# Germanium(II) hydride mediated reduction of carbon dioxide to formic acid and methanol with ammonia borane as the hydrogen source†‡

**Anukul Jana, Gašper Tavčar, Herbert W. Roesky* and Michael John***

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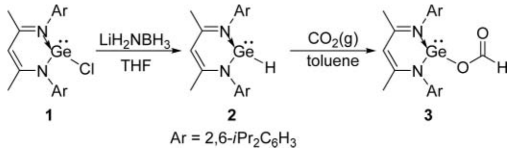
**LGeOC(O)H (3) (L = CH{(CMe)(2,6-*i*Pr$_2$C$_6$H$_3$N)}$_2$), from the straightforward conversion of LGeH (2) with CO$_2$, reacts with LiH$_2$NBH$_3$ giving 2 and LiOC(O)H (4), while the corresponding reaction of 3 with H$_3$NBH$_3$ after aqueous workup releases 2 and CH$_3$OH (5). This opens the possibility to use hydride 2 as a mediator in the reduction of carbon dioxide to formic acid and methanol.**

Carbon dioxide is nowadays recognised as a major contributor to global warming.[1] Processes that store or chemically transform carbon dioxide and help to reduce its concentration in the atmosphere are therefore urgently sought after.[2] On the other hand formic acid and methanol are outstandingly important compounds because of their extensive use in the laboratory as well as in industry. Traditionally the synthesis of formic acid involves the reaction of methanol and carbon monoxide, followed by hydrolysis.[3] The direct catalytic reduction of carbon dioxide with dihydrogen results in the formation of a mixture of products, including methanol.[4] Hydrogenation of carbon dioxide to generate formic acid and methanol is an interesting option, because carbon dioxide is readily accessible, inexhaustible, of low toxicity and therefore an ideal environmentally friendly C$_1$ building block. However the kinetic and thermodynamic stability of carbon dioxide presents significant challenges in designing efficient chemical transformations.

In the literature, the hydrogenation of carbon dioxide has been widely investigated using transition metal complexes.[5] Recently, the groups of Stephan and Erker reported the activation of carbon dioxide with a frustrated Lewis pair[6] and its reduction to methanol with ammonia borane in 37–51% yield.[7] Ashley *et al.*[8] outlined a completely metal-free hydrogenation of carbon dioxide to methanol in 6 days at 160 °C (24% yield). In our laboratory we discovered a very simple synthesis of germanium(II) formate[9] and tin(II) formate[10] using gaseous carbon dioxide with germanium(II) hydride and tin(II) hydride,[11] respectively, under mild conditions without any additional catalyst. Herein, we report the conversion of germanium(II) and tin(II) formate back to germanium(II) and tin(II) hydride and formic acid or methanol using ammonia borane as the hydrogen source.

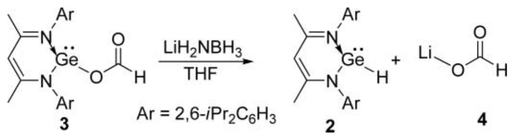
Ammonia borane (AB) is currently receiving enormous attention as a safe hydrogen storage material.[12] For example, the hydrogenation of N-heterocyclic carbene (1,3-di-*tert*-butylimidazole-2-ylidene) to 2,3-dihydro-1,3-di-*tert*-butylimidazole and N-heterocyclic germylene to germanium(II) hydride has been achieved by applying ammonia borane as the hydrogen source,[13] instead of hydrogen gas in the presence of finely divided Pd or Pt metal. The ammonia borane molecule contains both hydridic B–H and protic N–H polarised bonds and a strong B–N bond so that hydrogen release from solid AB is more favorable than the dissociation into ammonia and borane under non-catalytic conditions. We have replaced one of the protic hydrogen atoms of ammonia borane with an alkali metal. The reaction of *n*BuLi with ammonia borane leads to LiH$_2$NBH$_3$,[14] which is a highly nucleophilic reducing reagent.

The reaction of LGeCl, (L = CH{(CMe)$_2$(2,6-*i*Pr$_2$C$_6$H$_3$N)$_2$}) (**1**)[15] with lithium amidoborane (LiH$_2$NBH$_3$) yields LGeH (**2**),[16] which was previously prepared using NaBH$_4$–Me$_3$P,[17] AlH$_3$·NMe$_3$,[11] and K-selectride,[9] respectively (Scheme 1). In the course of this reaction there is no indication of the formation of germanium(II) amidoborane (LGeNH$_2$·BH$_3$), similar to observations made during the recent synthesis of zinc hydride (LZnH).[18] LGeH (**2**) reacts with carbon dioxide under ambient conditions to give germanium(II) formate (LGeOC(O)H) (**3**) (Scheme 1).[9]



