C,N-Chelated Organogermanium(II) Hydride as Catalyst for Esterification of Aldehydes

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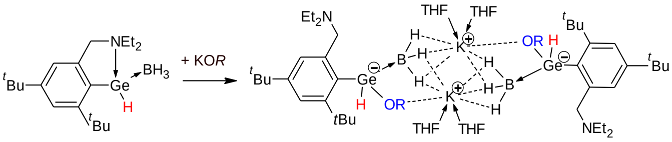
Abstract: The reactions of the monomeric C,N-chelated organogermanium(II) hydride L(H)Ge·BH$_3$ (**1**) with potassium alkoxides KOR provided potassium hydrido-alkoxo-germanato-borates {K(THF)$_2$[BH$_3$·Ge(L)(H)(OR)]}$_2$ (R = ^{t}Bu (**2**), C(CH$_3$)$_2$CH$_2$CH$_3$ (**3**)) as products of KO*R* addition. Compounds **2** and **3** react with benzaldehyde under formation of alkyl esters of benzoic acid along with elimination of a neutral complex L(H)Ge·BH$_3$ (**1**). Thus complex **1** was tested as a useful catalyst for esterification of aldehydes by KO^{t}Bu. The GC-MS analysis revealed formation of *t*-butyl esters of appropriated carboxylic acids. The mechanistic studies for the esterification of benzaldehyde with KO^{t}Bu catalysed by **1** were also performed either theoretically (DFT calculations), or experimentally (NMR and IR spectroscopy).

Introduction

Reactivity of tetrylene-hydrides RE(II)*H* (E is Si, Ge, Sn, Pb) towards unsaturated bonds classifies them as a very important class of organometallic compounds, which can be even compared to transition metal hydrides.[1] Studies made by groups of Power,[2] Aldridge,[3] Rivard,[4] Weseman,[5] Jones[6] or Roesky[7] nicely clarified that the hydroelementation may proceed also without the addition of catalyst. Substrate insertions into the E–H bond should be the first step of potential hydroelementation catalytic cycles. However, the recovering of the low-valent group 14 hydrides usually remains main disadvantage, despite the progress made by above mentioned groups.[2-7] Nowadays, tetrylene-hydrides RE(II)*H* are studied as active sites for catalysis. Depending on the system, these compounds are either used as isolable species, or are formed *in situ* from pre-catalysts.[1a,b] The foundation of their use was laid by the group of Jones, who demonstrated that two-coordinate tetrylenes hydrides [(N^{Ar})(H)E:] (E = Ge, Sn, N^{Ar} = [N(Ar)(SiMe$_3$)], Ar = [C$_6$H$_2$Me{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] Since that time, tetrylenes hydrides or their pre-catalysts have been tested more frequently as suitable catalysts for hydroboration, hydrosilylation, or cyanosilylation of aldehydes, ketones, pyridine or nitriles.[5, 8, 9] The conversion of CO$_2$ into the methanol equivalents MeOBR$_2$ (R = Bpin or Bcat) using the HBpin or HBcat was achieved either by tetrylenes hydrides pre-catalysts [(L´)(O^{t}Bu)E:] (E = Ge, Sn, L´ = [N(Ar*)(Si^{i}Pr$_3$)], Ar* = [C$_6$H$_3${C(H)Ph$_2$}$_2$-2,4,6]) reported by Jones, Maron and coworkers[10],or by Si(II) hydride complex [(ImMe$_4$)$_2$SiH]I [ImMe$_4$ = :C(NMe)$_2$(CMe)$_2$] reported by So and co-workers.[11] The Power group also successfully used Sn(II) hydride pre-catalysts [(Ar^{Me6})(μ-OMe)Sn:]$_2$ and [(Ar^{iPr4})(μ-OMe)Sn:]$_2$ (Ar^{Me6} = Ar^{Me6} = [C$_6$H$_3${C(H)Ph$_2$}$_2$-2,4,6]) in dehydro-coupling reactions of amines R$_2$NH (R = H, alkyl, aryl) with HBpin.[12] Finally, the Driess group opened another direction of tetrylene-hydride catalysis when they have reported on the cooperative activation of H$_2$ by a bimetallic Ni(0)/Si(II) system, and postulated active Ni(μ-H)$_2$Si structure.[13] Recently, we have started with studies including N→Ge coordinated germanium hydride L(H)Ge (L is [2-(CH$_2$NEt$_2$)-4,6-*t*Bu$_2$-C$_6$H$_2$]$^-$) and its adducts with ZnCl$_2$ and BH$_3$.[14] While the [L(H)Ge·ZnCl$_2$]$_2$ is an active catalyst in the ring-opening polymerization of the lactide, [14a] the borane adduct L(H)Ge·BH$_3$ (**1**) reacted with organolithium salts RLi (R = Ph, *t*Bu, *n*Bu) to produce lithium hydrido-germanato-borates {Li(THF)$_2${BH$_3$[L(H)GeR]}}$_2$.[14b] Here we report on the reactivity studies of **1** with potassium alkoxides, and subsequent use of **1** as an unpreceded catalyst in a direct esterification of aldehydes.

