

Germlyiumylidene: A Versatile Low Valent Group 14 Catalyst

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Abstract: Bis-NHC stabilized germlyiumylidenes $[\text{RGe}(\text{NHC})_2]^+$ are typically Lewis basic (LB) in nature, owing to their lone pair and coordination of two NHCs to the vacant p-orbitals of the germanium center. However, they can also show Lewis acidity (LA) via $\text{Ge}-\text{C}^{\text{NHC}} \sigma^*$ orbital. Utilizing this unique electronic feature, we report the first example of bis-NHC-stabilized germlyiumylidene $[\text{MesTerGe}(\text{NHC})_2]\text{Cl}$ (**1**), ($\text{MesTer} =$

2,6-(2,4,6-Me₃C₆H₂)₂C₆H₃; NHC = $\text{IMe}_4 = 1,3,4,5$ -tetramethylimidazol-2-ylidene) catalyzed reduction of CO₂ with amines and arylsilane, which proceeds via its Lewis basic nature. In contrast, the Lewis acid nature of **1** is utilized in the catalyzed hydroboration and cyanosilylation of carbonyls, thus highlighting the versatile ambiphilic nature of bis-NHC stabilized germlyiumylidenes.

Introduction

The ability of main group complexes to mimic transition metals has gained tremendous attention in recent years, driven by the desire for new sustainable processes.^[1] Activation of small molecules by low-valent main group centers has been achieved and is the preliminary step towards transition metal-free catalysis.^[1a,e] However, their catalytic application is still limited due to challenges in reductive elimination from the resultant high-oxidation state complex.^[1d,e,2] Recently, low valent germanium compounds have found themselves to be a diverse tool in enabling chemical transformations, attributed to the relative ease in which the +II and +IV oxidation states can be accessed.^[2b-9,3] This includes the first example of low-valent main group dihydrogen activation and the use of multiple bonds (digermynes) in catalysis.^[2f,3a] Among the low valent germanium compounds, germlyiumylidenes $[\text{R}-\text{Ge}]^+$ possess a unique electronic feature,^[4] due to the presence of a lone pair

and two vacant p-orbitals at the germanium center. It, therefore, combines the characteristics of germlyium cations $[\text{R}_3\text{Ge}]^+$ and germlyenes $[\text{R}_2\text{Ge}]$ (Scheme 1a) and can simultaneously act as an electrophile and nucleophile,^[4] which has been further utilized in the activation of various small molecules,^[3e,5] including the thermodynamically robust H–H bond.^[3e]

The reactivity of germlyiumylidenes can be tuned depending on the number of donor ligands employed to stabilize the vacant p-orbitals (Scheme 1b). Based on this, germlyiumyli-

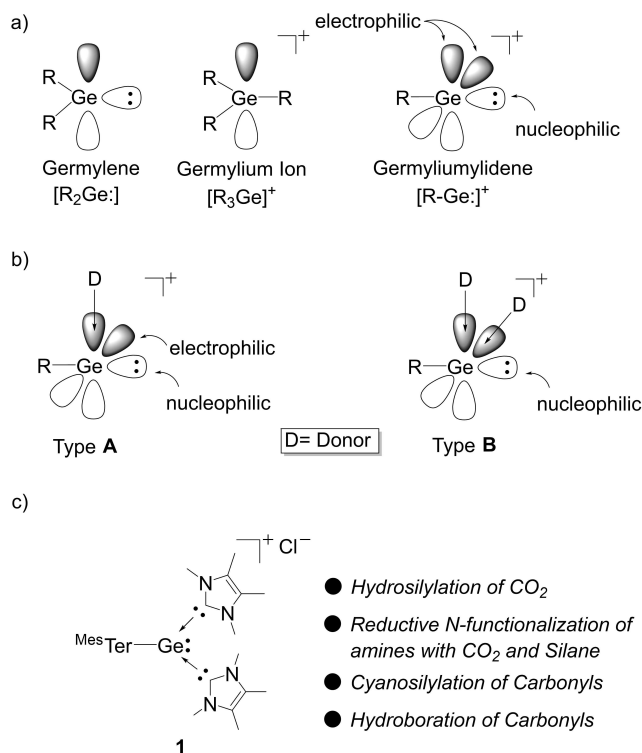
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Scheme 1. (a) Electronic features of germlyiumylidene, (b) Lewis based stabilized germlyiumylidenes, and (c) this work.

