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ARTICLE

Mechanistic studies of CO₂ reduction to methanol mediated by an *N*-heterocyclic germylene hydride

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The labile germylene hydride L^{Cy}GeH is capable to activate CO₂ affording the corresponding formate L^{Cy}GeOCH(=O) (**2**) (L^{Cy} = cyclo-C₆H₈-1-NAr-2-C(Ph)NAr, Ar = 2,6-*i*Pr₂C₆H₃). Compound **2** and the previously reported LGeOCH(=O) (L = CH(MeC=NAr)₂, Ar = 2,6-*i*Pr₂C₆H₃) (**2'**) could be further converted to methanol with the AlH₃•NMe₃ alane-amine adduct as hydrogen source upon workup with water. A plausible mechanism for the conversion of the formate complexes to methanol is proposed based on additional results from the conversion of **2'** with the milder hydride delivery agent LAIH₂.

Introduction

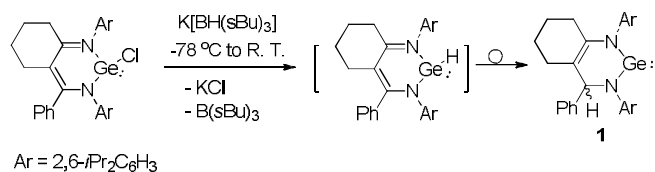
The activation and conversion of carbon dioxide to valuable chemicals is attracting increasing attention in chemical research due to the energy and climate crisis.¹ Hydrogenation of carbon dioxide to other C1 feedstocks, such as formic acid, methanol and methane is one of the most straightforward approaches in utilising CO₂.² The process, which is catalysed by transition metal complexes, has been well developed in the last decade.²⁻³ Small molecule activation represents one of the most crucial research topics in contemporary main group chemistry.⁴ However, the examples of CO₂ hydrogenation mediated by main-group pre-catalysts are still scarce. Recently, *N*-Heterocyclic Carbenes (NHCs) as demonstrated by Ying et al.⁵ and 'Frustrated Lewis Pair' (FLP) systems reported by Stephan,⁶ and Piers⁷ were shown to serve as suitable hydrogenation systems. In line with that, Roesky et al. has demonstrated that the germylene hydride LGeH (L = CH(MeC=NAr)₂, Ar = 2, 6-*i*Pr₂C₆H₃) can activate CO₂ affording a germylene formate complex LGeOCH(=O) (**2'**),⁸ which can be further converted to formic acid and methanol upon hydrolysis with water using LiNH₂•BH₃ and NH₃•BH₃ adducts as hydride sources.⁹ In addition, they proposed a possible mechanism for the latter case based on NMR spectroscopic investigations, but no intermediates were isolated in this study. Very recently, a theoretical study by Sakaki et al. has shown that LGeH could also act as a catalyst for CO₂ hydrosilylation to F₃SiOCH(=O) when HSiF₃ is used as the hydride source.¹⁰ Until now, there are only two examples using the germylene hydride complexes bearing β-diketiminato ligands for CO₂ activation,¹¹ so it seems desirable to apply varied ligand scaffolds to stabilise the highly active germylene hydride species and investigate their ability in CO₂ activation.

In 2010, we introduced the 2-iminocyclohexylidenebenzylamine ligand L^{Cy}H (L^{Cy} = cyclo-C₆H₈-1-NAr-2-C(Ph)NAr, Ar = 2,6-*i*Pr₂C₆H₃) for stabilising a germylene complex, and studied its reactivity towards water and ammonia.¹² Since the successful application of this ligand, we wanted to apply it also as a supporting ligand for the corresponding germylene hydride and the potentially isolable corresponding formate complexes. Herein, we report the use

of this ligand (L^{Cy}H) for the synthesis of a new germylene hydride derivative and its application in CO₂ hydrogenation to the germylene formate L^{Cy}GeOCH(=O) (**2**). Complex **2** and the reported LGeOCH(=O) (**2'**) react readily with alane (AlH₃•NMe₃) to afford deuterated methanol (CH₃OD) upon hydrolysis with D₂O. The trapping and full elucidation of key intermediates in the conversion of **2'** to methanol is also reported and sheds light on the mechanism of CO₂ reduction mediated by germylene hydrides.

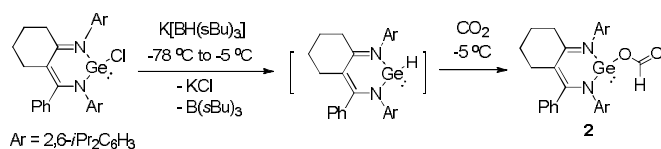
Results and discussion

Accordingly, the synthesis of the L^{Cy}H stabilised germylene hydride complex was first investigated. Akin to the preparation of LGeH,⁸ L^{Cy}GeCl was treated with one molar equivalent of K[BH(sBu)₃] in toluene at -78 °C and allowed to warm to room temperature. Unexpectedly, after a reaction time of 12 hours at ambient temperature, the anticipated germylene hydride complex (L^{Cy}GeH) was not isolated. Instead, L^{Cy}(H)Ge (**1**) was isolated as the single product with 84% yield (Scheme 1).