Results and Discussion

The monomeric germanium hydride L(H)Ge·BH$_3$ (**1**) was prepared according to our previous procedure.[14b] Complex **1** was then treated with different alkali alkoxides MO*R* (M = Li, Na, K; R = ^{t}Bu, C(CH$_3$)$_2$CH$_2$CH$_3$). While no reactions were observed for M = Li or Na, reactions of potassium alkoxides KOR provided potassium hydrido-alkoxo-germanato-borates {K(THF)$_2$[BH$_3$·Ge(L)(H)(OR)]}$_2$ (R = ^{t}Bu(**2**), C(CH$_3$)$_2$CH$_2$CH$_3$ (**3**)) as products of KO*R* addition (Scheme 2). These reactions thus mimic the addition of organolithium salts RLi (^{t}Bu, *n*Bu, Ph) into the **1**.[14b] Compounds **2** and **3** were characterized via NMR spectroscopy and X-ray diffraction analysis.



1

{K(THF)$_2${BH$_3$[L(H)GeOR]}}$_2$
R = ^{t}Bu (**2**), C(CH$_3$)$_2$CH$_2$CH$_3$ (**3**)

Scheme 1. Synthesis of {K(THF)$_2$[BH$_3$·Ge(L)(H)(OR)]}$_2$ (R = ^{t}Bu (**2**), C(CH$_3$)$_2$CH$_3$CH$_3$ (**3**)

The ^{1}H NMR spectra of THF-d_8 solutions of **2** and **3** showed that the Ge*H* proton resonates at δ 6.35 ppm and the ^{11}B{^{1}H} NMR spectra of **2** and **3** revealed the resonances at δ -37.6 (**2**) and -37.4 (**3**). The data correlate with those found for lithium germanato-borates $\{Li(THF)_2\{BH_3[L(H)GeR]\}\}_2$ (δ ^{1}H ranges from 4.93 to 5.65, δ ^{11}B ~ -41 ppm)[14b] and $[\{HC(C(CH_2)NAr)CMeNAr\}Ge(H)BH_3]Li(OEt_2)_3$ (Ar = 2,6-iPr$_2$C$_6$H$_3$, δ ^{1}H 6.70 ppm, δ ^{11}B at -43.7 ppm),[15] and proved existence of negatively charged $\{BH_3[L(H)GeR]\}^-$ moiety. The IR spectra showed typical vibrations of both B*H* and Ge*H* bonds at ν_{BH3} 2343 (**2**) or 2356 (**3**) cm^{-1}, and ν_{GeH} 1989 (**2**) or 1976 (**3**) cm^{-1}.[16]

Compounds **2** and **3** crystallize as discrete centrosymmetric dimers (Figure 1, for details see SI).[22] The $\{BH_3[L(H)GeR]\}^-$ ligand binds one potassium K1 through the O1 atom (2.700(2) Å in **2**, 2.706(2) Å in **3**), while the hydrogen atoms of borane coordinate second potassium K2. In addition, two hydrogens also coordinate the K1 ion and thus the borane group forms bridge between both potassium ions forming diamond-shaped $K_2(BH_3)_2$ core. The potassium ions are also coordinated by two THF molecules defining the potassium ions pseudo-eight coordinate. Similar arrangement was observed in potassium salts of amido-diphenylphosphine-borane ligands,[17] and thio-substituted phosphido-borane ligands.[18] The Ge atoms have the tetrahedral arrangement. The Ge–B bond distances (2.053(3) Å in **2**, 2.050(4) Å in **3**) suggest strong Ge→B interaction (Σ_{cov}Ge,B = 2.06 Å).[19] The Ge–O bond distances (1.8428(2) Å in **2**, 1.845(2) Å in **3**) are closed to the sum of the covalent radii of the parent atoms (Σ_{cov}Ge,O = 1.84 Å).[19]