denes can be classified into two types, i) two-coordinate germyliumylidenes, which have both electrophilic and nucleophilic centers (Scheme 1b, Type A), ii) three-coordinate germyliumylidenes where the nucleophilic character is more pronounced due to the occupancy of the two p-orbitals (Scheme 1b, Type B).^[4]

Among the type B classification, bis-NHC stabilized germyliumylidenes are comparatively Lewis basic and relatively more stable than type A germyliumylidenes, due to the occupied p-orbitals. Thus, on one hand they can be used as a robust Lewis base catalyst whilst on the other hand they can be used as a Lewis acid catalyst, due to the ability of the Ge–C^{NHC} σ^* orbitals to accept electrons, which provides an additional cooperative site for potential catalytic application. Despite these unique electronic features, the catalytic application of germyliumylidenes is in its infancy. Recent examples from the groups of Rivard and Nagendran have shown the role of type A and B germyliumylidenes, respectively, in the hydroboration of carbonyls.^[6] However, the catalytic application of bis-NHC-stabilized germyliumylidenes is still unknown.^[5]

Very recently, we have reported hydrosilylation of CO₂ with a germa-acylium ion (I, [MesTerGe(O)(NHC)₂]Cl) (^{Mes}Ter = 2,6-(2,4,6-Me₃C₆H₂)₂C₆H₃; NHC = IMe₄ = 1,3,4,5-tetramethylimidazol-2-ylidene) which proceeds through the active germylene species (II, ^{Mes}TerGe(OSiHPh₂)(NHC)).^[7] Importantly, in our case the Lewis basicity of the Ge(II) center facilitates the hydride transfer from silane to CO₂ via the formation of a hypercoordinate silane intermediate. Moreover, it has been shown that the Lewis acidity and Lewis basicity are both important for the catalytic transformation of CO₂.^[2d,e,h,8] This encouraged us to examine the recently reported bis NHC stabilized germyliumylidene [^{Mes}TerGe(NHC)₂]Cl (1) towards a range of catalytic reductive functionalization reactions, with a particular emphasis on C=O reduction i. e., CO₂ and carbonyls.

Results and Discussion

Following a similar protocol to the previous NHC-stabilized germa-acylium catalysis,^[7] compound 1 was found to transform CO₂ into the corresponding hydrosilylated products in both a stoichiometric and catalytic manner in the presence of phenylsilane (PhSiH₃). The ¹H NMR spectrum revealed the complete consumption of PhSiH₃ within 2.5 h at 60 °C, with the formation of silylformate, bis(silyl)acetal and silylated methanol observed (see Supporting Information, Figure S1). As expected, use of more sterically protected silanes required increased reaction times (PhSiH₃ 2.5 h vs. Ph₂SiH₂ 3.5 h), and in the case of Ph₃SiH, higher temperatures and prolonged reaction times are required (28 h at 80 °C). Furthermore, solvent optimization studies found increased rates of reaction in polar solvents (e.g., CD₃CN) compared to non-polar solvents (e.g., C₆D₆). This, however, can also be attributed to the low solubility of the catalyst in non-polar solvents. To consider the influence of the counter ion in catalysis, the reaction was performed using the anion-exchanged 1[BArF], [BArF = {(3,5-(CF₃)₂C₆H₃)₄B}], catalyst in CD₃CN, no significant change in the rate of reaction was found. This

points towards the dependence on the cationic germanium center during the catalysis. With the above points considered, use of 5 mol% of 1 with PhSiH₃ in CD₃CN at 60 °C provides the optimal reaction conditions for this study.

