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Organogermanium(II) Hydrides as a Source of Highly Soluble LiH

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Abstract: The reactions of the monomeric C,N-chelated organogermanium(II) hydride L(H)Ge·BH_3 with organolithium salts RLi yielded lithium hydrogermanatoborates {Li(THF)$_2${BH_3[L(H)GeR]}}$_2$. Compound {Li(THF)$_2${BH_3[L(H)GePh]}}$_2$ was used as a source of LiH for the reduction of organic C=O or C=N bonds in non-polar solvents accompanied by the elimination of a neutral complex L(Ph)Ge·BH_3. The interaction of {Li(THF)$_2${BH_3[L(H)GePh]}}$_2$ with the C=O polar bond was further investigated by computational studies revealing a plausible geometry of a pre-reactive intermediate. The experimental and theoretical studies suggest that while the Li atom of {Li(THF)$_2${BH_3[L(H)GePh]}} coordinates the C=O bond, the Ge*H* fragment is the active species in the reduction reaction. Finally, benzaldehyde was reduced by the mixture of L(H)Ge·BH_3 with PhLi in non-polar solvents.

Introduction

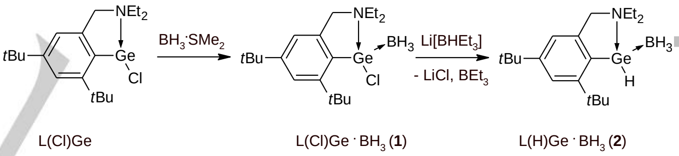
Low valent group 14 hydrides belong to an important class of organometallic compounds due to their reactivity towards various organic substrates.[1] It is well known that unsaturated organic bonds may interact with these compounds without any catalyst and that the substrate inserts into the E–H bond during the first step of a hydroelementation catalytic cycle.[2] However, the main disadvantage of this catalytic cycle is the recovering of the low-valent group 14 hydrides through metathesis reactions, which do not take place so prominently despite the progress made by groups of Power,[3] Aldridge,[4] Roesky,[5] Rivard[6] or Jones.[7]

Besides these stoichiometric reductions, the recent studies of Jones demonstrated that the two-coordinate (amido)(hydrido)-tetrylenes [(L*)(H)E:] (E = Ge, Sn, L* = [N(Ar)(SiMe$_3$)], Ar = [C_6H_2Me{C(H)Ph$_2$}$_2$-2,4,6]) may be used as efficient catalysts in the hydroboration of aldehydes or ketones RR^{1}C=O by the pinacol borane (HBpin).[8] It was reported that the [(L*)(H)E:] catalyst reacts with aldehydes or ketones RR^{1}C=O resulting in the formation of (amido)(alkoxy)tetrylene [(L*)(RR^{1}CHO)E:] in the first step.[8] The regeneration of the [(L*)(H)E:] catalyst was achieved through the reaction of [(L*)(RR^{1}CHO)E:] with HBpin along with the elimination of RR^{1}CHOBpin.[8] Moreover, the kinetic studies also suggested that the metathesis reaction is the rate determining step of this particular hydroboration.

As such, the studies of the reactions between the low valent group 14 compounds and various inorganic substrates may provide the last key aspect of the full catalytic cycle, which is essential for their application as catalysts in various organic transformations. Here we present our results of the reactivity studies of the borane adduct of the N→Ge coordinated germanium hydride L(H)Ge·BH_3 with organolithium salts RLi (L = [2-(CH_2NEt_2)-4,6-*t*Bu$_2$-C_6H_2]$^-$, R = Ph, *t*Bu, *n*Bu). These reactions yielded lithium hydrogermanatoborates {Li(THF)$_2${BH_3[L(H)GeR]}}$_2$ that were used as a source of highly soluble LiH in nonpolar solvents.