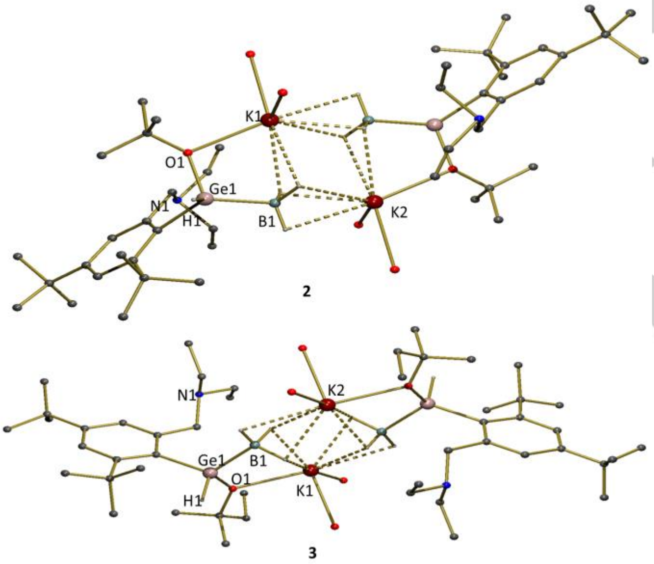
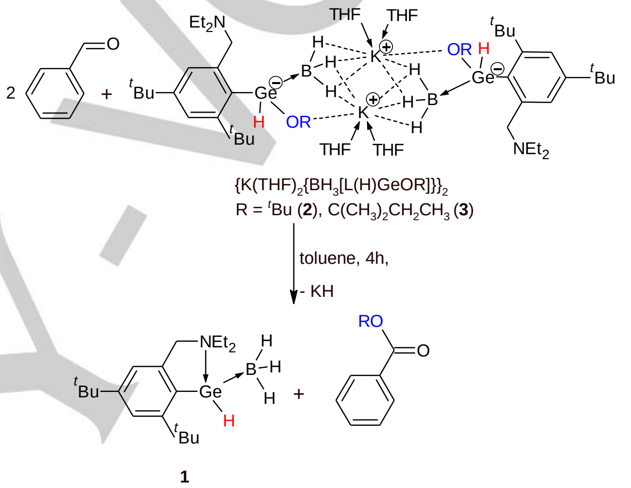


Figure 1. Molecular structures of **2** and **3.** Hydrogen atoms (except of the Ge*H*) and coordinated molecules of THF are omitted. Selected bond distances (Å) and angles (°): For **2**: Ge1-O1 1.8428(17), Ge1-B1 2.053(3), K1-O1 2.700(2), Ge1-H1 1.49(4), O1-Ge1-C1 105.99(9), O1-Ge1-B1 105.36(10). For **3**: Ge1-O1 1.845(2), Ge1-B1 2.050(4), K1-O1 2.706(2), Ge1-H1 1.48(4), O1-Ge1-C1 106.70(11), O1-Ge1-B1 106.04(13).

Thus, it seems that reactivity of **1** towards nucleophiles (Nu$^-$) has a general character. The Nu$^-$ group may coordinate the Ge(II) atom and convert a neutral L(H)Ge(II) moiety into the organogermanato anions $[L(H)Ge(II)R]^-$ (R is Nu$^-$). This process is accompanied with the de-coordination of the Et$_2$N arm of L. The flexibility and stability of **1** contrasts with a related germanium hydride $[\{HC(CMeNAr)_2\}GeH(BH_3)]$ (Ar = 2,6-iPr$_2$C$_6$H$_3$) that provided $[\{HC(C(CH_2)NAr)CMeNAr\}Ge(H)BH_3]Li(OEt_2)_3$ along with the elimination of ^{t}BuH.[15]