Whilst the catalytic activity of 1 is lower in comparison to our previously reported germa-acylium ion catalyst (TOF: 1 = 13.2 h⁻¹ vs. 1 = 7.9 h⁻¹ for PhSiH₃ at 60 °C),^[7] germyliumylidene 1 has the added advantage of being a more stable catalyst as well as requiring fewer synthetic steps. Using the optimized conditions mentioned above, the longevity of catalyst 1 was examined in which additional PhSiH₃ and 1 bar of CO₂ were added to the J-Young NMR tube at the end of the cycle. This process could be repeated four times before a small drop in turnover was observed (TOF: Run 1 = 8 h⁻¹ vs. Run 4 = 6 h⁻¹). In contrast, the previously reported germa-acylium ion catalyst decomposed after the third cycle.

A series of stoichiometric reactions were undertaken to probe the mechanism. No reaction was observed with 1 and CO₂ in the absence of silane, even after prolonged heating at 60 °C. Additionally, no reaction was observed with varying equivalents of hydrosilane under the optimal catalytic conditions. This suggests a cooperative silane/CO₂ mechanism, and therefore, the mechanism was investigated computationally (Figure S50). In a similar fashion to the previous case,^[7] the Si–H bond in PhSiH₃ is activated by the germanium lone pair in 1M⁺ and the hydride transfer from the hypercoordinate silane to the free CO₂ occurs in a concerted process via the transition state TS-1 (Figure 1). IRC calculations confirm the direct formation of the transition state from the separated species (1M⁺ + PhSiH₃ + CO₂) following a three-component mechanism. Additionally, participation of the germanium lone pair in “concerted S_N2@Si-acceptor” mechanism^[9] rather than the classical activation of hydrosilanes is also clearly evident from the substantially longer Ge–Si distance (2.787 Å) in TS-1. This step needs to surmount an energy barrier of 28.6 kcal mol⁻¹ to provide the resulting intermediate (INT-1). The Lewis basicity of NHC-stabilized germyliumylidene towards PhSiH₃ cannot be explained by drastically high energy separation (11.0 eV) between the germanium lone pair orbital in free 1M⁺ and Si–H σ^* orbital in free PhSiH₃ (Figure S51a). However, when the silane approaches the Ge center, significant stabilization of the Si–H σ^* orbital in the PhSiH₃ fragment of TS-1 results in favorable interaction (8.3 eV) with the germanium lone pair in the 1M⁺ fragment, thus enhancing the reactivity of germyliumylidene and highlighting the Lewis basic nature of 1M⁺ (Figure S51b). In the alternative pathway, oxidative addition of silane across the Ge center in 1M⁺ with concomitant liberation of IMe₄ demands slightly lesser energy barrier of 28.2 kcal mol⁻¹ (Figure S52), as suggested by favorable interaction (8.2 eV) between the Si–H σ and Ge–C^{IMe₄} σ^* orbitals in TS-7 (Figure S53b). However, CO₂ insertion into the Ge(IV) hydride species (INT-5) in the subsequent step demands drastically high intrinsic activation barrier of 44.9 kcal mol⁻¹ and can be safely discarded. Moreover, 1M⁺ does not coordinate with either CO₂ or silane. Thus 1[Cl] assisted hydrosilylation of CO₂ is proposed to occur through three-component pathway rather than a two component mechanism. In agreement with experimental findings, the

