined in Scheme 1, with calculated energies of reaction presented in Table 3.



**Scheme 1.** Two alternative reaction products for the reaction of  $\text{EH}_2$  ( $\text{E} = \text{Zn}, \text{Cd}, \text{Hg}$ ) with  $\text{NHC}^{\text{Me}}$ : (a) double deprotonation, and (b) NHC-mediated dehydrocoupling of  $\text{EH}_2$  to  $\text{E}_2\text{H}_2$ .

**Table 3.** SCS-MP2/def2-TZVP//M06-2X/def2-TZVP calculated relative free energies ( $\Delta G$ , kJ/mol) for reactions of group 12 hydrides in Scheme 1. Solvent effects (acetonitrile) included via MP2 electronic energies.

	A	1(a)	1(b)
$\text{ZnH}_2$	0 (+8.2) <sup>a</sup>	43.4	53.5
$\text{CdH}_2$	0 (+15.9)	-33.1	-18.4
$\text{HgH}_2$	0 (+45.0)	-131.5	-60.6

[a] Energies in parentheses are in relation to the free species.

In the first case (Scheme 1(a)) two H atoms are transferred from  $\text{EH}_2$  to the carbene carbon leaving the bare element metal. For  $\text{ZnH}_2$  the products are calculated to be higher in free energy than **A** by 43.4 kJ/mol, and are also higher in free energy than the reactants. For  $\text{CdH}_2$  and  $\text{HgH}_2$  the products are calculated to be lower in free energy than compound **A** by 33.1 kJ/mol (Cd) and 131.5 kJ/mol (Hg), respectively, and are also lower in free energy than the free reactants.

In the second case (Scheme 1(b)), NHC-mediated reductive dehydrocoupling of  $\text{EH}_2$  to  $\text{E}_2\text{H}_2$  yields products higher in energy than Scheme 1(a), although again they are higher in free energy than the reactants with  $\text{ZnH}_2$ . With Cd and Hg the products are lower in free energy than **A** by 18.4 and 60.6

kJ/mol, respectively, with both also lower in free energy than the reactants. For Cd and Hg, Scheme 1(a) is thermodynamically favoured over Scheme 1(b).

It is concluded that the insertion pathway for  $\text{ZnH}_2$ ,  $\text{CdH}_2$  or  $\text{HgH}_2$  is not competitive compared to the reactions in Scheme 1. It is likely that the reaction of  $\text{CdH}_2$  and  $\text{HgH}_2$  with either a single NHC or with two NHCs would favour production of the bare metal and the reduced carbene ring without the observation of adduct **A** or ring insertion. It may be possible to produce a Cd or Hg ring-expanded product such as that reported by Marder and coworkers.<sup>[15]</sup>

### Group 13

Rivard<sup>[7]</sup> reported the first example of boron hydride insertion into NHCs, which has been followed by a number of observations of analogous boron hydride reactivity.<sup>[16-18]</sup> As of yet there are no reports of analogous reactivity for the heavier group 13 elements. Numerous studies have also demonstrated that group 13 hydrides can be stabilised by NHCs, including the boron mediated reactions reported by Schaefer, Schleyer and Robinson to stabilise both a B=B double bond<sup>[26]</sup> and a bridged  $\text{BH}_2$  complex.<sup>[27]</sup> Extensive work has been carried out by Jones and co-workers in the stabilisation of the majority of the group 13 hydrides including Al,<sup>[28]</sup> Ga,<sup>[28a]</sup> In<sup>[28b, 29]</sup> and Tl.<sup>[30]</sup> Other notable outcomes include the  $\text{AlH}_3$  adduct of  $\text{NHC}^{\text{Mes}}$  reported by Cole and co-workers,<sup>[31]</sup> the  $\text{AlMe}_3$  adduct of  $\text{NHC}^{\text{tBu}}$  by Dagorne,<sup>[32]</sup> and the gallium-chloride species isolated by Nolan.<sup>[33]</sup>