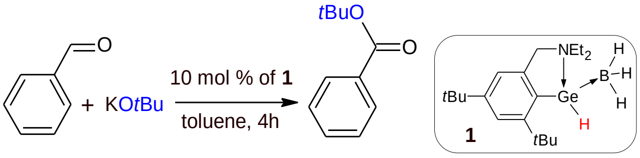
Since these compounds **2** and **3** contain both B-H and Ge-H bonds, their ability to reduce C=O bond was assessed by the stoichiometric reaction with benzaldehyde (Scheme 2, for experimental details see SI), similarly to their lithium analogues $\{Li(THF)_2\{BH_3[L(H)GeR]\}\}_2$.[14b] Interestingly, the GC-MS analysis of a reaction mixture showed formation of appropriate alkyl esters ROC(O)Ph (R = ^{t}Bu, C(CH$_3$)$_2$CH$_2$CH$_3$) with conversions up to 95% (Scheme 2, Figures S9 and S10 in SI). In addition, monitoring of stoichiometric reactions in C$_6$D$_6$ revealed signal of the Ge*H* proton at δ 6.54 ppm, characteristic for L(H)Ge·BH$_3$ (**1**), and suggested a recovery of neutral germanium hydride **1** during this reaction (Figure S11 in SI),



Scheme 2. Stoichiometric reaction of **2** and **3** with benzaldehyde.

The formation of **1** in the reaction mixture also suggests, that Ge*OR* group of the starting **2** or **3** is transferred to benzaldehyde and new C*OR* bond is formed to provide parent esters of benzoic acids, as detected by GC-MS analysis. Thus, compound **1** appears as a starting material for synthesis of **2**/**3**, as well as the product of abovementioned reactions of **2/3** with benzaldehyde.

Therefore, **1** could be a useful catalyst for esterification of benzaldehyde. Thus, the reaction of benzaldehyde with KO^{t}Bu in the presence of **1** as the catalyst (10 mol %) was done under same conditions (Scheme 3). Once more, the GC-MS analysis revealed formation of *t*-butyl ester of benzoic acid as the major product with conversion up to 95% (Figure S12 in SI). To see the effect of **1**, a blind experiment between benzaldehyde and KO^{t}Bu in an absence **1** was carried out as well. The GC-MS analysis revealed presence of benzyl ester of benzoic acid as the major product (conversion ~ 90%, Figure S15 in SI), typical for Tischenko reaction. Therefore, the presence of **1** shifts progress of the reaction toward alkyl esters of benzoic acid.



Scheme 3. Esterification reaction of benzaldehyde with KO^{t}Bu catalyzed by **1**.

It should also be noted, that the decrease of catalytic loading of **1** to 1 % provided mixture of *t*-butyl ester of benzoic acid (~70%) and benzyl alcohol (~ 30%, Figure S14 in SI). The effect of cations M (M = Li, Na, K) in MO^{t}Bu was also tested. Therefore, reactions of benzaldehyde with MO^{t}Bu (M = Li or Na) in the presence of **1** as the catalyst (10 mol %) were done, but no *t*-butyl ester of benzoic acid was detected by GC-MS analysis (Figure S13). However, this observation, fits well with low reactivity of **1** towards MO*R* for M = Li and Na. Therefore, **1** cannot be converted into the appropriate hydrido-alkoxo-germanato-borate.

The courses of studied reactions were also monitored by IR spectroscopy using ATR probe following the changes of the band area corresponding to C=O stretching mode of benzaldehyde (Figure 2). We have observed, that stoichiometric and catalytic (10 mol. % of **1**) reactions proceed very fast and starting compounds are converted into respective ester within 15 minutes. We note that using of catalytic amount of **1** lead to a slight decrease in the reaction rate when 70% of conversion is achieved. Thus we propose, that In the catalytic reaction catalyst **1** reacts with KO^{t}Bu to provide **2** that may react with the benzaldehyde as a rate determining step. The regeneration of **1** is the final step and it can repeatedly react with KO^{t}Bu to give **2**. A series of reactions performed at various stoichiometry proved that conversion of benzaldehyde corresponds to the amount of KO^{t}Bu used in the reaction, see Figure S16 in SI. This again confirms, that **1** reacts with KO^{t}Bu to provide **2**, and this step is then followed by the reaction with benzaldehyde.