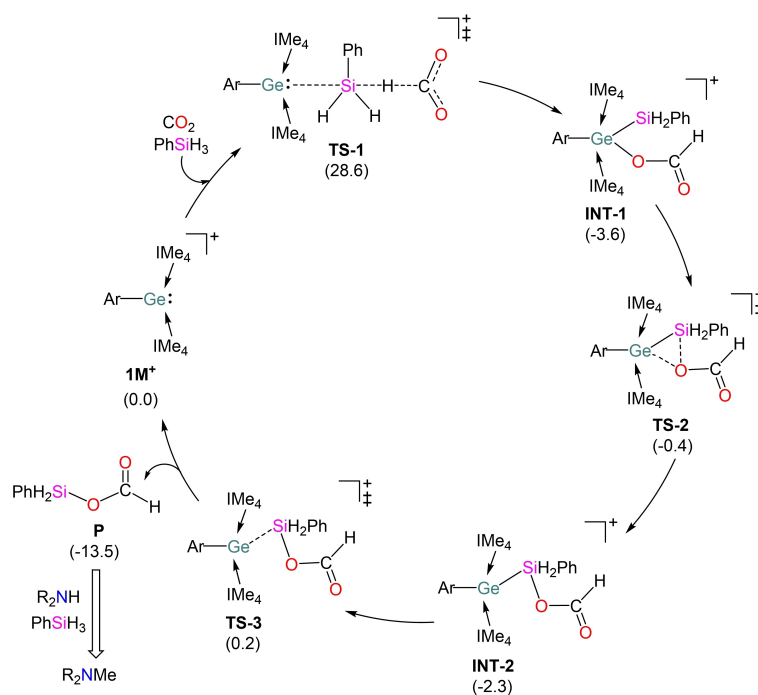


Figure 1. Proposed mechanism of $1M^+$ -catalyzed N-functionalization of amines with CO_2 and $PhSiH_3$. ΔG_L^\ddagger ($kcal\ mol^{-1}$) values are given in brackets. Ar = 2,6-dimethylphenyl; R = -Et.

computed activation barriers for **TS-1** increase with decreasing number of hydrides on the silane ($PhSiH_3$: $28.6\ kcal\ mol^{-1}$ < Ph_2SiH_2 : $31.4\ kcal\ mol^{-1}$ < Ph_3SiH : $34.7\ kcal\ mol^{-1}$, Figure S54). **INT-1** finally delivers the formoxysilane (**P**) accompanying an energy barrier of $3.8\ kcal\ mol^{-1}$.

Further comparisons to the previous germa-acylium ion catalysis were sought through the extension to reductive N-functionalization of amines.^[7] Accordingly, following an initial optimization study, we examined the scope of the reaction with various amines as listed in Table 1. The study revealed that aliphatic secondary amines proceed smoothly compared to aromatic secondary amines. For example, the aliphatic amines (Table 1, Entry 1–4) are converted to corresponding $2e^-$ (formamide), $4e^-$ (aminal) and $6e^-$ (methylamine) reduced products within 2 h, whereas N-methylaniline (Table 1, Entry 5) requires 16 h. This is possibly attributed to the low nucleophilicity of the

aromatic amine arising from the higher inductive effects of the phenyl ring compared to alkyl groups.^[10] In comparison to the previous germa-acylium ion lower activity was again observed for reductive N-functionalization catalysis. This may, in part, be due to the role of the Ge center in the subsequent conversion of the formoxysilane product to the functionalized amine. In this system no metal center is implicated in the computed mechanism and formation of $PhSiH_2OH$ requires a slightly higher energy barrier for the reduction of formamide compared to the former germa-acylium ion system.^[7]

Germlyumylidene catalyst **1**, whilst not as active as the germa-acylium system,^[7] its increased stability with regard to subsequent cycles prompted us expand the scope of the reactivity towards alternative reductive catalytic cycles. Cyanosilylation is one of the most fundamental carbon-carbon bond forming reactions in organic chemistry, where the resulting cyanohydrin silyl ether $[R_2C(OTMS)CN]$ serves as a synthon for numerous biologically relevant molecules such as α -hydroxyacids, α -amino acids, and β -amino alcohols.^[11] Catalysts for cyanosilylation of carbonyls typically utilize transition metals,^[11] whilst in contrast, only a handful of heavier p-block compounds have been exploited as a single site cyanosilylation catalyst.^[2c,g,12] In this context, Khan and co-workers recently demonstrated the role of a neutral NHC-stabilized germylene in the catalyzed cyanosilylation of aldehydes. Here, the Lewis acidity of germanium facilitated the cyanide transfer to the carbonyl moiety via formation of a donor-accepter complex $[TMSCN \rightarrow Ge(II)]$.^[2g] We, therefore, envisaged enhanced activity of germlyumylidenes over germlylenes, due to the cationic

Table 1. N-Methylation of amines using 1 bar CO_2 , 3 equiv. $PhSiH_3$, in CD_3CN and 5 mol% of **1** (All reactions carried out at $60^\circ C$). TOF = (Conversion/catalyst loading)/time.