Results and Discussion

We have previously reported on the synthesis of monomeric germanium hydride complexes L(H)Ge·W(CO)$_5$ and L(H)Ge·Cr(CO)$_5$.[9] Similarly, the reaction of L(Cl)Ge[10] with BH_3 yielded complex L(Cl)Ge·BH_3 (**1**) that was converted by the subsequent reaction with Li[Et_3BH] into the monomeric germanium hydride L(H)Ge·BH_3 (**2**) (Scheme 1). Complex **2** was characterized by the help of NMR spectroscopy and X-ray diffraction analysis. The most relevant NMR data are the ^{1}H NMR resonance at δ 6.59 ppm attributed to the Ge*H* hydridic proton and a signal of the BH_3 group at δ –38.3 ppm in the ^{11}B{^{1}H} spectrum.



Scheme 1. Synthesis of the monomeric L(H)Ge·BH_3 (**2**)

The molecular structure of the germanium(II) hydride **2** showed that it retains its monomeric form in the solid state as well (Figure 1, Left). The selected bond lengths and angles are given in the caption of Figure 1, while the M06/cc-pVDZ(-PP) optimized geometry of **2** along with relevant bonding distances is shown in the right part of Figure 1.

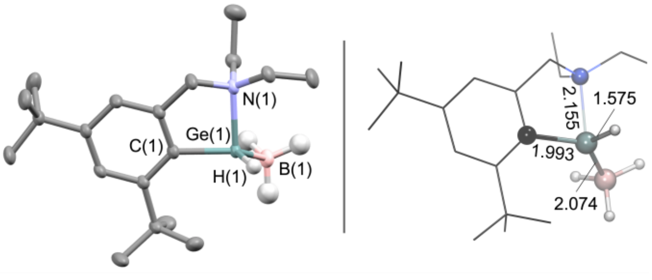


Figure 1. (Left) ORTEP presentation of the molecular structure of **2**. Selected bonding distances (in Å): Ge(1)-C(1) 1.9674(18); Ge(1)-N(1) 2.0686(16); Ge(1)-H(1) 1.54(2); Ge(1)-B(1) 2.050(2). (Right) M06/cc-pVDZ(-PP) optimized geometry of **2** along with relevant distances (in Å).

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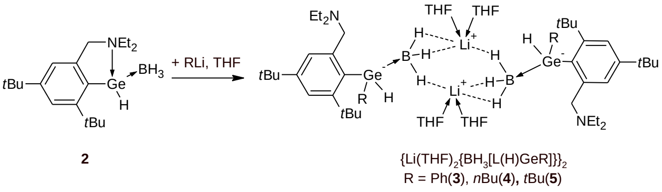
The Ge(1) atom is four coordinate by the C(1) and N(1) atom of the ligand L and by the B(1) and H(1) atoms. The Ge(1)-H(1) bond distance of 1.54 Å and the Ge(1)-B(1) bond length of 2.050(2) Å, which is close to the sum of the covalent radii of the parent atoms (Σ_{cov}Ge,B = 2.06 Å),[11] are similar to those found in related BH_3 complexes of the germanium(II) hydrides [2,6-$(Me_2N)_2C_6H_3]_2Ge\cdot BH_3$[12], $IPr\cdot GeH_2\cdot BH_3$,[13] $IPr\cdot GeH_2\cdot W(CO)_5$,[14] $IPr\cdot GeH(BH_3)NHDipp$,[15] $IPrCH_2\cdot H_2Ge{-}GeH_2\cdot W(CO)_5$,[16] $Ph_3PCMe_2\cdot GeH_2\cdot BH_3$,[17] and $IPr\cdot GeH(OSiMe_3)\cdot BH_3$[18] (IPr = $[(HCNDipp)_2C{:}]$; Dipp = 2,6-$i$$Pr_2C_6H_3$) with the Ge-B and Ge-H distances in the range of 2.032(3) - 2.0786(17) and 1.42(3) - 1.60(4) Å, respectively. It should also be noted that compound **2** is air and moisture stable.

The reaction of **2** with organolithium salts RLi (R = Ph, *n*Bu, *t*Bu) provided lithium hydrogermanatoborates $\{Li(THF)_2\{BH_3[L(H)GeR]\}\}_2$ (R = Ph(**3**), *n*Bu(**4**), *t*Bu(**5**)) as the addition products (Scheme 2). Compounds **3** - **5**, characterised by the help of NMR spectroscopy and X-ray diffraction analysis, are highly soluble in non-polar solvents such as hexane or toluene.