**Scheme 1** Preparation of **2** and **3**.

The 1 : 1 reaction of LGeOC(O)H (**3**) with LiH$_2$NBH$_3$ in THF at −78 °C leads to the re-formation of LGeH (**2**) and lithium formate (LiOC(O)H) **4** (Scheme 2).[16]



**Scheme 2** Preparation of **4**.

The $^1$H NMR spectrum of the crude reaction mixture in C$_6$D$_6$ indicates the conversion of LGeOC(O)H (**3**) to LGeH (**2**) in almost quantitative yield. After workup with D$_2$O and addition of 1,4-dioxane as an external standard, the formation of LiOC(O)H (**4**) was confirmed by $^1$H (singlet at 8.37 ppm), $^7$Li (−0.15 ppm), and $^{13}$C (171.0 ppm) NMR spectra. The average calculated yield of lithium formate was in the range of 85–95%. Lithium formate is easily converted to formic acid by reaction with hydrochloric acid.

After the successful reaction of LGeOC(O)H (**3**) with LiH$_2$NBH$_3$ we were interested in whether **3** would also react

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*Institut für Anorganische Chemie, Universität Göttingen, Tammannstrasse 4, 37077, Göttingen, Germany. E-mail: hroesky@gwdg.de, michael.john@gwdg.de; Fax: +49 551-39-3373*

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directly with $H_3NBH_3$ using THF and benzene as solvents. As confirmed by $^1H$ NMR spectroscopy, conversion of **3** was very slow at room temperature, presumably due to the limited solubility of $H_3NBH_3$. However heating to 60 °C greatly accelerated the reaction, and after 2 h (THF) and 18 h (benzene) nearly quantitative conversion of **3** to LGeH (**2**) and a little amount of free ligand LH was observed (Fig. 1).

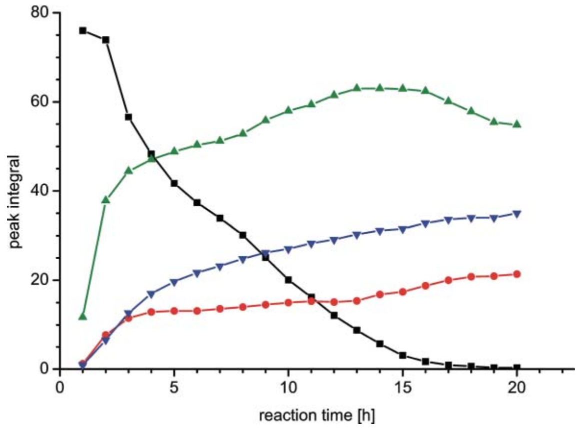
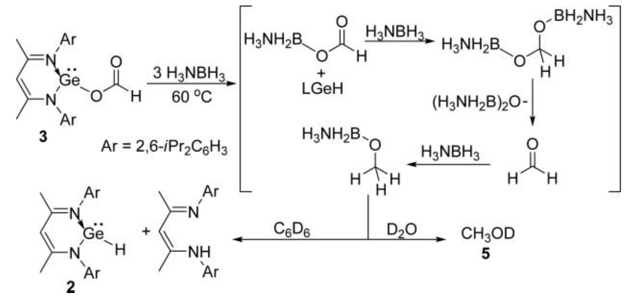


**Fig. 1** Reaction of **3** with 3 eq. $H_3NBH_3$ at 60 °C in $C_6D_6$ monitored by $^1H$ NMR (■: **3**, ▲: **2**, ▼: unidentified second product, ●: LH). The γ-H resonances at 5.07 ppm, 4.93 ppm, 4.94 ppm and 4.86 ppm, respectively, were used for integration. Start of heating to 60 °C was at $t = 0$.

The workup was again accomplished with $D_2O$, and the resulting $D_2O$ phase contained $CH_3OD$ (**5**) (yield: 33–43%, $^1H$ NMR: singlet at 3.27 ppm, $^{13}C$ NMR: quartet at 48.7 ppm, $^1J_{CH}$ = 142 Hz) as the major product. To investigate the mechanism of methanol formation, we ran several reactions in $C_6D_6$ and THF-$d_8$ at the NMR scale, using $^{13}C$-labelled formate **3** (obtained from $^{13}CO_2$ as described above). Initially, with the formation of LGeH (**2**) the $^{13}C$-label appears in several formate species (the resonances are somewhat broad), suggesting that the Ge–O bond is cleaved prior to reduction of the –OC(O)H group (Scheme 3).



**Scheme 3** Proposed mechanism of the formation of methanol from **2** and ammonia borane.

The reduction then presumably proceeds *via* several intermediates that are short-lived and could not be detected by NMR spectroscopy. The finally $^{13}C$-labelled compounds are mostly (B)–O–$CH_3$ derivatives that appear around 3–3.5 ppm and 48–52 ppm in the $^1H$ and $^{13}C$ NMR spectrum, respectively (Fig. 2). These compounds are expected to yield methanol upon workup with $D_2O$. As side-products, small amounts of N-methylated compounds are formed.