Scheme 1. Synthesis of compound **1** via Ge(II) hydride.

However, when the reaction process was monitored by ¹H NMR spectroscopy, after the mixture was stirred for 3 hours at room temperature, the characteristic resonance signal for Ge–H proton could indeed be observed at δ = 7.96 ppm which is comparable to that of LGeH (δ = 8.08 ppm).^{11a} This indicates that the L^{Cy}GeH is formed during the reaction, but it is labile and ultimately undergoes a 1,3-hydrogen transfer from the germanium centre to the backbone of the ligand to give the germylene **1** with hydrogenated ligand scaffold as the thermodynamic product. A similar reaction mode was reported

by Jones et al. when they attempted to use $t^{\text{Bu}}\text{NacnacH}$ ($t^{\text{Bu}}\text{Nacnac} = \text{CH}(t^{\text{Bu}}\text{CNAr})_2$, Ar = 2,6-*i*Pr₂C₆H₃) and $t^{\text{Bu}}\text{MesNacnacH}$ ligands ($t^{\text{Bu}}\text{MesNacnac} = \text{CH}(t^{\text{Bu}}\text{CNMes})_2$, Mes = 2,4,6-Me₃C₆H₃) to stabilise a germylene hydride. In both cases the only isolated products are diamido germylene complexes with 1,3-hydride migration to the backbone of the ligands.^{11b,13} However, compound **1** can not activate CO₂ even at elevated temperatures in toluene or benzene.

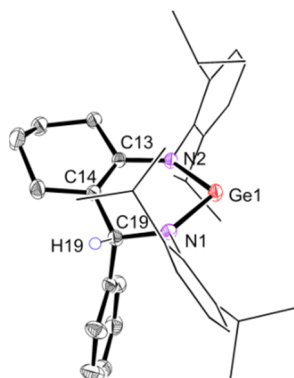


Scheme 2. Synthesis of compound **2**.

Although L^{Cy}GeH is only the kinetic product, we reasoned that it could be employed for hydrogenation of CO₂ to afford the germylene formate complex L^{Cy}GeOCH(=O) (**2**). Following this idea, L^{Cy}GeCl was reacted with K[BH(*s*Bu)₃] in toluene at -5 °C for 12 hours under N₂ atmosphere, and then the gas atmosphere was changed with CO₂ through a freeze-pump-thaw cycle, and the reaction mixture further stirred for five hours. From the reaction mixture, the germylene formate L^{Cy}GeOCH(=O) (**2**) could indeed be isolated in 77% yield (Scheme 2).

Both compounds **1** and **2** are yellowish solids, and are thermally robust (Mp. 178 °C (**1**); 165 °C (**2**)) without any decomposition when stored under N₂ atmosphere at room temperature for several months. They are soluble in toluene, benzene and THF, and slightly soluble in *n*-hexane. They were fully characterised with NMR spectroscopy (¹H, ¹³C), mass spectrometry, elemental analyses as well as single crystal X-ray diffraction analyses. The resonance signal for the γ -H proton (PhCHNAr) in complex **1** is observed at $\delta = 4.75$ ppm as a singlet in the ¹H NMR spectrum in C₆D₆ at room temperature. The corresponding carbon nucleus resonates at $\delta = 74.8$ ppm in the ¹³C{¹H} NMR spectrum. In the APCI-HR-MS spectrum, the signal for the molecular ion peak of **1** is found at m/z 595.3082 (caclcd: m/z 595.3102), whereas the molecular ion peak for compound **2** is not found, but the signal for the molecule fragment corresponding to loss of the formate group is observed at m/z 593.2936 (caclcd: m/z 593.2946). The resonance signal for the proton at formate group in **2** is shown at $\delta = 8.78$ ppm in the ¹H NMR spectrum, which is comparable to that of the formate group in **2'** ($\delta = 8.4$ ppm), the corresponding ¹³C signal is revealed at $\delta = 164.4$ ppm in ¹³C NMR spectrum. The molecular structures of complex **1** and **2** are shown in Figure 1.

a)



b)

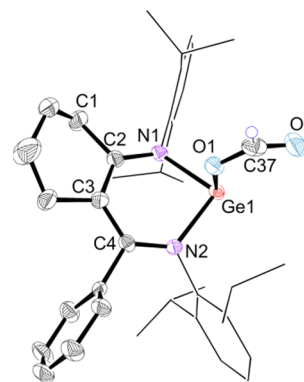


Fig. 1. Molecular structures of compounds **1** (a) and **2** (b) in solid state. Thermal ellipsoids are drawn in 50% probability level; the Dipp groups are depicted in wireframe style. Disorders at C36 and C38 of compound **2** and hydrogen atoms (except those at C19 of compound **1** and C37 of compound **2**) are omitted for clarity.