Scheme 2. Synthesis of hydrogermanatoborates $\{Li(THF)_2\{BH_3[L(H)GeR]\}\}_2$ (R = Ph(**3**), *n*Bu(**4**), *t*Bu(**5**)) as the addition products of RLi to **2**.

The ^1H NMR spectra of C_6D_6 solutions of **3** – **5** showed that the Ge*H* hydridic proton resonates at δ 5.65 (**3**), 5.03 (**4**) and 4.93 (**5**) ppm, respectively, as a consequence of different R group in **3** – **5**. All signals are shifted upfield as compared with the neutral complex **2** (δ 6.59). The ^1H NMR also showed the presence of a quartet of the B*H₃* protons at δ 0.34 (**3**), 0.12 (**4**), 0.19 (**5**) ppm with $^1J(^{11}B, ^1H) \sim 80$ Hz. The ^{11}B NMR spectra of **3** – **5** proved the presence of the BH_3 group by showing quartets at δ -41.4 (**3**), δ -40.7 (**4**), δ -41.5 (**5**), shifted upfield in comparison with **2.** These data indicate the higher electron density on the BH_3 moiety. For comparison, the B*H* protons in the neutral borane adduct η^2-$B_5H_8GeHMe_2$ resonate at $\delta \sim 7$ ppm.[19] The only analogue, monomeric complex $[\{HC(C(CH_2)NAr)CMeNAr\}Ge(H)BH_3]Li(OEt_2)_3$ (Ar = 2,6-$i$$Pr_2C_6H_3$), showed similar resonances for the BH_3 group (δ ^1H ranging from -0.65 to -1.15 ppm, δ ^{11}B at -43.68 ppm),[20] but the Ge*H* proton resonated downfield at δ 6.70 ppm in comparison to **3** – **5**. Finally, the $^7Li\{^1H\}$ NMR spectrum showed the signals at δ -0.03 (**3**), - 0.16 (**4**), -0.14 (**5**), shifted downfield in comparison with the monomeric $[\{HC(C(CH_2)NAr)CMeNAr\}Ge(H)BH_3]Li(OEt_2)_3$ (δ -1.41).[20]

Single crystalline material suitable for XRD analysis was grown from the hexane/toluene solutions of **3** – **5** at -20°C (Figures 2, 3 and Figures S1, S2 in SI); selected bond lengths are summarized in Table 1. The Li atom is six-coordinate by two oxygen atoms from the THF and by hydrogen atoms of two μ^2-BH_3 groups. The range of the Li–H distances in **3** - **5** (1.97 (5) – 2.12(4) Å is comparable with those found in the hexane-soluble LiH complexes $[\{(DippNPPh_2)Li\}_4(LiH)_4]\cdot C_6H_6$[21] $[\{[(Me_3Si)_2N]_2AlH\}_3(LiH)_4]$[22] and $[[\{(Me_3Si)_2N\}_2AlH_2]Li]_n$ [22] (a range of 1.81(4) – 2.26(2) Å). The hydrogen atoms of BH_3 groups in the dimeric structures of **3** – **5** are involved in the Li–H–B contacts (the Li–B distances range from 2.434(10) to 2.523(7) Å) resulting in a formation of the ten-membered $Li_2B_2H_6$ cluster (Figure 2). The Li and B atoms are placed at antipodal positions with the Li–Li distances ranging from 3.087(12) to 3.244(11) Å and the B–B distances in the range of 3.777(7) – 3.844(6) Å, structurally resembling the arrangement of the inorganic complex $\{TMEDA\cdot LiBH_4\}_2$,[23] but deviating from the monomeric structure of alkyltrihydroborate $[(THF)_3Li(\mu\text{-}H)_3BC(SiMe_2Ph)_3]$[24] or dimeric structure of $[\{[(Me_3Si)_2N]AlH_3Li\cdot 2OEt_2\}_2]$ with eight-membered $Li_2Al_2H_4$ ring.[25]