In this work we considered  $\text{EH}_3$  as a model hydride for each element. For boron, the experimentally observed insertion reaction employed  $\text{H}_2\text{BNH}(\text{Dipp})$  ( $\text{Dipp} = 2,6\text{-diisopropylphenyl}$ ), with only two hydrides bound to the boron. We have demonstrated previously<sup>[10]</sup> that the presence of the N atom bearing a donor lone-pair serves to stabilise the electron-deficient boron, especially in an unfavourable three-coordinate configuration that is common in the reaction pathway. Calculated reaction energetics with  $\text{BH}_3$  result in higher reaction barriers (15-45 kJ/mol) and less favourable product formation by 74 kJ/mol in comparison with and  $\text{BH}_2\text{NH}^{\text{Me}}$ . As such, the present calculated results with  $\text{BH}_3$  (and all group 13  $\text{EH}_3$ ) may be considered an upper bound of the barrier heights of the reaction of experimentally applicable group 13 hydrides ( $\text{EH}_2\text{NHR}$ ) with  $\text{NHC}^{\text{Me}}$ .

The five species investigated from group 13 include  $\text{BH}_3$ ,  $\text{AlH}_3$ ,  $\text{GaH}_3$ ,  $\text{InH}_3$  and  $\text{TlH}_3$ , with results collated in Table 1. There remains significant debate around the stability of In and Tl trihydrides,<sup>[34]</sup> which have recently been synthesized in the gas phase but despite early claims by Wiberg of their isolation (that have been unable to be reproduced<sup>[35]</sup>), it would appear that solid phase isolation of  $\text{InH}_3$  and  $\text{TlH}_3$  is unlikely. Nevertheless, the heavier trihydrides are included for comparison in the present study, and may potentially be isolatable as adducts with NHCs with the reaction of lithium complexes such as  $\text{LiInH}_4$ , which Jones and co-workers employed in the isolation of an  $\text{NHC-InH}_3$  adduct.<sup>[29]</sup>

The formation of adduct **A** is exergonic for all group 13 elements, and decreases monotonically in magnitude from  $\text{BH}_3$  (-176.7 kJ/mol) to  $\text{TlH}_3$  (-37.2 kJ/mol). The E-C bond distance in **A** reflects the relative stability of the adducts, with bond distances increasing going down the group: 1.60 Å (B), 2.08 Å (Al), 2.12 Å (Ga), 2.36 Å (In) and 2.50 Å (Tl). The respective sum of covalent single-bond radii for E-C bonds are 1.60 Å (B), 2.01 Å (Al), 1.99 Å (Ga), 2.17 Å (In) and 2.19 Å (Tl), from which it may be concluded that the covalent character of the E-C bond decreases going down the group. For the lighter elements of the group, the E-C bond is best described as covalent in nature.

The calculated E-C bond distances are comparable to available experimental values, such as the boron-carbon interactions of 1.58-1.62 Å in the  $\text{NHC}^{\text{iPr}}$  stabilized adducts reported by Schaefer, Schleyer and Robinson.<sup>[26-27]</sup> Jones' aluminium hydrides afforded Al-C interactions of 2.05-2.06 Å,<sup>[28]</sup> while the gallium hydride adduct yielded a Ga-C distance of 2.07 Å.<sup>[28a]</sup> Their  $\text{NHC}^{\text{Mes}}$  stabilised  $\text{InH}_3$  species exhibited an In-C distance of 2.253(5) Å and provided increased thermal stability at raised temperatures (115 °C)<sup>[29]</sup> compared to the analogous chlorinated species ( $\text{NHC}^{\text{Mes-InCl}_3}$ ) that exhibited a shortened interaction of 2.20 Å.<sup>[29]</sup> The Tl-C distance of 2.18 Å between the bulky  $\text{NHC}^{\text{Mes}}$  and thallium-chloride species is contracted, however it is comparable to the less sterically demanding carbene.<sup>[30]</sup>