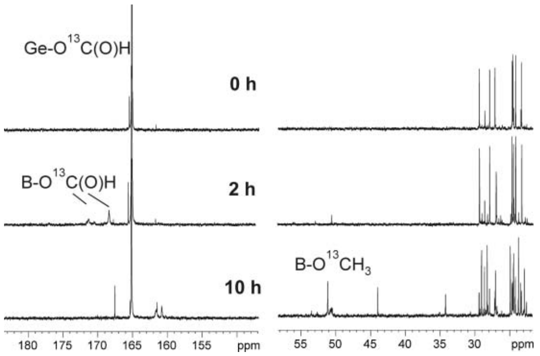


**Fig. 2** $^{13}C$ NMR spectra of $^{13}C$-labelled **3** with 3 eq. $H_3NBH_3$ in $C_6D_6$ directly, 2 h and 10 h after heating to 60 °C.

The conversion of LGeOC(O)H (**3**) to LGeH (**2**) regenerates the primary $CO_2$-capturing agent. Here it is worth mentioning that LGeH is stable towards water and can therefore be easily separated from the other reaction products by extraction with benzene. Currently we are trying to optimise the conditions for the catalytic conversion of carbon dioxide to its derivatives under ambient conditions. Initial results indicate that the reaction of the tin(II) analogue LSnOC(O)H with ammonia borane is complete within a few hours at room temperature and yields similar methyl derivatives. However, in contrast to LGeH (**2**), the corresponding tin hydride is not stable under the reaction conditions and decomposes to the free ligand LH and metallic Sn. In conclusion we have shown the possibility of a germanium(II) hydride mediated synthesis of formic acid and methanol from gaseous carbon dioxide using ammonia borane as the hydrogen source.

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16 (*a*) *Preparation of LGeH* (**2**): *n*BuLi (0.62 mL, 1.6 M in *n*-hexane) was added to a solution of $H_3NBH_3$ (0.030 g, 1.0 mmol) in THF (15 mL) at −78 °C. The resulting solution was allowed to warm slowly to room temperature and stirred for another 30 min. This solution was added drop by drop to a solution of LGeCl (**1**) (0.52 g, 1.0 mmol) in THF (15 mL) at −78 °C. The resulting solution was allowed to warm slowly to room temperature and stirred for another 30 min. During this period the colour of the reaction mixture changed to red. Then the solvent was removed under vacuum and the residue was extracted with *n*-hexane (60 mL). Yield: 0.43 g (88%); mp 170 °C. $^1$H NMR (200 MHz, $C_6D_6$): $\delta$ 7.10–7.15 (m, 6H, Ar-*H*), 4.86 (s, 1H, C*H*), 3.59 (sept, 2H, C*H*($CH_3)_2$), 3.37 (sept, 2H, C*H*($CH_3)_2$), 1.60 (s, 6H, C$H_3$), 1.35 (d, 6H, CH(C$H_3)_2$), 1.22 (d, 6H, CH(C$H_3)_2$), 1.19 (d, 12H, CH(C$H_3)_2$) ppm; (*b*) *Conversion to LiOC(O)H* (**4**): *n*BuLi (0.31 mL, 1.6 M in *n*-hexane) was added to a solution of $H_3NBH_3$ (0.015 g, 0.5 mmol) in THF (10 mL) at −78 °C. The resulting solution was allowed to warm slowly to room temperature and stirred for another 30 min. This solution was added drop by drop to a solution of LGeOC(O)H (**3**) (0.26 g, 0.5 mmol) in THF (10 mL) at −78 °C. The resulting mixture was allowed to warm slowly to room temperature and stirred for another 30 min. During this period the colour of the reaction mixture changed from colourless to red. Then the solvent was removed under vacuum and the residue was dissolved in toluene (10 mL) and $D_2O$ (10 mL). The $D_2O$ phase was separated and added to a measured amount of 1,4-dioxane as an internal standard. Yield: 85–95%. $^1$H NMR $\delta$ 8.37 ppm. $^7$Li NMR $\delta$ −0.15 ppm. $^{13}$C NMR 171.0 ppm; (*c*) *Conversion to $CH_3OD$* (**5**): LGeOC(O)H (**3**) (0.26 g, 0.5 mmol) and $H_3NBH_3$ (0.044 g, 1.5 mmol) were suspended in benzene (10 mL) at room temperature and heated in an oil bath to 60 °C. After 18 h, the brownish mixture was allowed to cool down, and 10 mL of $D_2O$ were added to form two phases. The $D_2O$ phase was separated and a measured amount of 1,4-dioxane was added. Yield: 33–43%. $^1$H NMR $\delta$ 3.25 ppm. $^{13}$C NMR $\delta$ 48.7 ppm.

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