Entry	Amine	$CO_2 + PhSiH_3 + R_2NH \xrightarrow{5\ mol\% \ 1} R_2NCHO + R_2NCH_2NR_2 + R_2NMe$ (a) (b) (c)			TOF [h^{-1}]
		NMR Yield [%]			
		a	b	c	
1	diethylamine	73	4	22	9.4
2	piperidine	82	0	16	9.4
3	morpholine	81	0	16	9.4
4	dicyclohexylamine	47	0	47	19.8
5	N-methylaniline	70	25	4	1.25

germanium center. Accordingly, cyanosilylation was performed with various carbonyls, as listed in Table 2.

Catalytic cyanosilylation of aldehydes and ketones, mediated by **1**, proceeds under mild conditions compared to the previously reported germlyenes and transition metal catalysts.^[2c,9,13] Notably, in our case, low catalyst loadings (0.1 mol%) and reduced reaction times (≤ 90 min) are required for complete conversion of both aromatic and aliphatic aldehydes, yielding the corresponding cyanohydrin silylether (for aliphatic aldehydes TOF = ≥ 1800 h⁻¹ and aromatic aldehyde TOF = 900 h⁻¹). For benzophenone, increased catalyst loadings (1 mol%) and higher temperatures (50 °C) are required, likely due to the increased steric protection around the carbonyl moiety.

DFT studies indicate that initial coordination of Me₃SiCN to the Ge center via **TS-14** followed by de-coordination of IMe₄, leads to the formation of **INT-10** (Figure 2, Figure S57). The intermediate **INT-10** lies 15.4 kcal mol⁻¹ higher in energy than the initial reactants and several attempts to isolate the **INT-10** in presence of stoichiometric or excess Me₃SiCN were unsuccessful. The transition vector in **TS-14** animates the Ge–N bond formation (2.692 Å) with concomitant elongation of the Ge–C^{IMe₄} bonds (2.372/2.313 Å) compared to those in **1M⁺** (2.076/2.066 Å). The significant weakening of the C^{IMe₄}–Ge interactions in **TS-14** is also reflected in the Wiberg bond indices calculated for these bonds (**TS-14**: 0.486/0.529; **1M⁺**: 0.715/0.720). NOCV calculations reveal that the strongest orbital interaction in **TS-14** originates from the σ -donation of nitrogen

Table 2. Cyanosilylation: carbonyl (1.00 mmol), TMSCN (1.02 mmol), solvent (0.4 mL CD₃CN), temperature (28 ± 2 °C) and 0.1 mol% of **1**. TOF = (Conversion/catalyst loading)/time.^[a]

Entry	Aldehyde	Conversion [%]	Time [h]	TOF [h ⁻¹]
1	propanal	> 99	0.55	1800
2	pivaldehyde	> 99	0.50	1900
3	cyclohexanecarboxaldehyde	> 99	0.55	1800
4	4-pyridinecarboxaldehyde	> 99	0.50	1900
5	benzaldehyde	> 99	1.1	900
6	4-cyanobenzaldehyde	> 99	1.5	660
7	2-naphthalenecarboxaldehyde	> 99	1.5	660
8	benzophenone	> 99	4	25
9	acetophenone	> 99	14	7
10	4-fluoroacetophenone	> 99	16	6
11	4-methoxyacetophenone	> 99	15	6.6

[a] For ketones 1.00 mol% of **1** and 50 °C temperature was required.