Complex **1** crystallizes in the triclinic space group *P1*, which is a chiral crystal system. The germanium centre is coordinated by the N1 and N2 atoms. The distances of Ge1 to N1 and N2 are 1.8250(19) Å and 1.867(2) Å, respectively. They are comparable to those in L^{Cy}Ge (L^{Cy} = cyclo-C₆H₇-1-NAr-2-C(Ph)NAr, Ar = 2,6-*i*Pr₂C₆H₃) which bears a dianionic ligand (1.861 and 1.843 Å).¹² The bond distances of C14–C19 (1.513 (3) Å) and C13–C14 (1.346(3) Å) indicate the single and double bond character, respectively. This is in accordance with the structure portrayed for **1** in Scheme 1. Compound **2** crystallises in the monoclinic space group *P2/c* and the germanium atom is tetrahedral coordinated. The Ge1 centre deviates from the plane defined by N1-C2-C3-C4-N2 by 0.534 Å. The distances of Ge1–N1, Ge1–N2 (1.976(2) and 1.988(2) Å) and Ge1–O1 (1.958(2) Å) are consistent with those observed in **2'** (Ge–N: 1.969(2) and 1.968(2) Å, Ge–O: 1.9339(18) Å).⁸

Roesky et al. demonstrated that the germylene formate **2'** could be converted to formic acid and methanol with LiNH₂•BH₃ and NH₃•BH₃ as the hydride sources upon workup with water, respectively.⁹ Very recently, Sakaki et al showed that LGeH can act as a catalyst in CO₂ hydrogenation when a suitable silane is applied as the hydride source based on theoretical study.¹⁰ Inspired by these results, we were interested in introducing alane as a hydride transfer source for CO₂ hydrogenation and elucidating the mechanism of the reaction.

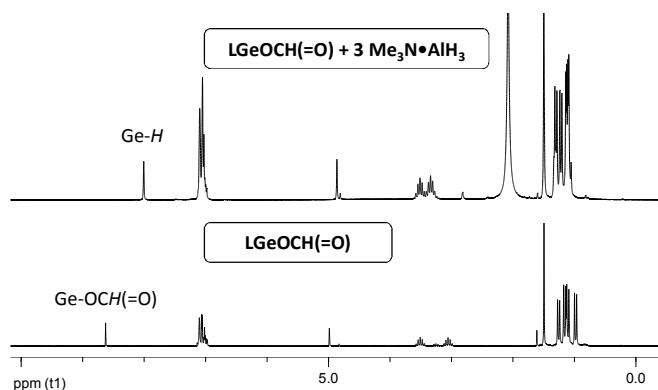
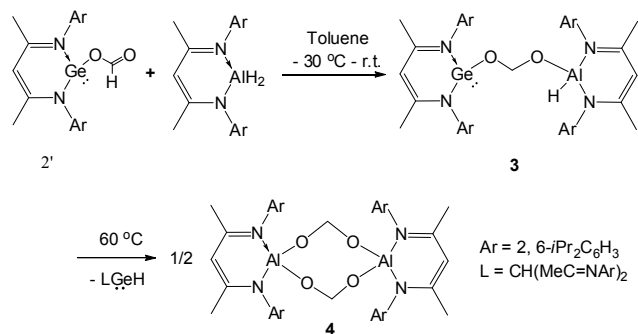


Fig. 2. ¹H NMR spectra of the reaction of **2'** with 3 molar equivalents of NMe₃•AlH₃ for 60 min (top) and **2'** in C₆D₆ (bottom).

We chose Me₃N•AlH₃ as the hydride source and used it to react with 1/3 molar equivalent of **2'** and compound **2**, respectively. The ¹H NMR spectra in C₆D₆ showed that both the reactions proceeded

smoothly to give the corresponding germylene hydride complexes in almost quantitatively yields within one hour at room temperature (Fig. 2 and ESI†).¹⁴ After stirring for two hours in toluene, the reactions were quenched with D₂O at 0 °C. The yields of CH₃OD were determined as 46% (**2'**) and 42% (**2**) by ¹H NMR spectroscopy with 1,4-dioxane as internal standard.



Scheme 3. Synthesis of compounds **3** and **4**.

After obtaining these results, we proceeded to elucidate the stepwise process of this reaction. For this purpose, LAIH₂ (L = CH(MeC=NAr)₂, Ar = 2,6-*i*Pr₂C₆H₃)¹⁵ was applied as a milder hydride delivery agent to react with **2'** with one molar equivalent of LAIH₂, the carbonyl group is further hydrogenated to afford the striking compound **3** as an OCH₂O bridged heterobimetallic complex (Scheme 3). The resonance signal for the protons at OCH₂O group is observed at δ = 4.48 ppm, the γ -H protons of the β -diketiminato ligands resonate at δ = 4.90 and 5.02 ppm, respectively, their integrate ratio is 2:1:1, which is in accordance with the structure depicted for compound **3**. Hence, the hydrogenation of the formate group to OCH₂O group represents the second step for CO₂ hydrogenation. While there is still one Al–H in compound **3**, and the yellow solution of **3** in THF gradually turned to red at room temperature, and so we tested the thermal stability of **3**. From a ¹H NMR spectroscopic investigation, compound **3** decomposed to give LGeH and compound **4** after heating at 60 °C for 3 hours in THF (Scheme 3). From the reaction mixture compound **4** was isolated as a colorless crystalline product in 60% yield. The proton signals for OCH₂O group and γ -H proton in the β -diketiminato ligand are observed at δ = 4.74 and 5.00 ppm, respectively, with the integrate ratio of 4:2. In this step, the LGeH is regenerated. Moreover, we tried to cleave the O–CH₂O bond in **4** with various hydride sources, but all attempts failed, probably due to the steric crowding resulting from the bulky β -diketiminato ligand.