For all group 13 hydrides the formation of compound **A** is very favourable, however the subsequent barrier height associated with the first hydrogen migration (**T1**) is significant when a single NHC is included. The **T1** barrier is the rate-determining step, consistent with previous results for Si, Be and B hydrides.<sup>[10]</sup> The barrier is a maximum with BH<sub>3</sub> (204.6 kJ/mol) and decreases moving down the group to TlH<sub>3</sub> (162.2 kJ/mol). Hydrogen migration leads to minimum **B**, which for B lies below the energy of the free reactants. For the other element hydrides, minima **B** lies higher in energy than the free reactants, being 13.4 kJ/mol for Al and 46-61 kJ/mol for the heavier elements.

Subsequent activation and expansion of the C–N bond provides an optimal **T2** orientation for subsequent insertion of the main-group hydride. A minor energetic barrier of 15.6 kJ/mol for BH<sub>3</sub> increasing to 107.8 kJ/mol for the TlH<sub>3</sub> species is required for **T2**. The calculations indicate that all of the group 13 species then form structure **C**, a highly stretched six-membered ring (which may indicate instability of the structure). The energy for the **C** complexes are also slightly less stable when compared to the initial adduct **A**, ranging from +20.2 kJ/mol (Al) to +90.0 kJ/mol (Tl). The final transition (**T3**) associated with secondary hydrogen migration is sizable: B (+64.8 kJ/mol), Al (+119.1 kJ/mol), Ga (+120.9 kJ/mol), In (+125.8 kJ/mol) and Tl (+113.9 kJ/mol). All of these compounds then lead to the final formation of a disordered and slightly expanded **D** structure. As shown from Table 1, the final inserted products are stable, ranging from B (-183.2 kJ/mol) to In (-16.4 kJ/mol), in relation to the initial adducts.

While the barrier heights and the energetics of final product formation do not appear particularly favourable, it should be noted that the reaction with BH<sub>3</sub> (and possibly all EH<sub>3</sub>) represents an upper limit of calculated barrier heights, and would be expected to be more favourable with experimentally relevant hydrides such as BH<sub>2</sub>R.<sup>[10]</sup> In that case, while reaction with the simple group 13 EH<sub>3</sub> hydrides is unlikely due to the large barriers for the initial hydrogen migration, it could be expected that insertion reactivity is achievable with the majority of group 13 element hydrides.

Indeed, we have very recently reported the first observation of the insertion of an aluminium hydride at room temperature,<sup>[36]</sup> which was assisted by the use of a NacNac ligand that serves to increase the hydridic character in comparison with NHC ligands.

## Group 14

Ring expansion of NHCs via activation of the C–N bond was first observed with a silicon hydride, with Radius reporting the insertion of PhSiH<sub>3</sub> into NHC<sup>*i*Pr</sup>.<sup>[6]</sup> Radius and co-workers<sup>[37]</sup> have subsequently reported further unusual reactivity of silanes with NHCs, in which a stable (NHC*i*Pr)-SiCl<sub>2</sub>Ph<sub>2</sub> adduct underwent an unusual rearrangement with the silicon species migrating from the carbene carbon and inserting between the C=C backbone of two NHC species when heated in THF. While not directly related to the pathway in the current paper, the unusual reactivity is intriguing and justifies continued interest in exploring the reactivity of silanes and heavier group 14 analogues with NHCs.

For the investigation of NHC insertion, we considered SiH<sub>4</sub>, SiH<sub>2</sub>, GeH<sub>2</sub>, SnH<sub>2</sub> and PbH<sub>2</sub> hydrides, with results presented in Table 1. The two-coordinate hydrides are considered due to our interest in low-oxidation state main-group chemistry, and for consistency with the experimentally relevant +2 oxidation state for the heavier group 14 hydrides. Results for SiH<sub>4</sub> and SiH<sub>2</sub>Ph<sub>2</sub> are included for comparison.