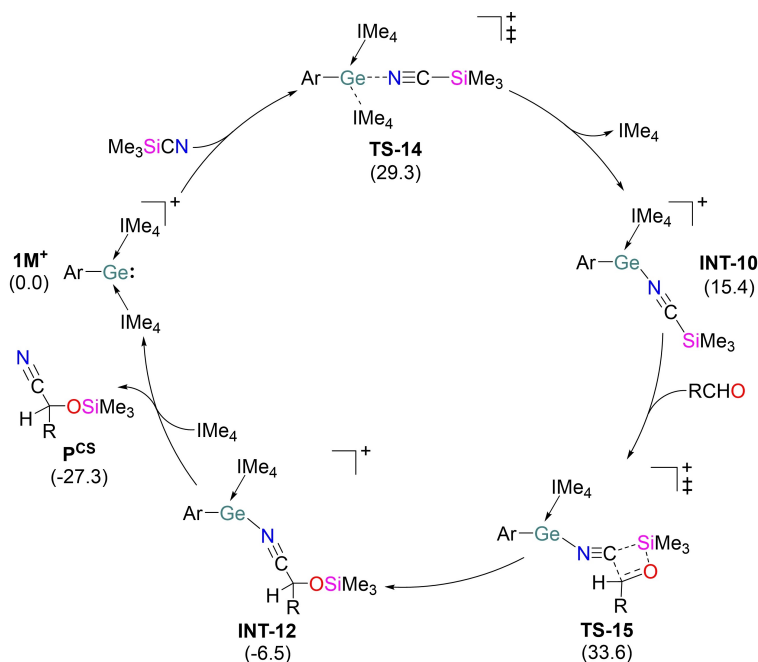


Figure 2. Proposed mechanism of **1M⁺**-catalyzed cyanosilylation of aldehyde. ΔG_L^{\ddagger} (kcal mol⁻¹) values are given in brackets. R = ^tBu.

lone pair in Me_3SiCN to the $\text{Ge}-\text{C}^{\text{IMe}_4} \sigma^*$ orbitals in 1M^+ (Figure S58). Analogous to the previous hydrosilylation mechanism, the electrophilic nature of 1M^+ cannot be explained by the orbital interactions between free 1M^+ and Me_3SiCN species (Figure S60a). The promotion of the 1M^+ fragment from its ground state equilibrium geometry to the perturbed form in TS-14 , as Me_3SiCN approaches the Ge center, results in lowering of the $\text{Ge}-\text{C}^{\text{IMe}_4} \sigma^*$ orbital from the LUMO + 10 in the free 1M^+ to LUMO in the 1M^+ fragment of TS-14 (Figure S60b).^[14] The significant stabilization of the $\text{Ge}-\text{C}^{\text{IMe}_4} \sigma^*$ orbital in TS-14 allows the germyliumylidene to exhibit its Lewis acidic nature towards Me_3SiCN . The incoming carbonyl essentially inserts into the C–Si bond of NCSiMe_3 via a 4-membered cyclic transition state (TS-15). This step needs to overcome overall energy barrier of $33.6 \text{ kcal mol}^{-1}$ to furnish the substantially more stable intermediate (INT-12). Similar moderately high activation barrier for cyanosilylation reactions at room temperature have been reported earlier.^[12a,b] Finally, re-coordination of IME_4 and a product de-coordination step to deliver the desired cyanohydrin product accompanies an energy barrier of $7.5 \text{ kcal mol}^{-1}$. In the alternative pathway, the substitution of IME_4 in 1M^+ by RCHO demands slightly lower energy barrier of $28.6 \text{ kcal mol}^{-1}$ compared to that by Me_3SiCN (Figure S62). However, the Si–CN bond activation in the incoming Me_3SiCN by free NHC in the subsequent step needs to surmount a significantly higher energy barrier of $37.1 \text{ kcal mol}^{-1}$ and hence, the initial coordination of RCHO to the Ge center in 1M^+ via ligand exchange can be safely discarded. Moreover, theoretical endeavor to optimize the transition state similar to TS-1 (Figure 1), depicting the activation of Si–CN bond in Me_3SiCN by the germanium lone pair in 1M^+ and concomitant –CN transfer to RCHO remained unsuccessful. Special attention is also directed towards the nucleophilic attack of germanium lone pair in 1M^+ to the silicon center in Me_3SiCN (Figure S73). However, geometry optimization of such hypercoordinate silane adduct (INT-37) remained unsuccessful at the R-BP86/def2-SVP level. Importantly, we were able to optimize INT-37 at the R-M06-2X-D3/def2-TZVP level. Our calculations suggest that the formation of INT-37 is extremely endergonic by $29.5 \text{ kcal mol}^{-1}$ and its generation also demands an activation barrier of $30.8 \text{ kcal mol}^{-1}$ (Figure S74). The subsequent –CN transfer to the carbonyl carbon in the incoming substrate demands an energy barrier of $32.9 \text{ kcal mol}^{-1}$. Importantly, the favorable pathway for the