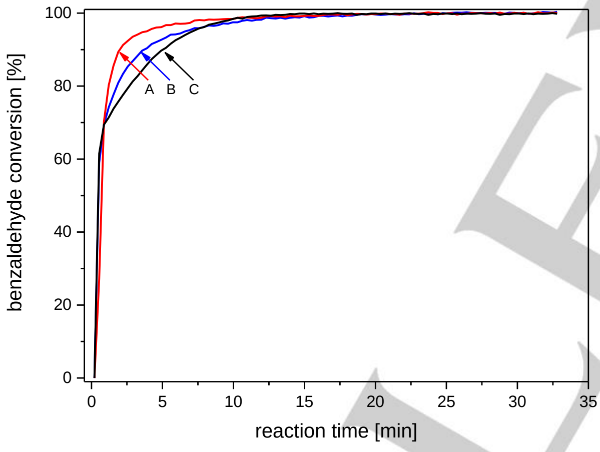
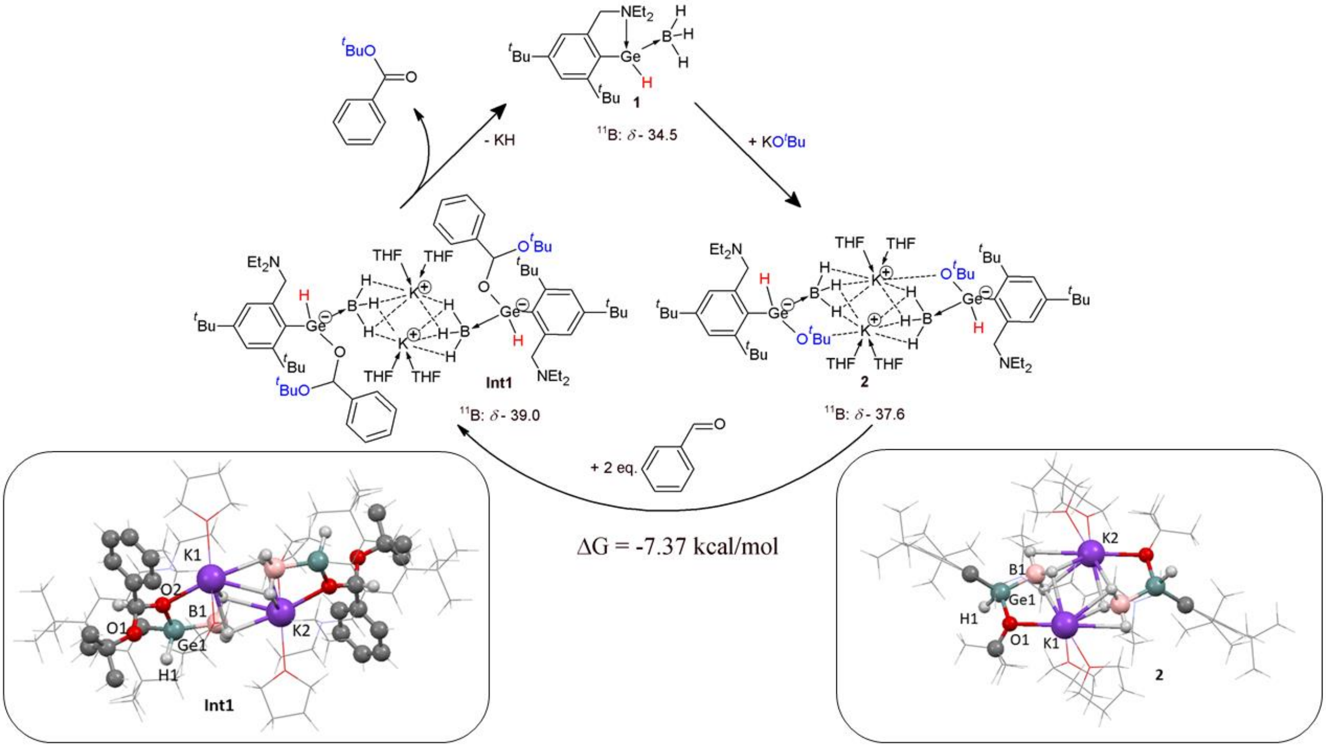


Figure 2. The courses of stoichiometric (**A**, **B**) and catalytic (**C**) reactions monitored by time-resolved FTIR spectroscopy. Experimental conditions: B) benzaldehyde + KO^{t}Bu + **1**, B) benzaldehyde + **2**, **C**) benzaldehyde + KO^{t}Bu + 10 mol% of **1.**