With SiH<sub>2</sub>Ph<sub>2</sub>, for which ring-insertion has been observed, the common four-step pathway is predicted to be favourable with a rate-determining **T1** barrier of 106.8 kJ/mol from the initial reactants. With SiH<sub>4</sub>, initial adduct formation is favourable by 21.2 kJ/mol. With M06-2X/def2-TZVP a structure for **A** was only able to be located with tighter integration grids and geometry convergence thresholds – default parameters failed to locate a minimum on the potential energy surface, which is consistent with the results we obtained with Me<sub>2</sub>SiH<sub>2</sub> and MeSiH<sub>3</sub>.<sup>[9]</sup> The barrier from the initial reactants is 115.6 kJ/mol with SiH<sub>4</sub> (gas phase is 112.1 kJ/mol), which may be compared to the (gas phase) MP2/def2-TZVP//M06-2X/6-31G(d) calculated barriers of 153.9 and 154.9 kJ/mol for Me<sub>2</sub>SiH<sub>2</sub> and MeSiH<sub>3</sub>,

respectively.<sup>[9]</sup> It is clear that Ph-substituents on the silane stabilize the initial adduct (**A**) and reduce the barrier for initial hydride migration.

For each group 14 dihydride (EH<sub>2</sub>) the formation of adduct **A** is favourable, and more so than the analogous group 13 hydrides of the same row. The free energy change in forming **A** decreases in magnitude going down the row, from -167.5 kJ/mol (SiH<sub>2</sub>) to -56.6 kJ/mol (PbH<sub>2</sub>). The interaction distance between the carbene and each of the elemental hydrides is marginally longer than the sum of single-bond covalent radii of E-C bonds, being 1.920 Å (Si), 2.046 Å (Ge), 2.323 Å (Sn) and 2.487 Å (Pb). The optimised Si-C distance of 1.920 Å falls between distances noted by Filippou and co-workers<sup>[38]</sup> in their isolated (NHC<sup>iPr</sup>)SiI<sub>3</sub> compound (1.91 Å) and that of Rivard and co-workers<sup>[39]</sup> in their (NHC<sup>iPr</sup>)SiW(CO)<sub>5</sub> compound (1.93 Å). Similarly, the interaction distance calculated for the germanium adduct **A**, (NHC<sup>Me</sup>)GeH<sub>2</sub> (2.046 Å), lies between those reported by Rivard and co-workers<sup>[20]</sup> (2.00 Å) involving a chloride-substituted Ge(II) compound and the mesityl-substituted germanium compound (2.07 Å) synthesized by Baines.<sup>[40]</sup> The elongated Ge-NHC interaction found by Frenking, Jones and Stasch<sup>[41]</sup> could be reasoned by the use of the bulkier NHC<sup>iPr</sup> substituent. The tin-carbene interaction distance (2.29 Å) found in the organotin complex isolated by Wagner *et al.*<sup>[42]</sup> also compares well with the theoretical value (2.323 Å) for the initial adduct.

Initial hydrogen migration from adduct **A** requires a moderate (+126.3 kJ/mol, Pb) to substantial (+215.7 kJ/mol, Si) amount of energy, which is reasonable due to the strong interaction observed within the group 14 hydrides. For all group 14 dihydrides, the initial hydrogen migration barrier (**T1**) is the rate-determining step. For Si and Ge the **T1** barrier is greater than for the respective group 13 species (Al, Ga), however for the heavier elements the trend is reversed and the Sn and Pb barriers are lower than the respective group 13 elements (In, Tl). The barrier for the experimentally observed Si<sub>2</sub>Ph<sub>2</sub> species is 106.8 kJ/mol, which is comparable to the barrier for PbH<sub>2</sub> (126.3 kJ/mol).

The barrier to ring opening (**T2**) is typically much smaller, although SiH<sub>2</sub>Ph<sub>2</sub> is an exception, with a **T2** barrier (109.5 kJ/mol) that is marginally greater than for **T1** (106.8 kJ/mol). For the dihydrides, the **T2** barrier is much smaller than **T1**, and increases with elemental mass (34.5 to 71.2 kJ/mol), which is consistent with the case for group 13 element hydrides. The barrier for the second hydrogen migration (**T3**) is similar in magnitude to the ring-opening barrier for the dihydrides, and generally increases going down the group from 48.4 kJ/mol (SiH<sub>2</sub>) to 61.9 kJ/mol (PbH<sub>2</sub>).