cyanosilylation reaction (Figure S57) shows the rate-limiting energy barrier of $31.8 \text{ kcal mol}^{-1}$ at the same level of theory. Moreover, structural optimization of the intermediate generated by the nucleophilic attack of 1M^+ to the RCHO failed despite several attempts (Figure S73). Hence, the Lewis basicity of the germyliumylidene for the cyanosilylation reaction is less likely to operate on kinetic ground.

Given the current interest in hydroboration as an attractive method for mild and selective reduction of carbonyls, we were interested to see how our germyliumylidene catalyst performed. Most relevant to this work is the previous reports of neutral tetrylene catalysts (R_2E , $\text{E}=\text{Si}-\text{Sn}$)^[2b,15] and the recent examples of cationic Ge(II) metal centers for hydroboration of carbonyls.^[6] Encouraged by these studies, we screened catalytic activity of **1** towards various aldehydes with pinacol borane (HBpin) as the hydroboration reagent. In line with previous studies, less bulky substituents (e.g., propanal, Table 3, entry 1) proceed rapidly with low catalyst loadings (0.1 mol%), whereas more sterically demanding substrates (e.g., $^t\text{BuCHO}$, Table 3, entry 2) require longer reaction times. Notably, this catalysis proceeds with much lower catalyst loadings than those previously reported for cationic germanium catalysts.^[6b]

Similar to the cyanosilylation mechanism, the favorable pathway of hydroboration of aldehyde shows the initiation of the reaction by substitution of IME_4 by RCHO via TS-22 accompanying the rate-limiting activation barrier of $29.2 \text{ kcal mol}^{-1}$ (Figure 3 and S64). The strongest orbital interaction in TS-22 is associated with the charge flow from the oxygen lone pair in RCHO into the $\text{Ge}-\text{C}^{\text{IMe}_4} \sigma^*$ orbitals in 1M^+ , as suggested by NOCV calculations (Figure S65). Similar to TS-14 , the unique bonding features of the 1M^+ and RCHO fragments in TS-22 can nicely explain electrophilic nature of germyliumylidene in hydroboration reactions. The significant stabilization of $\text{Ge}-\text{C}^{\text{IMe}_4} \sigma^*$ orbital in the 1M^+ fragment of TS-22 compared to that in the free 1M^+ facilitates the nucleophilic attack of aldehyde (Figure S66). The subsequent B–H bond activation in HBpin is mediated by the free IME_4 .^[14b,16] The adduct INT-21 transfers the hydride to the carbonyl carbon in INT-20 . This is followed by the coordination of boron to the oxygen center generating the substantially stable intermediate INT-23 . Finally, the IME_4 ligand transfer to the Ge center demands an energy barrier of $26.8 \text{ kcal mol}^{-1}$ to afford the desired product and regenerate 1M^+ . Notably, unlike transition

Table 3. Hydroboration: Aldehyde (1.00 mmol), HBpin (1.02 mmol), solvent (0.4 mL CD_3CN), temperature ($28 \pm 2^\circ\text{C}$) and 0.1 mol % of catalyst. TOF = (Conversion/catalyst loading)/time.