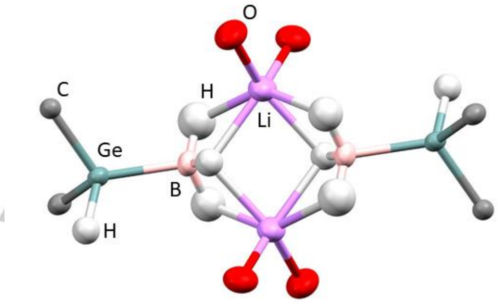


Figure 2. General motif of $Li_2B_2H_6$ core found in the molecular structures of **3** – **5**

The Ge atom is four-coordinate by two carbon atoms of the L and R groups, and by the hydrogen and boron atom. As suggested by the NMR data, the R group influences the Ge*H* moiety. In **3** (R = Ph), the Ge*H* atom has the longest Ge(1)-H(1) (1.50(3) Å) and B(1)-H(1) (2.94(4) Å) bond distances, while shorter Ge(1)-H(1) and B(1)-H(1) distances were found in **4** (R = *n*Bu; 1.46(4) and 2.85(4) Å, respectively) and **5** (R = *t*Bu; 1.41(4) and 2.86(5) Å). The B*H₃* protons have the B–H distances in the range of 1.09(4) – 1.15(5) Å, while the Ge–C bond lenghts are ranging from 1.972(3) to 2.028(4) Å (values typical for a covalent bond).[11] The Ge–B bond distances of 2.058(5) - 2.069(4) Å indicate the presence of a strong Ge→B donation in **3** – **5** (Σ_{cov}Ge,B = 2.06 Å).[11] Since the similar value was found in starting **2** (2.050(2) Å), one can propose that the Ge→B donation is not affected by the addition of RLi. This strongly contrasts with the N→Ge donation, that is present in **2** (2.069(2) Å), but is missing in **3** – **5** (distances up to 4 Å). Consequently, the addition of the R group is accompanied by the decoordination of the NEt_2 group from the Ge coordination sphere emphasizing the importance of the flexibility of the ligand L.

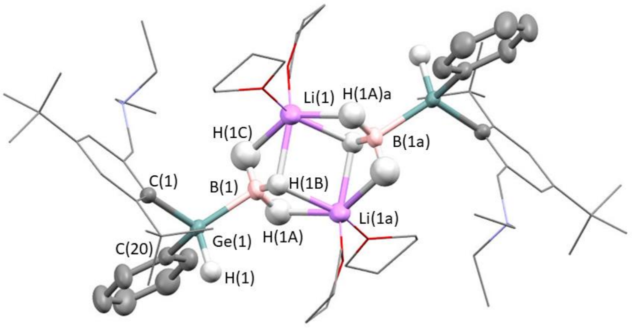


Figure 3. ORTEP presentation of the molecular structure of **3**

It is evident that the reaction of **2** with RLi salts is of a general character. The RLi salt attacks compound **2** and the nucleophilic addition of the R group to the Ge(II) atom takes place. This converts the neutral L(H)Ge(II) moiety into the organogermanato [L(H)Ge(II)R]$^-$ anion. As the latter moiety contains the Ge(II) atom, it may coordinate to the BH_3 group to provide hydrogermanato-borates {BH_3[L(H)GeR]}$^-$ compensated by the Li^+ cation.