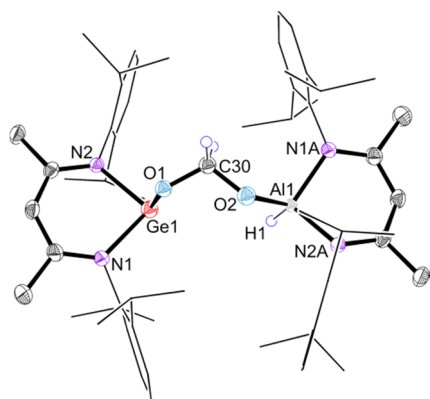


Fig. 3. Molecular structures of compounds **3** in solid state. Thermal ellipsoids are drawn in 50% probability level; the Dipp groups are depicted in wireframe style. Disorders at the core part GeOCH₂OAl

of compound **3** and hydrogen atoms (except those at C30 and Al1) are omitted for clarity. Operation symmetry for all atoms labelled with "A": $-x+1/2, -y+1/2, -z+2$ (**3**).

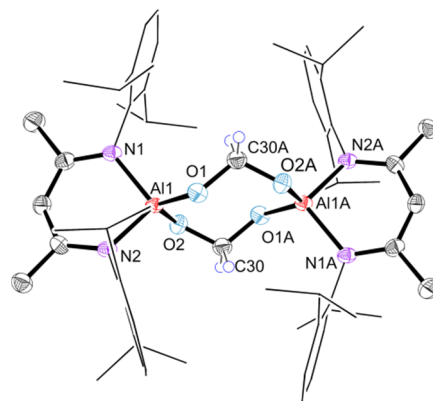
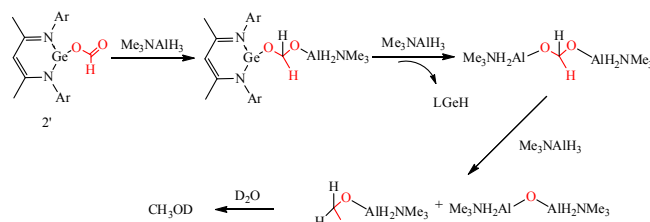


Fig. 4. Molecular structures of compounds **4** in solid state. Thermal ellipsoids are drawn in 50% probability level; the Dipp groups are depicted in wireframe style. Hydrogen atoms (except those at C30 and C30A) are omitted for clarity. Operation symmetry for all atoms labelled with "A": $-x+1/2, -y+1/2, -z+1$ (**4**).

The molecular structures of compound **3** and **4** are shown in Figure 3 and 4. Complex **3** and **4** crystallise in monoclinic space group *C2/c*. The Ge1 has a trigonal pyramidal geometry and Al1 feature a tetrahedral coordination in **3**, and they are bridged by the OCH₂O group. The Ge1–O1 bond length (1.854(4) Å) is shorter than that in the starting material **2'** (1.9339(18) Å),⁸ whereas it is comparable to that in LGeOiPr (1.821(2) Å).¹⁶ The Al1–O2 bond distance (1.807(3) Å) is akin to those in [{LAlMe(μ -O)AlMe₂}]₂ (av. 1.8493 Å).¹⁷ Compound **4** is a binuclear aluminium complex with a (AlOCH₂O)₂ core structure. The Al–N (1.8979(13) and 1.8963(13) Å) and Al–O (1.7123(11) and 1.7239(11) Å) bond lengths are similar to those in LAI[OB(3-MeC₆H₄)₂(μ -O)] (Al–N: 1.872(2) and 1.862(2) Å; Al–O: 1.7362(17) and 1.7418(17) Å).¹⁸



Scheme 4. Plausible reaction mechanism for germylene mediated CO₂ reduction to CH₃OD with alane.

Based on the model reaction of LAIH₂ with **2'** and the isolation of complexes **3** and **4**, the stepwise process of the conversion of **2** or **2'** with Me₃N•AlH₃ to methanol upon hydrolysis with water could be explained as follows (Scheme 4): complex **2'** is hydrogenated to form the adduct LGeOCH₂OAlH₂•NMe₃, and the subsequent Al–H hydride of Me₃N•AlH₃ transfer to the Ge centre regenerates LGeH. Concomitantly, Me₃N•AlH₂OCH₂OAlH₂•NMe₃, is formed which is continuously converted to Me₃N•AlH₂–OMe and Me₃N•AlH₂OH₂Al•NMe₃ with O–CH₂O bond cleavage. Hydrolysis of Me₃N•AlH₂–OMe with D₂O then yields CH₃OD as C1 product.