Entry	Aldehyde	Conversion [%]	Time [h]	TOF [h^{-1}]
1	propanal	> 99	0.1	> 5900
2	pivaldehyde	> 92	24	38
3	cyclohexanecarboxaldehyde	> 99	4	250
4	4-pyridinecarboxaldehyde	> 99	3.5	280
5	benzaldehyde	> 85	0.5	1700
6	4-cyanobenzaldehyde	> 99	0.6	1600
7	2-naphthalenecarboxaldehyde	> 99	0.6	1600

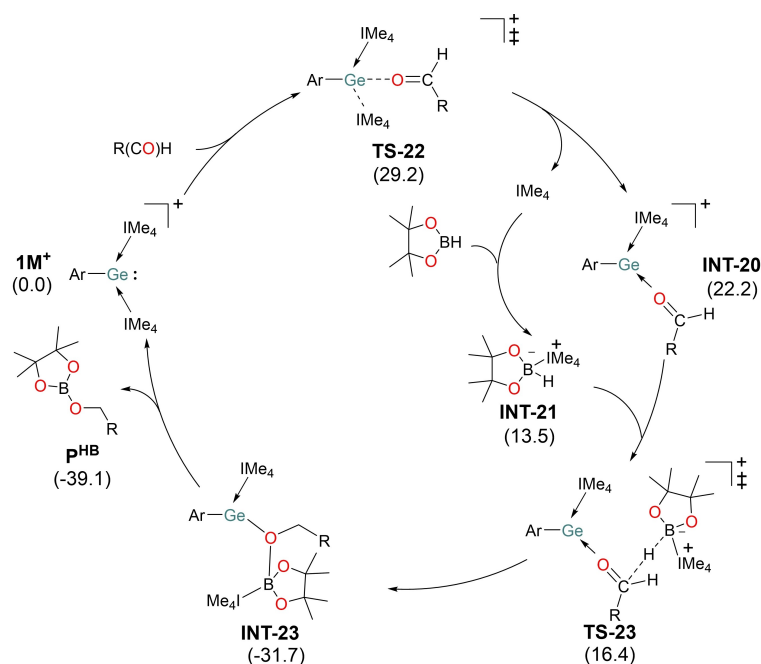


Figure 3. Proposed mechanism of $1M^+$ -catalyzed hydroboration of aldehyde. ΔG_L^{\ddagger} (kcal mol $^{-1}$) values are given in brackets. R = –Et.

metals,^[17] metal-ligand cooperativity in low valent group 14 complexes is rare^[15a] and this provides a unique example of this cooperativity and its pivotal role in catalysis. Whilst the IMe_4 ligand plays a key role in this transformation, subsequent control experiments highlight the requirement for the Ge center (0.1 mol% of IMe_4 the TOF for hydroboration of benzaldehyde 50 h $^{-1}$).

Conclusion

In conclusion, we have demonstrated for the first time the utilization of a well-defined low valent group 14 tetryliumylidene complex for diverse organic transformations. This includes the germyliumylidene (1)-catalyzed hydrosilylation of CO $_2$ and N-methylation of amines using CO $_2$ as a C1 source, where 1 acts as a Lewis base towards silane due to the presence of a lone pair on the germanium atom. Additionally, exploiting the electronic features of 1 other organic transformations, such as cyanosilylation and hydroboration of carbonyls, have been achieved under mild conditions. This is possible due to the accessible Ge–C^{NHC} σ^* orbitals, which allow 1 to exhibit its electrophilic nature in cyanosilylation and hydroboration reactions. With the observed high catalytic activity and versatile transformations, this NHC-stabilized germyliumylidene catalyst provides a viable alternative towards transition metal-free catalysis.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: catalysis · cations · CO $_2$ conversion · DFT · germanium · N-heterocyclic carbenes

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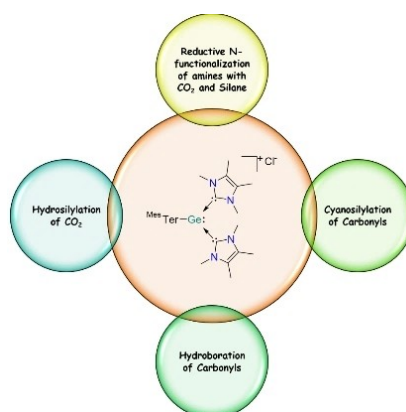
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FULL PAPER

The versatile ambiphilic catalytic application of a bis-NHC-stabilized germyliumylidene enables a range of reductive functionalization reactions, with a particular emphasis on C=O reduction that is, CO₂ and carbonyls.



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**Germyliumylidene: A Versatile Low
Valent Group 14 Catalyst**