Table 1. Selected bond lengths of **3** – **5** (in Å)

Compound/ Bond length	**3**	**4**	**5**
Ge(1)-B(1)	2.069(4)	2.058(5)	2.068(5)
Li(1)-B(1)	2.481(9)	2.482(9)	2.460(9)
Li(1)-B(1A)	2.523(7)	2.497(9)	2.434(10)
Ge(1)-C(1)	2.007(3)	2.023(4)	2.028(4)
Ge(1)-C(20)	1.973(3)	1.988(5)	2.022(4)
Ge(1)-H(1)	1.50(3)	1.46(4)	1.41(6)
B(1)-H(1)	2.94(4)	2.85(4)	2.86(5)
B(1)-H(1A-1C)	1.15(5) – 1.14(4)	1.09(4) – 1.10(5)	1.10(6) – 1.14(6)
Li(1)-H(1A)a	1.98(5)	1.99(6)	2.04(5)
Li(1)-H(1B)a	2.05(6)	1.98(4)	2.04(5)
Li(1)-H(1C)	2.10(4)	2.12(4)	2.02(5)
B(1)-B(1a)	3.844(6)	3.777(7)	3.797(7)
Li(1)-Li(1a)	3.203(8)	3.244(11)	3.087(12)

This strongly contrasts with the reaction of *t*BuLi and [{HC(CMeNAr)$_2$}GeH(BH_3)] (Ar = 2,6-*i*$Pr_2C_6H_3$) that provided [{HC(C(CH_2)NAr)CMeNAr}Ge(H)BH_3]Li(OEt_2)$_3$ along with the elimination of *t*BuH, without any evidence of *t*Bu addition to the Ge(II) centre.[20] Similarly, the reaction of [Ge{N($SiMe_3$)C(Ph)C($SiMe_3$)(C_5H_4N-2)}Cl] with an excess of PhC≡CLi afforded the lithium germinate [{(PhC≡C)$_3$Ge}$_3$GeLi(Et_2O)$_3$] as the side product of the elimination of the amido ligand.[26] These rare examples demonstrate the stability of **2** that can be easily transformed by nucleophilic addition of RLi to **3** – **5**, without any side reactions.

Given the unique structural motif of **3** – **5**, a DFT computational study was performed to gain a better understanding of their molecular structure and bonding. The geometries of all studied complexes were fully optimized at the M06/cc-pVDZ(-PP)[27] level of theory, which was chosen on the basis of our previous studies of the transition metal complexes of the type L(H)Ge·TM(CO)$_5$.[9] The agreement between the experimental X-ray diffraction data and the calculated structural parameters is very good (Figures 1 and 5, Figure S3 in SI). The structure of all compounds is very similar, showing a four-coordinate Ge centre with a distorted tetrahedral geometry. In line with the experimental data, a minor elongation of the Ge–C^R bond was observed going from **3** to **5**, while the Ge→B interaction was not affected by the different R substituents. Since the only structurally related compound was shown to be monomeric,[20,25] we have also optimized a plausible monomeric compound **3-mon**. As shown in Figure 4, the bonding pattern in the monomeric compound is almost identical as in the dimer, apart from the obvious shortening of the B···Li contact of *ca.* 0.1 Å. Interestingly, the μ^2-coordination of the BH_3 group resulting in the bending of the Ge→B···Li angle (130.9°) is also preserved in **3-mon** in contrasts to the angle of 161.0° found for [{HC(C(CH_2)NAr)CMeNAr}Ge(H)BH_3]Li(OEt_2)$_3$.[20] Moreover, the relative Gibbs free energy of **3** was found to be 2.6 kcal mol^{-1} lower in energy than that of **3-mon**, which confirms the formation of the dimeric compounds both in solution and solid state.