Conclusion

In conclusion, we demonstrated that the novel formate compound L^{Cv}GeOCH(=O) (**2**) and the previously reported LGeOCH(=O) (**2'**) can both be efficiently hydrogenated to yield methanol using alane

as the hydride source upon workup with water. The germylene hydrides are concomitantly regenerated in this process. Based on the reaction of the mild hydrogen delivery agent (LAlH₂) with LGeOCH(=O) (**2**^{*}) as a model reaction, we suggested a plausible mechanism for the formation of methanol with the isolation of LGeOCH₂OAl(H)L (**3**) and (LAlOCH₂O)₂ (**4**) respectively. These studies shed new light on the reduction of CO₂ mediated by germylene hydrides.

Experimental section

All experiments were carried out under dry oxygen-free nitrogen using standard Schlenk techniques. Solvents were dried by standard methods and freshly distilled and degassed prior to use. The NMR spectra were recorded on Bruker spectrometers (AV400 or AV200) referenced to residual solvent signals as internal standards (¹H NMR: CDCl₃, 7.26 ppm; C₆D₆, 7.16 ppm and ¹³C{H} NMR: CDCl₃, 77.0 ppm; C₆D₆, 128.1 ppm) or with an external standard. Concentrated solutions of samples in C₆D₆ or CDCl₃ were sealed off in a Young-type NMR tube for measurements. Melting points were recorded on a "Melting point tester" device from BSGT company and are uncorrected. All the samples are sealed off in capillary under vacuum and each sample was measured in duplicate. High resolution mass spectra (atmosphere pressure chemical ionization) were recorded on an Orbitrap LTQ XL of Thermo Scientific mass spectrometer and the raw data evaluated using the Xcalibur computer program. For the single crystal X-ray structure analyses the crystals were each mounted on a glass capillary in perfluorinated oil and measured in a cold N₂ flow. The data of compounds **1** and **2** were collected on an Oxford Diffraction Xcalibur S Sapphire at 150 K (Mo-Kα radiation, λ = 0.71073 Å), the data of compounds **3** and **4** were collected on an Oxford Diffraction Supernova, Single source at offset, Atlas at 150 K (Cu-Kα-radiation, λ = 1.5418 Å). The structures were solved by direct methods and refined on F² with the SHELX-97¹ software package. The positions of the H atoms were calculated and considered isotropically according to a riding model.

Commercially available reagents were purchased from Aldrich, Acros and used as received. L^{Cy}H, L^{Cy}GeCl (L^{Cy} = cyclo-C₆H₈-1-NAr-2-C(Ph)NAr, Ar = 2,6-*i*Pr₂C₆H₃),¹² LGeOCH(=O) (**2**^{*})⁸ and LAlH₂¹⁵ (L = CH[C(Me)NAr]₂, Ar = 2,6-*i*Pr₂C₆H₃) were synthesized according to published procedures.

Compound L^{Cy}(H)Ge (**1**):

L^{Cy}GeCl (0.628 g, 1 mmol) was placed in a schlenk flask (100 mL) in the glovebox. Toluene (30 mL) was transferred into the flask via cannula under stirring at room temperature and a clear yellow solution was formed. The solution was cooled to -78 °C, and K[BH(sBu)₃] (1 mL, 1 mmol, 1 M solution in THF) was added dropwise to the solution via syringe. The mixture was allowed to warm to room temperature and stirred for another 12 hours. The obtained red solution was concentrated to 10 mL and filtered. The filtrate was left at 0 °C for 24 hours to afford a yellow crystalline product (**1**). The product was collected by decantation of the supernatant and the obtained solid was dried in vacuo for several hours. Yield: 0.50 g (0.84 mmol, 84%). Mp. 178 °C (dec.). ¹H NMR (200.1 MHz, C₆D₆, 298 K): δ = 0.53 (d, 3 H, ³J_{H-H} = 6.8 Hz, CH(CH₃)₂), 1.10 (d, 3 H, ³J_{H-H} = 7.0 Hz, CH(CH₃)₂), 1.25 (d, 3 H, ³J_{H-H} = 6.6 Hz, CH(CH₃)₂), 1.28 (d, 9 H, ³J_{H-H} = 6.8 Hz, CH(CH₃)₂), 1.37-1.44 (m, 7 H, Cy-CH₂ (4 H) + CH(CH₃)₂ (3 H)), 1.47 (d, 3 H, ³J_{H-H} = 6.8 Hz, CH(CH₃)₂), 1.75-2.01 (m, 4 H, Cy-CH₂), 3.13 (sept, 1 H, ³J_{H-H} = 6.8 Hz, CH(CH₃)₂), 3.55 (sept, 1 H, ³J_{H-H} = 6.8 Hz, CH(CH₃)₂), 3.91 (sept, 2 H, ³J_{H-H} = 7.0 Hz, CH(CH₃)₂), 4.75 (s, 1 H, γ-H (PhCHNAr)), 7.04-7.41 (m, 11 H, Ar-H and Ph-H). ¹³C{¹H} NMR (50.3 MHz, C₆D₆, 298 K): δ = 22.5, 22.9 (*i*Pr-CH₃), 23.0 (Cy-