The final products (**D**) are thermodynamically favoured for all dihydrides, being exergonic by 66.9 to 155.7 kJ/mol from the initial reactants. Of the dihydrides, only PbH<sub>2</sub> yields a product **D** that is lower in free energy than **A** (-10.3 kJ/mol). It is concluded that ring insertion is energetically feasible for the heavier EH<sub>2</sub> hydrides, and possibly also for the lighter EH<sub>2</sub> hydrides.

## Group 15

For the investigation of NHC insertion, we considered EH<sub>3</sub> (E = N, P, As, Bi), with results presented in Table 1. It is important to note that for all group 15 hydrides the initial adduct **A** is not a covalently bound adduct, but is optimized as a van der Waals cluster with a C-H(E) interaction rather than a C-E interaction as calculated for group 12-14 hydrides. This is consistent with the results of Rullich *et al.*,<sup>[43]</sup> who identified C-H(E) interactions in the initial adduct formation of NH<sub>3</sub> with an NHC bearing only a single N atom in the ring. The formation of the adduct **A** is also calculated to be endergonic by at least 32 kJ/mol for N-Bi.

In each case a minimum structure corresponding to **B** (initial H-migration) was able to be located, however it generally coincided with a loss of planarity of the N-methyl groups. Attempts to locate **T1** (linking **A** and **B**) led to a TS associated with ring opening, with barriers of 141.2 kJ/mol (NH<sub>3</sub>), 129.9 kJ/mol (PH<sub>3</sub>) and 136.9 kJ/mol (AsH<sub>3</sub>). The ring-open species is thermodynamically unfavoured compared to both **A** and the reactants, suggesting that insertion reactivity is not expected for group 15 hydrides. Moreover, compound **C** lies 371 kJ/mol above the reactants for NH<sub>3</sub>, with P-Bi analogues similarly high in free energy. Compound **D** is only calculated to be exergonic with BiH<sub>3</sub>, however the high relative energy of **C** (+187 kJ/mol) suggests that insertion with BiH<sub>3</sub> is not likely.

## Group 16

There are very few experimental reports of the stabilisation of group 16 elements solely through the use of carbenes.<sup>[44]</sup> While there are no reports of NHC-element hydrides, NHC-element halide adducts have been isolated.<sup>[45]</sup> Driess and co-workers<sup>[46]</sup> have demonstrated that NHC adducts of the heavier group 16 species could be isolated through complexation with silanone. The synthesis involves combining the silanone with either an NHC<sup>Me</sup> or NHC<sup>iPr</sup> and the elemental species of interest (in this case S, Se or Te), which affords the NHC-coupled silanochalcogenone.

For the investigation of NHC insertion, we considered OH<sub>2</sub>, SH<sub>2</sub>, SeH<sub>2</sub> and TeH<sub>2</sub> hydrides, with results presented in Table 1. The results for H<sub>2</sub>O indicate behavior more in common with the group 15 hydrides than the heavier group 16 hydrides (Table 1). The initial adduct **A** is a van der Waals cluster with a (O)H-C interaction, and lies 31 kJ/mol higher in energy than the free reactants. Compound **B** exhibits non-planarity of the N-methyl groups, while any additional reactivity leads to ring opening, analogous to results for group 15. A 6-membered ring product (**D**) was located, however it is endergonic by 233 kJ/mol from the initial reactants.

For SH<sub>2</sub>, SeH<sub>2</sub> and TeH<sub>2</sub> formation of the adduct (**A**) is thermodynamically unfavourable, with the change in free energy calculated to be at least +160 kJ/mol. As such, experimental observation of adduct formation and subsequent ring expansion is very unlikely, even at elevated temperatures. Nevertheless, the calculated insertion pathway for group 16 element hydrides offers interesting insights in comparison to groups 12-15.