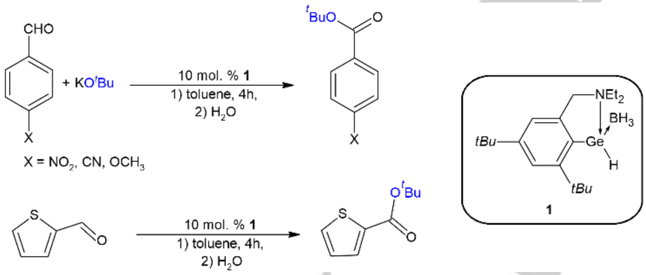
To explain the rapid consumption of the C=O bond of the benzaldehyde together with the formation of new CO^{t}Bu bond, we tentatively propose, that reaction might proceed *via* a pre-reactive intermediate **Int1**, as the addition product of the GeO^{t}Bu bond of **2** to the C=O bond of the benzaldehyde (Scheme 4). To support this proposed mechanism, DFT computational studies were performed to gain a better understanding of the molecular structure of **2** and suggested **Int1**. The geometries of both complexes were fully optimized at the M06/cc-pVDZ(-PP)[20] level of theory, which was chosen on the basis of our previous studies of lithium organogermanato compounds $\{Li(THF)_2\{BH_3[L(H)GeR]\}\}_2$ (R is Ph, *t*Bu, *n*Bu),[14b] or of the transition metal complexes of the type L(H)Ge·TM(CO)$_5$.[21] We have previously demonstrated, that dimeric structures of the lithium organogermanato compounds $\{Li(THF)_2\{BH_3[L(H)GeR]\}\}_2$ (R is Ph, *t*Bu,*n*Bu),[14b] analogues of **2**, are more stable than its monomers $Li(THF)_2\{BH_3[L(H)GeR]\}$. In the case of studied complex **2** and plausible corresponding monomer (**2-mon**, see SI) the DFT calculations confirmed stabilization of dimeric structure by 4.55 kcal/mol. Therefore, here we have focused mainly on the optimalization of the dimeric structure of **2** and on its interaction with benzaldehyde. The agreement between the experimental X-ray diffraction data of **2** and the calculated structural parameters was deemed satisfactory (Scheme 4). The structure is very similar, showing a diamond-shaped $K_2(BH_3)_2$ core and four-coordinate Ge center with a distorted tetrahedral geometry with bond lengths Ge-O 1.889 Å; Ge-C 2.029 Å; Ge-B 2.073 Å. According to the DFT calculations, reaction of **2** with two eq. of benzaldehyde might process *via* a pre-reactive intermediate **Int1** (Scheme 4), where new C-O bond C-O 1.376 Å) interacts either with potassium cation (K-O 2.665 Å) or Ge atom under the formation of a new Ge-O-C(H)Ph bond (Ge-O 1.912 Å). The original GeO^{t}Bu bond of **2** is cleaved during the reaction and a new Ph(H)C-*O*^{t}Bu (1.416 Å) is formed in **Int1**. The structure of **Int1** resembles **2** and remains as hydrido-alkoxo-germanatoborate $\{K(THF)_2[BH_3·Ge(L)(H)(OR)]\}_2$ (R = C(O*t*Bu)(H)Ph) having four-coordinate Ge center with Ge→B interaction (2.073 Å). Moreover, according to the DFT calculations, reaction of **2** with 2 eq. of PhCHO to yield **Int1** is a thermodynamically favored with ΔG = -7,37 kcal/mol.

To slow down the reaction rate, both stoichiometric (Scheme 2) and catalytic (Scheme 3) reactions were done at -50°C in THF and were monitored by ^{11}B NMR spectroscopy. After 10 minutes, the stoichiometric reaction revealed signals at δ -37.6 of starting **2** together with a new signal at δ -38.6 (Figure S17 in SI). This new signal corroborates formation of new $\{BH_3[L(H)GeR]\}^-$ moiety (**Int1**) in reaction. In contrast after 60 minutes, the ^{11}B NMR spectrum showed signals at δ -38.6 of **Int1** and at δ -34.5 ppm of **1**, while the signal of starting **2** disappeared (Figure S18 in SI). Similarly, catalytic reaction reveled signals at δ -34.5 (**1**), -38 (**2**) and -38.6 ppm (major signal of **Int1**) after 10 minutes (Figure S19 in SI), and at δ -35.5 (**1**) and -39.6 ppm (major signal of **Int1**) after 60 minutes (Figure S20 in SI). All these data support the mechanism proposed in Scheme 4, where **1** is converted to **2** *via* reactions with KO^{t}Bu, which is followed by the reaction with benzaldehyde to give aa new hydrido-alkoxo-germanato-borate **Int1**. This species is unstable and decomposes to **1** and *t*-butyl ester of benzoic acid.