CH₂), 23.5(*i*Pr-CH₃), 23.7 (Cy-CH₂), 23.8 (*i*Pr-CH₃), 25.2, 26.1, 26.2, 26.9 (*i*Pr-CH), 27.9 (Cy-CH₂), 28.1, 28.2, 28.3, 28.4(*i*Pr-CH₃), 29.9 (Cy-CH₂), 74.8 (γ-C), 109.1 (CH₂CCNAr), 123.2, 123.8, 124.0, 124.2, 126.4, 127.0, 127.1, 128.2, 128.3 (Ar-CH), 134.4, 140.3, 143.7, 145.0, 146.9, 147.1, 147.2, 148.1 (Ar-C and CH₂CCNAr). Elemental analysis for C₃₇H₄₈GeN₂: calcd: C, 74.89; N, 4.72; H, 8.15; found: C, 74.19; N, 4.48; H, 8.30. APCI-HR-MS: calcd for [C₃₇H₄₉GeN₂(M + H)]⁺: *m/z* 595.3102; found: *m/z* 595.3082.

Compound L^{Cy}GeOCH(=O) (**2**):

L^{Cy}GeCl (1.26 g, 2 mmol) was placed in a schlenk flask (100 mL) in the glovebox. Toluene (30 mL) was transferred into the flask via cannula under stirring at room temperature and a clear yellow solution was formed. The solution was cooled to -78 °C, and K[BH(sBu)₃] (2 mL, 2 mmol, 1 M solution in THF) was added dropwise to the solution via syringe. The mixture was then placed in a cooled water-salt bath (ca. -5 °C), and allowed to stir at this temperature for 12 hours. Then the atmosphere was changed to CO₂ by a freeze-pump-thaw cycle, and the mixture was stirred at CO₂ atmosphere for 12 hours. All the volatiles were removed in vacuo and the residue was washed with hot (ca. 50 °C) *n*-hexane (20 mL), the solution was filtrated. The remaining residue is the pure product (**2**) on the basis of ¹H NMR spectroscopy. The filtrate was left at room temperature for 12 hours to yield the crystals of **2**, which are suitable for X-ray single crystal diffraction analysis. Total yield: 1.01 g (1.55 mmol, 77%). Mp. 165 °C (dec.). ¹H NMR (200.1 MHz, C₆D₆, 298 K): δ = 0.91 (d, 3 H, ³J_{H-H} = 6.6 Hz, CH(CH₃)₂), 1.02 (d, 3 H, ³J_{H-H} = 6.8 Hz, CH(CH₃)₂), 1.12-1.23 (m, 16 H, Cy-H (4 H) + CH(CH₃)₂ (12 H)), 1.27 (d, 3 H, ³J_{H-H} = 6.6 Hz, CH(CH₃)₂), 1.33 (d, 3 H, ³J_{H-H} = 6.6 Hz, CH(CH₃)₂), 1.86-2.21 (m, 4 H, Cy-H), 3.03-3.31 (m, 2 H, CH(CH₃)₂), 3.44-3.72 (m, 2 H, CH(CH₃)₂), 6.67-6.92 (m, 7 H, Ar-H and Ph-H), 7.03-7.22 (m, 4 H, Ar-H and Ph-H), 8.78 (s, 1 H, -OCH(=O)). ¹³C{¹H} NMR (50.3 MHz, C₆D₆, 298 K): δ = 21.0 (Cy-CH₂), 22.3(Cy-CH₂), 22.9, 23.3, 24.2, 24.3, 24.4, 26.8 (*i*Pr-CH₃), 27.2, 27.6 (*i*Pr-CH), 27.9 (*i*Pr-CH₃), 28.6, 28.7(*i*Pr-CH), 28.8 (Cy-CH₂), 28.9(*i*Pr-CH₃), 31.1(Cy-CH₂), 107.0 (γ-C), 123.2, 124.2, 125.3, 126.9, 127.0, 127.5, 127.7, 127.8, 127.9, 128.0, 128.6 (Ar-CH), 137.9, 139.9, 140.4, 143.0, 145.1, 146.0, 146.7 (Ar-C), 164.4 (-OCH(=O)), 165.8 (Cy-CN), 168.7 (Ph-CN). Elemental analysis for C₃₈H₄₈GeN₂O₂ (%): calcd: C, 71.60; N, 4.39; H, 7.59; found: C, 71.56; N, 4.37; H, 7.93. APCI-HR-MS: calcd for [C₃₇H₄₇GeN₂(M - CO₂H)]⁺: *m/z* 593.2946; found: *m/z* 593.2936. IR (KBr): ν = 2870 (OC(=O)-H), 1657(OC(=O)-H) cm⁻¹.