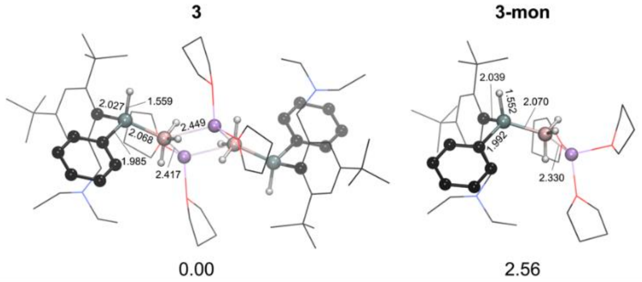
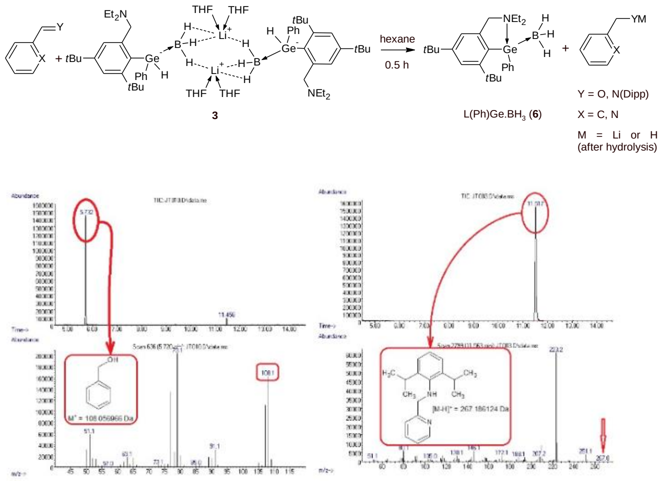


Figure 4. Optimized geometries of **3** and **3-mon** along with the selected distances (in Å) and relative Gibbs free energies (in kcal mol^{-1}; calculated in THF at the M06/cc-pVTZ(-PP) level)

The natural bond orbital (NBO) analysis[28] of the starting compounds **1** and **2** (Figure S4 in SI) revealed a strong intramolecular $n_N \rightarrow p^*_{Ge}$ donor-acceptor interaction that provides a stabilization energy of 56.6 and 79.8 kcal mol^{-1} for **1** and **2**, respectively. The strength and a high degree of covalent character of the Ge→B interaction is supported by the computed Wiberg bond index (WBI)[29] showing $WBI_{Ge\text{-}B}$ values higher than 0.9 (Table S2 in SI). This also results in the increase of the positive natural population analysis (NPA)[28] charge on the germanium centre in comparison to L(Cl)Ge. The NBO analysis of **3 – 5** showed an additional σ(Ge–C^R) NBO, which is highly polarized with the electron density mainly localized on the carbon atom (*ca.* 70 %) (Figure S4 in SI). The formation of the new Ge–C^R covalent bond in **3** – **5** instead of the N→Ge interaction in **1** and **2** leads to the higher energies of σ(Ge–H) and σ(Ge→B) NBOs. However, in agreement with the geometrical data, the $WBI_{Ge\text{-}B}$ (0.97) and $WBI_{Ge\text{-}H}$ (0.90) values of **3 – 5** are equal to those found for **2**. The negative NPA charge on the boron atom (*ca.* -0.8 *e*), as a result of a strong Ge→B interaction, is compensated by the positive NPA charge on the lithium atom (*ca.* 0.9 *e*), which suggest an ionic interaction between the BH_3 group and the lithium atom in **3 – 5** (This is further confirmed by a molecular electrostatic potential map of the simplified complex **3'**; Figure S5 in SI).

As the compounds **3** – **5** contain either B-H or Ge-H bonds, the ability of **3** to reduce C=O and C=N bonds in nonpolar solvents (hexane or toluene) was assessed in the stoichiometric reaction of **3** with benzaldehyde or iminopyridine (Scheme 3, for experimental details see SI). Interestingly, a new complex L(Ph)Ge·BH_3 (**6**) was isolated from this reaction (for experimental detail see SI), while the GC-MS analysis of the hydrolysed mixture proved complete reduction of the starting material (Scheme 3, Figures S6 and S7 in SI).



Scheme 3. Reduction ability of **3** towards C=Y polar bonds along with the GC-MS analysis of the reduced materials obtained from the reaction mixture.

Complex **6** was fully characterised by NMR spectroscopy, XRD analysis (Figure 5, Left) and DFT calculations (Figure 5, Right). The Ge atom in **6** is four-coordinate, proving again the importance of the flexibility of the pendant NEt$_2$ group (for the NBO analysis of **6** see Figure S4 and Table S2 in SI).