Scheme 4. Catalytic cycle for the esterification of benzaldehyde with KO^{t}Bu catalysed by **1** proposed by DFT calculations (optimalization of **2**, **Int1** and ΔG) in the combination with the experimental studies (NMR and IR spectroscopy)

We have also done some preliminary tests for the scope of substrates. Therefore, reactions of substituted aldehydes with KO^{t}Bu in the presence of **1** as the catalyst (10 mol %) were done under same conditions (Scheme 5). The GC-MS analysis of the reaction mixtures revealed nearly quantitative formation of appropriate *t*-butyl esters with conversion up to 95% (Figures S21-S24 in SI).



Scheme 5. Esterification of substituted aldehydes by KO^{t}Bu catalyzed by **1**

Finally, we have also run the esterification reaction of 4-CN benzaldehyde as the up-scale experiment (200 mg) and corresponding *t*-butyl ester of 4-CN-benzoic acid was isolated and characterized by ^{1}H NMR spectroscopy (Figure S25 in SI)

Conclusion

In conclusion, we have reported on the synthesis of potassium hydrido-alkoxo-germanato-borates K(THF)$_2$[BH$_3$·Ge(L)(H)(OR)]}$_2$ (R = ^{t}Bu(**2**), C(CH$_3$)$_2$CH$_2$CH$_3$ (**3**)) as products of KO*R* addition to neutral L(H)Ge·BH$_3$ (**1**). Both compounds **2** and **3** react with benzylaldehyde to provide appropriate alkyl esters of benzoic acid and eliminates starting **1.** This demonstrates possible application of **1** as a catalyst for esterification of benzaldehyde by KO^{t}Bu. This unique application of tetrylene hydrides was not reported up to date. The possible application of **1** as a catalyst for the esterification of several substrates was demonstrated and it was also clearly proven, that the presence of 10 mol. % of **1** shifts progress of the reaction toward alkyl esters of benzoic acid from the Tischenko reaction. Mechanistic studies also support formation of **2** by the reaction of **1** and KO^{t}Bu in the catalytic cycle. Reaction of **2** with the C=O bond of the benzaldehyde may process as addition reaction of the GeO^{t}Bu bond of **2** to the C=O bond of the benzaldehyde *via* a pre-reactive intermediate **Int1**. The addition reactions of the GeO*R* bond in N-coordinated germylenes are thus of current interest.

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Keywords: hydride • germylene • esterification • IR spectroscopy • NMR spectroscopy

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[22] Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 2372333 and 2372334 for **2** and **3**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EY, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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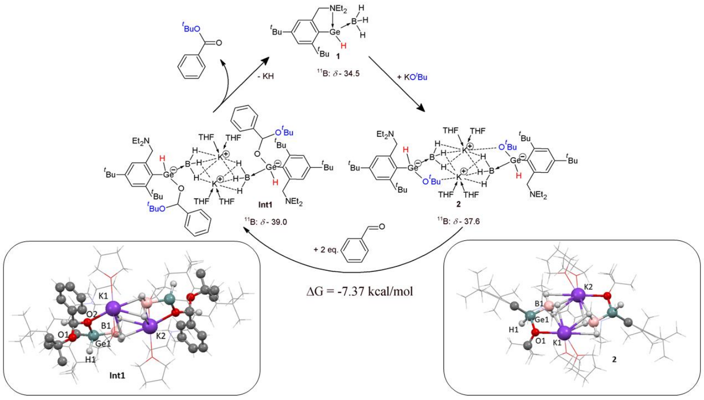

Monomeric C,N-chelated organogermanium(II) hydride L(H)Ge·BH$_3$ (**1**) reacts with potassium alkoxides to give potassium hydrido-alkoxo-germanato-borates {K(THF)$_2$[BH$_3$·Ge(L)(H)(OR)]}$_2$ (R = ^{t}Bu (**2**), C(CH$_3$)$_2$CH$_2$CH$_3$ (**3**)) as products of KO*R* addition. Moreover, Complex **1** was tested as useful catalyst for esterification of aldehydes by KO^{t}Bu to yield *t*-butyl esters of appropriated carboxylic acids.