Compound LGeOCH₂OAl(H)L (**3**):

LGeOCH(=O) (**2**^{*}) (0.268 g, 0.5 mmol) and LAlH₂ (0.224 g, 0.5 mmol) were placed in a schlenk flask (100 mL) in the glovebox. Toluene (30 mL) was transferred to the mixture via cannula under stirring at -50 °C. The solution was allowed to warm to room temperature and stirred for another 12 hours to give a clear yellow solution. The solution was concentrated to ca. 5 mL and filtrated. The obtained filtrate was left at 0 °C for 24 hours to give yellow crystals of compound **3**. The product was collected by decantation of the supernatant and dried in vacuo for several hours. Yield: 0.36 g (0.37 mmol, 74%). Mp. 96 °C (dec.). ¹H NMR (400.2 MHz, CDCl₃, 298 K): δ = 0.62 (d, 6 H, ³J_{H-H} = 6.4 Hz, CH(CH₃)₂), 0.79 (d, 6 H, ³J_{H-H} = 6.8 Hz, CH(CH₃)₂), 0.94 (d, 6 H, ³J_{H-H} = 6.8 Hz, CH(CH₃)₂), 1.01 (d, 6 H, ³J_{H-H} = 6.8 Hz, CH(CH₃)₂), 1.02 (d, 6 H, ³J_{H-H} = 6.8 Hz, CH(CH₃)₂), 1.07 (d, 6 H, ³J_{H-H} = 6.8 Hz, CH(CH₃)₂), 1.15 (d, 6 H, ³J_{H-H} = 6.8 Hz, CH(CH₃)₂), 1.21 (d, 6 H, ³J_{H-H} = 6.8 Hz, CH(CH₃)₂), 1.62 (s, 6 H, α-CH₃), 1.67 (s, 6 H, α-CH₃), 2.98-3.12 (m, 6 H, CH(CH₃)₂), 3.17 (sept, 2 H, ³J_{H-H} = 6.8 Hz, CH(CH₃)₂), 4.48 (s, 2 H, OCH₂O), 4.90 (s, 1 H, γ-H), 5.02 (s, 1 H, γ-H), 6.84-6.86 (m, 2 H, Ar-H), 6.98-7.03 (m, 2 H, Ar-H), 7.06-7.26 (m, 8 H, Ar-H). The

resonance signal for Al-H is not observed in the spectrum. $^{13}\text{C}\{^1\text{H}\}$ NMR (100.1 Hz, CDCl_3 , 298 K): δ = 23.1 ($\alpha\text{-CH}_3$), 23.4($\alpha\text{-CH}_3$), 24.1, 24.2, 24.6, 24.7, 25.1, 25.8 (*i*Pr- CH_3), 27.3, 27.7, 28.0, 28.7 (*i*Pr-*CH*), 85.9 (OCH_2O), 96.2 ($\gamma\text{-C}$), 96.4 ($\gamma\text{-C}$), 123.3, 123.9, 124.1, 124.8, 126.3, 126.7, 126.8, 128.2, 129.0 (Ar-*CH*), 139.4, 140.7, 143.1, 143.8, 143.9, 146.0 (Ar-*C*), 163.2 (CNAr), 169.9 (CNAr). Elemental analysis for $\text{C}_{59}\text{H}_{85}\text{AlGeN}_4\text{O}_2$ (%): calcd: C, 72.17; N, 5.71; H, 8.72; found: C, 72.40; N, 5.86; H, 8.55. APCI-HR-MS: calcd for $[\text{C}_{59}\text{H}_{86}\text{AlGeN}_4\text{O}_2 (\text{M} + \text{H})]^+$: m/z 983.5772; found: m/z 983.5751.

Compound LAI(OCH_2O)₂AIL (4):

Compound **3** (0.491 g, 0.5 mmol) is placed in a schlenk flask (50 mL) in the glovebox. THF (10 mL) was transferred to the flask via cannula at room temperature. The yellow solution was heated at 60 °C for 12 hours under stirring, and an orange-red solution was formed. All volatiles were removed in vacuo. The residue was extracted firstly with *n*-hexane (10 mL) (to remove the LGeH), and then it was extracted with toluene (10 mL) to give a yellow filtrate. The toluene solution was concentrated to ca. 5 mL and filtrated. The filtrate was left at 0 °C for 24 hours to give colorless crystals of compound **4**. The product was collected by removing the mother liquor and dried under vacuum for several hours. The mother liquor was further concentrated to ca. 3 mL, and afforded another portion of product after crystallization at -30 °C. Total yield: 0.15 g (0.15 mmol, 60%). Mp. 191 °C. ^1H NMR (200.1 MHz, CDCl_3 , 298 K): δ = 0.78 (d, 24 H, $^3J_{\text{H-H}} = 6.6$ Hz, $\text{CH}(\text{CH}_3)_2$), 0.95 (d, 24 H, $^3J_{\text{H-H}} = 6.8$ Hz, $\text{CH}(\text{CH}_3)_2$), 1.55 (s, 12 H, $\alpha\text{-CH}_3$), 3.06 (sept, 8 H, $^3J_{\text{H-H}} = 6.8$ Hz, $\text{CH}(\text{CH}_3)_2$), 4.74 (s, 4 H, OCH_2O), 5.00 (s, 2 H, $\gamma\text{-H}$), 6.96 (s, 3 H, Ar-*H*), 7.00 (s, 4 H, Ar-*H*), 7.14-7.21 (m, 5 H, Ar-*H*). $^{13}\text{C}\{^1\text{H}\}$ NMR (50.3 Hz, CDCl_3 , 298 K): δ = 23.5 ($\alpha\text{-CH}_3$), 24.4($\text{CH}(\text{CH}_3)_2$), 24.7($\text{CH}(\text{CH}_3)_2$), 27.9 ($\text{CH}(\text{CH}_3)_2$), 85.7 (OCH_2O), 97.1 ($\gamma\text{-C}$), 124.1, 126.8 (Ar-*CH*), 140.4, 144.2 (Ar-*C*), 170.3 (CNAr). Elemental analysis for $\text{C}_{60}\text{H}_{86}\text{Al}_2\text{N}_4\text{O}_4$ (%): calcd: C, 73.44; N, 5.71; H, 8.83; found: C, 73.72; N, 5.89; H, 8.65. APCI-HR-MS: calcd for $[\text{C}_{60}\text{H}_{87}\text{Al}_2\text{N}_4\text{O}_4 (\text{M} + \text{H})]^+$: m/z 981.6353; found: m/z 981.6340.