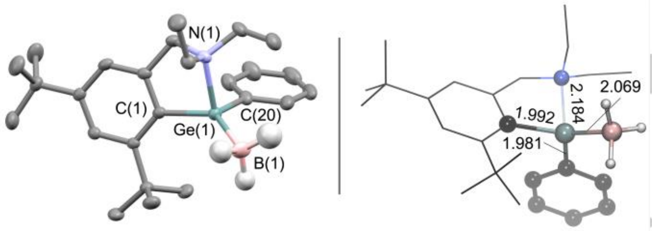


Figure 5A. (Left) ORTEP presentation of the molecular structure of **6**. Selected bonding distances (in Å): Ge(1)-C(1) 1.976(2); Ge(1)-N(1) 2.0844(17); Ge(1)-C(1) 1.966(2); Ge(1)-B(1) 2.047(3). (Right) M06/cc-pVDZ(-PP) optimized geometry of **6** along with relevant distances (in Å).

The isolation of **6** from the reaction mixture suggests that *LiH* eliminates from **3** during the reaction and therefore the unsaturated C=Y bonds are reduced by LiH. According to the DFT calculations, the reduction of the C=O polar bond of benzaldehyde by **3** might proceed *via* a pre-reactive intermediate where one of the THF molecules is replaced by the benzaldehyde (Figure 6 and Table S2 in SI). Analogous to **3**, the intermediate **3INT** is suggested to retain its dimeric structure with the related monomer **3INT-mon** being higher in energy by 6.7 kcal mol^{-1}. The structure of **3INT** closely resembles that of **3** with elongated B-Li distances, which is most probably caused by a stronger interaction of the benzaldehyde with the Li atom in comparison to the THF. Furthermore, the orientation of the carbonyl function towards the Ge*H* hydridic proton (Ge-H···CHO distance of 2.75 Å) is in line with the formation of **6**.

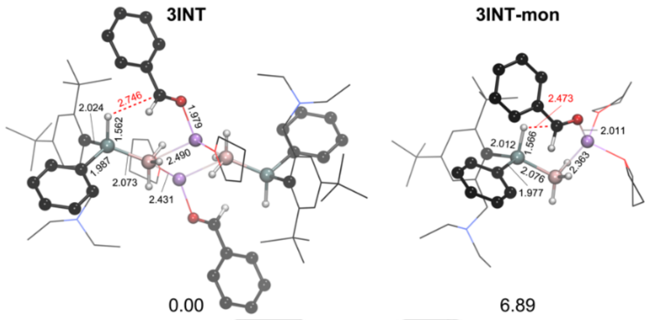
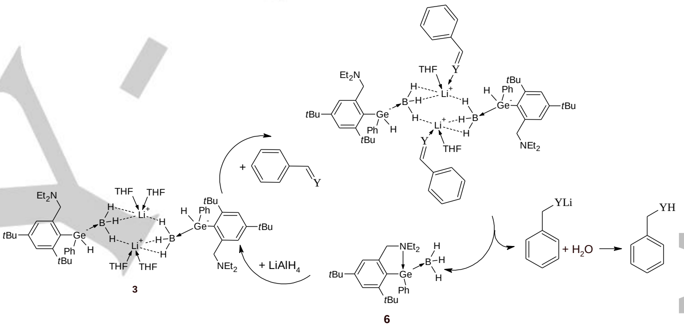


Figure 6. Optimized geometries of a pre-reactive intermediate **3INT** and its monomeric analogue **3INT-mon** along with the selected distances (in Å) and relative Gibbs free energies (in kcal mol^{-1}; calculated in hexane at the M06/cc-pVTZ(-PP) level)

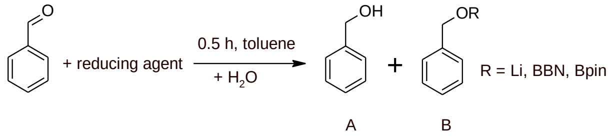
Since we have also found out that complex **3** can be recovered by the reaction of **6** with LiAlH$_4$ (for experimental details see SI), a plausible reaction mechanism of the reduction can be described according to Scheme 4, based on experimental and theoretical studies.