A marked difference to other groups is observed with the barrier for initial hydrogen migration (**T1**). With SH<sub>2</sub>, SeH<sub>2</sub> and TeH<sub>2</sub> the **T1** transition state is marginally lower in energy than **A** for S (-2.9 kJ/mol) and Se (-6.9 kJ/mol), while the barrier is only +36.2 kJ/mol with Te. The low (or negative) barrier for S and Se arises from the instability of **A** relative to **T1**: consideration of the electronic energy yields a minimal positive barrier, while inclusion of thermodynamic corrections results in **T1** being lower in energy than **A**. For comparison, the barriers are much greater with group 12 (115-133 kJ/mol), group 13 (162-195 kJ/mol) and group 14 (107-216 kJ/mol) hydrides.

Minima **B** is very stable, which in part brings about the large barriers (146-250 kJ/mol) for subsequent ring opening and EH insertion (**T2**). For each group 16 hydride, this barrier is the rate-determining step, which differs to that of group 12 (**T3**) and groups 13 and 14 (**T1**). The barrier for secondary hydrogen migration (**T3**) decreases going down the group from 110.3 kJ/mol (S) to 87.9 kJ/mol (Te), while the final product **D** is calculated to be highly stable.

One should note however, that while the final compound **D** is thermodynamically favourable compared to **A**, it is still less favourable (in relation to the initial adduct **A**) than the first hydrogen migrated structure **B**, making the final structure unlikely to be isolatable even if the initial adduct could be formed. It is clear that NHC ring-expansion and hydride insertion will not occur with group 16 hydrides.

## Rationale for hydride reactivity

The difference in reactivity of the group 12-16 hydrides can be rationalized by consideration of the protic or hydridic character of the hydrogen atoms in the reactant element hydride, EH<sub>n</sub>. Formation of the initial adduct **A** with an E-C requires hydridic H atoms and an electrophilic E element. For Group 15 (and especially NH<sub>3</sub>), the hydrogen atoms have protic character, which limits their ability to undergo hydride reactions. The protic nature may be characterized by the atomic charge of the hydrogen in the hydride (Table 4). For NH<sub>3</sub> the hydrogen atoms carry a positive charge, consistent with a protic description. Consistent with this is the observation that the initial NH<sub>3</sub> adduct forms not with an E-C interaction but with a (E)H-C interaction. Similarly for group 16, the H<sub>2</sub>O hydrogen atoms are clearly protic, which also leads to an initial van-der Waals adduct with a (O)H-C interaction.

For group 12-14  $\text{EH}_n$ , the hydrogen atoms all carry a negative charge that is also smaller in magnitude for the lighter elements, consistent with greater hydridic character. From this result it is concluded the group 12-14 hydrides represent the best avenue to achieve NHC insertion reactivity. The heavier group 15 hydrides demonstrate hydridic character (negative charge on hydrogen), which offers some hope of observing insertion reactivity with  $\text{BiH}_3$ . For the group 16 hydrides, ring insertion is not expected for any of the elements in the group.

**Table 4.** M06-2X/def2-TZVP calculated Natural Population Analysis (NPA) charges of hydrogen atom in  $\text{EH}_n$ . Solvent effects (acetonitrile) included.

$\text{ZnH}_2$	-0.60	$\text{SiH}_2\text{Ph}_2$	-0.16	$\text{NH}_3$	0.37
$\text{CdH}_2$	-0.58	$\text{SiH}_4$	-0.28	$\text{PH}_3$	0.01
$\text{HgH}_2$	-0.44	$\text{SiH}_2$	-0.30	$\text{AsH}_3$	-0.03
$\text{BH}_3$	-0.11	$\text{GeH}_2$	-0.41	$\text{BiH}_3$	-0.18
$\text{AlH}_3$	-0.41	$\text{SnH}_2$	-0.46	$\text{OH}_2$	0.48
$\text{GaH}_3$	-0.38	$\text{PbH}_2$	-0.16	$\text{SH}_2$	0.16
$\text{InH}_3$	-0.42			$\text{SeH}_2$	0.13
$\text{TlH}_3$	-0.32			$\text{TeH}_2$	0.01