Conversion of **2** and **2'** to CH_3OD with $\text{Me}_3\text{N}\cdot\text{AlH}_3$

The germylene-formate **2** or **2'** (0.25 mmol) and $\text{Me}_3\text{N}\cdot\text{AlH}_3$ (0.75 mmol) was placed in a schlenk flask in the glovebox. Toluene (10 mL) was added to the flask via syringe at room temperature under stirring. The mixture was allowed to stir for another two hours, and cooled to 0 °C, D_2O was added to the solution and stirred for 10 minutes. The formed solid was separated by centrifuge, and a clear two phase was formed. The aqueous phase was collected and 1,4-dioxane was added to it as an internal standard to determine the yields of CH_3OD by ^1H NMR spectroscopy.⁹ Yields of CH_3OD : 42% (**2**) and 46% (**2'**).

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Notes and references

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1 (a) T. J. Marks et al. (for full author list see ESI†), *Chem. Rev.*, 2001, **101**, 953; (b) *Carbon Dioxide as Chemical Feedstock*, ed. M. Aresta, Wiley-VCH, Weinheim, 2010.

2 P. G. Jessop, T. Ikariya and R. Noyori, *Chem. Rev.*, 1995, **95**, 259.

3 (a) F. Gassner and W. Leitner, *J. Chem. Soc. Commun.*, 1993, **19**, 1465; (b) R. Tanaka, M. Yamashita and K. Nozaki, *J. Am. Chem. Soc.*, 2009, **131**, 14168; (c) C. Ziebart, C. Federsel, P. Anbarasan, R. Jackstell, W. Baumann, A. Spannenberg and M. Beller, *J. Am. Chem. Soc.*, 2012, **134**, 20701.

4 S. Yao, Y. Xiong and M. Driess, *Organometallics*, 2011, **30**, 1748.

5 S. N. Riduan, Y. Zhang and J. Y. Ying, *Angew. Chem., Int. Ed.*, 2009, **48**, 3322.

6 G. Ménard and D. W. Stephan, *J. Am. Chem. Soc.*, 2010, **132**, 1796.

7 A. Berkefeld, W. E. Piers and M. Parvez, *J. Am. Chem. Soc.*, 2010, **132**, 10660.

8 A. Jana, D. Ghoshal, H. W. Roesky, I. Objartel, G. Schwab and D. Stalke, *J. Am. Chem. Soc.*, 2009, **131**, 1288.

9 A. Jana, G. Tavčar, H. W. Roesky and M. John, *Dalton Trans.*, 2010, **39**, 9487.

10 N. Takagi and S. Sakaki, *J. Am. Chem. Soc.*, 2013, **135**, 8955.

11 (a) L. W. Pineda, V. Jancik, K. Starke, R. B. Oswald and H. W. Roesky, *Angew. Chem., Int. Ed.*, 2006, **45**, 2602; (b) S. L. Choong, W. D. Woodul, C. Schenk, A. Stasch, A. F. Richards and C. Jones, *Organometallics*, 2011, **30**, 5543.

12 W. Wang, S. Inoue, S. Yao and M. Driess, *Organometallics*, 2011, **30**, 6490.

13 W. D. Woodul, E. Carter, R. Müller, A. F. Richards, A. Stasch, M. Kaupp, D. M. Murphy, M. Driess and C. Jones, *J. Am. Chem. Soc.*, 2011, **133**, 10074.

14 In the latter case, the germylene hydride complex is unstable, so compound **1** is the final product.

15 C. Cui, H. W. Roesky, H. Hao, H.-G. Schmidt and M. Noltemeyer, *Angew. Chem., Int. Ed.*, 2000, **39**, 1815.

16 L. Ferro, P. B. Hitchcock, M. P. Coles and J. R. Fulton, *Inorg. Chem.*, 2012, **51**, 1544.

17 Y. Yang, H. Zhu, H. W. Roesky, Z. Yang, G. Tan, H. Li, M. John and R. Herbst-Irmer, *Chem. Eur. J.*, 2010, **16**, 12530.

18 X. Ma, Z. Yang, X. Wang, H. W. Roesky, F. Wu and H. Zhu, *Inorg. Chem.*, 2011, **50**, 2010.

The mechanism of CO₂ reduction to methanol mediated by germylene hydrides is elucidated based on the model reaction of LAIH₂ with LGeOCH(=O) (L = CH(MeCNAr)₂, Ar = 2,6-iPr₂C₆H₃).