Scheme 4. Suggested mechanism of the reduction of C=Y bonds by **3**

Compounds **3** – **5** represent a good hydrocarbon-soluble LiH source, which can be used for the reduction of C=Y polar bonds in non-polar solvents, similarly to systems reported by Stach[21] or Mulvey[30], who used either [{(DippNPPh$_2$)Li}$_4$(LiH)$_4$]·C$_6$H$_6$[21] or 1-lithio-2-alkyl-1,2-dihydropyridine 2-*t*BuC$_5$H$_5$NLi·Me$_6$TREN (Me$_6$TREN is tris(N,N-dimethyl-2-aminoethyl)amine)[30] for the reduction of benzophenone in the non-polar solvents.

Finally, to prove the simplicity of the reduction process, the PhLi was mixed with complex **2** to generate complex **3** *in situ*, and the benzaldehyde was added. The organic fraction was examined by GC-MS analysis after 30 minutes (Scheme 5, Entry 2) and the peak of the benzyl alcohol (R_t ~ 5.7 min, [M]$^+$ = 108 Da) was determined in ~ 90% (Figure S8 in SI). For comparison, the reduction of benzaldehyde with 9-borabicyclo(3.3.1)nonane (9-BBN) was performed under the same conditions and the GC-MS analysis provided the evidence of benzyl alcohol (R_t ~ 5.7 min, [M]$^+$ = 108 Da, ~ 10%) and its boronic ester (R_t ~ 13.5 min, [M-2H]$^+$ = 226 Da, ~ 88%) (Figure S9 in SI) due to the insufficient hydrolysis of the B-*O* bond (Scheme 5, Entry 3). The reduction of benzaldehyde by HBpin is much slower and with a conversion of 95% after 8 hours.[31]



Entry	Reducing agent	Time (h)	% conversion (ratio of A:B)
1	**3**	0.5	>99 (100:0)
2	**2**/PhLi	0.5	>90 (100:0)
3	9-BBN	0.5	>90 (10:90)
4[31]	HBpin	8	95 (0:100)

benzaldehyde (1 mmol) and reducing agent (1.1 mmol); % conversions and ratios were obtained by GC MS

Scheme 5. Reduction ability of system **2/PhLi** towards C=O polar bond.

Thus, the complex **3** is a very strong reducing agent in non-polar solvent and its key advantage is that it can be easily prepared by mixing of **2** with PhLi in hexane.

Conclusion

In conclusion, we have reported on the synthesis of complexes $\{Li(THF)_2\{BH_3[L(H)GeR]\}\}_2$ that are easily formed by the reaction of $L(H)Ge\cdot BH_3$ with RLi. The polarity of their Ge-H bonds depends on the R group, based on NMR and XRD analysis. These compounds represent a non-polar solvent-soluble LiH source that can be further used for the reduction of organic C=O or C=N bonds together with the elimination of a neutral complex $L(Ph)Ge\cdot BH_3$. As the complexes $\{Li(THF)_2\{BH_3[L(H)GeR]\}\}_2$ may be easily prepared, the system of **2**/PhLi was successfully tested in the reduction of the benzaldehyde as well. Reactions of **2** with nucleophiles of different alkali metals to obtain soluble Group 1 metal hydrides are of our current interest.

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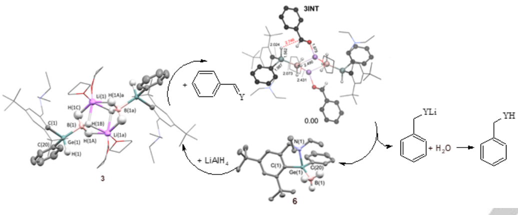

The reduction of C=Y polar bonds by RLi in the presence of monomeric germanium hydride is possible. The combination of PhLi with L(H)Ge·BH_3 yielded {Li(THF)$_2${BH_3[L(H)GePh]}} (**3**), a source of *LiH* for the reduction of benzaldehyde in non-polar solvents. The reaction proceeds *via* intermediate **3INT** accompanied by the elimination of a neutral complex L(Ph)Ge·BH_3 (**6**).