## Conclusions

The ring-insertion energetics of group 12-16 hydrides reacting with  $\text{NHC}^{\text{Me}}$  have been investigated to explore the potential for new observations of ring-opening and hydride insertion reactivity. The majority of the hydrides closely follow the four-step reaction pathway previously determined for Si, Be and B hydrides, with initial hydrogen migration typically being the rate-determining step. While transition barriers along the insertion route may be energetically large, it is proposed that these still may be experimentally possible as shown through precedent reactions such as silicon insertion.<sup>[6]</sup>

With group 12 hydrides (Zn, Cd, Hg), it was determined that a reaction pathway with two NHCs was preferred over the reaction with a single NHC, analogous to the case with Be. However, in each case ring-insertion with NHCs is calculated to be unfavourable, but rather a double hydrogen transfer to the NHC leaving elemental metal (or  $\text{E}_2\text{H}_2$ ) would result.

With group 13 hydrides, the  $\text{EH}_3$  results are expected to provide an upper bound to the experimentally relevant  $\text{EH}_2\text{NHR}$  hydrides, and as such it could reasonably be expected that while NHC insertion is unexpected with group 13  $\text{EH}_3$  hydrides, insertion reactivity might be observed with alternative ligands that maximize the hydridic character of the element hydride.

For the group 14 dihydrides, ring-insertion reactivity is predicted to be feasible with the heavier Sn and Pb hydrides. With group 15-16 initial adduct formation is calculated to be unfavourable, for which subsequent ring-insertion will not occur.

The results for group 12-16 may be rationalized by consideration of the hydridic and protic character of the hydrogen atoms in the element hydrides, with greater hydridic character required for insertion reactivity.

## Computational Methods

All geometries were optimised using the M06-2X density functional<sup>[47]</sup> with a def2-TZVP<sup>[48]</sup> basis set within Gaussian 09 using default integration grids and convergence criteria.<sup>[49]</sup> Optimization of the initial adduct **A** with SiH<sub>4</sub> required non-default tighter thresholds, with opt=tight and grid=ultrafine Gaussian keywords; for consistency the entire pathway with SiH<sub>4</sub> was calculated with the ultrafine grid. Structures were characterised as minima or transition states by analytical calculation of the Hessian. The optimised M06-2X/def2-TZVP geometries were used to calculate the single-point energies with MP2 and SCS-MP2,<sup>[50]</sup> with the def2-TZVP basis set, including solvent effects (acetonitrile solvent) with the polarizable continuum model (PCM)<sup>[51]</sup> self-consistent reaction field (SCRF) together with Truhlar's SMD solvation model.<sup>[52]</sup> SCS-MP2 energies are calculated from the reported SCF and same/opposite spin electron correlation components. All of the tabulated SCS-MP2  $\Delta G$  values were determined from the combination of the SCS-MP2/def2-TZVP electronic energy (inclusive of solvent effect) and the thermochemical correction calculated from M06-2X/def2-TZVP. Other density functionals (B3LYP,<sup>[53]</sup> PBE1PBE<sup>[54]</sup>) and basis sets (6-31G(d), def2-SVP)<sup>[55]</sup> were considered and found to provide very similar optimised structures and energies and are thus not described in detail. Quadratic synchronous transit (QST)<sup>[56]</sup> analysis was used to determine the transition steps between minima structures, with all transitions displaying one imaginary frequency. Intrinsic reaction coordinate (IRC)<sup>[57]</sup> analysis was also performed to ensure that transition states linked the energetic barriers. Natural bond orbital (NBO)<sup>[58]</sup> calculations were carried out with M06-2X/def2-TZVP at the optimised geometries, including natural population analysis (NPA) charges and Wiberg bond indices (WBIs).

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