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# Reactivity of Digermylenes toward Potassium Graphite: Synthesis and Characterization of Germylidenide Anions

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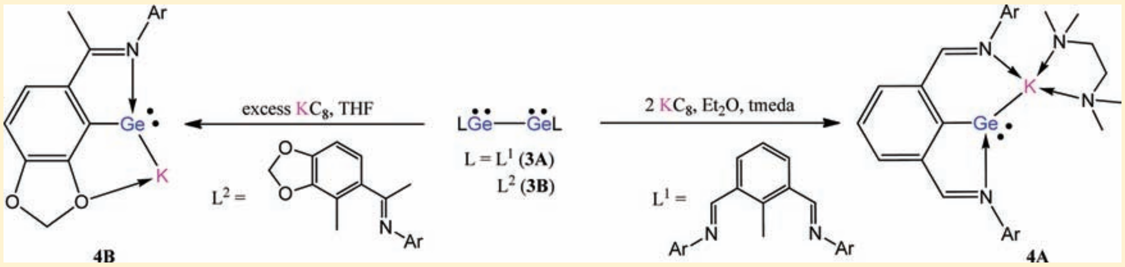
*Supporting Information*

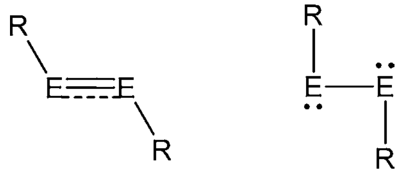


**ABSTRACT:** The synthesis and characterization of the digermylenes [LGe–GeL] [L = **L**$^1$ (**3A**), **L**$^2$ (**3B**)] supported by the 2,6-diiminophenyl (**L**$^1$) and 2-imino-5,6-methylenedioxylphenyl (**L**$^2$) ligands are described. Their reactivities toward potassium graphite are also reported. The reaction of [LGeCl] [L = **L**$^1$ (**2A**), **L**$^2$ (**2B**)] with KC$_8$ in tetrahydrofuran (THF) at room temperature afforded the digermylenes [LGe–GeL] [L = **L**$^1$ (**3A**), **L**$^2$ (**3B**)], which are the first examples of diaryldigermylenes stabilized by *o*-imino donor(s). The treatment of **3A** with 2 equiv of KC$_8$ in Et$_2$O, followed by the addition of excess tetramethylethylenediamine (TMEDA), results in cleavage of the Ge$^I$–Ge$^I$ bond to afford the germylidenide anion [**L**$^1$GeK·TMEDA] (**4A**). Similarly, the reaction of **3B** with excess KC$_8$ in THF afforded the germylidenide anion [**L**$^2$GeK] (**4B**). The molecular structures of compounds **4A** and **4B** as determined by single-crystal X-ray diffraction analysis show that the K atoms are $\eta^1$-coordinated with the low-valent Ge atoms. Moreover, the negative charges at the Ge atoms in compounds **4A** and **4B** are stabilized by electron delocalization in the germanium heterocycles.

## INTRODUCTION

Stable heavier group 14 alkyne analogues of composition REER (R = bulky terphenyl or silyl ligand; E = Si, Ge, Sn, Pb) have attracted much attention in the past decades.[1] These complexes can be synthesized by incorporating sterically hindered substituents at the heavier group 14 elements.[2] The X-ray structures of heavier group 14 alkyne analogues show that they have a trans-bent and planar geometry in which the R–E–E angle decreases from silicon to lead. It was also demonstrated that the heavier alkyne analogues can undergo one- and two-electron reduction to give the radical anions [REER]$^{\bullet -}$ and the doubly reduced species [REER]$^{2-}$.[2g,3] A comparison of their structural data with those of the heavier alkyne analogues can provide insight into the E–E bonding.[4,5] For example, the one-electron reduction of the distannyne [Ar′SnSnAr′] [Ar′ = C$_6$H$_3$-2,6-(C$_6$H$_3$-2,6-Pr$^i{}_2$)$_2$] with potassium afforded [K(THF)$_6$]-[Ar′SnSnAr′] (THF = tetrahydrofuran), in which the Sn–Sn bond is lengthened significantly from 2.6675(4) to 2.8081(9) Å and the Ar′–Sn–Sn angle is narrowed appreciably from 125.24(7) to 97.91(16)°.[2g] When two electrons are added to [Ar′SnSnAr′], the doubly reduced species [Ar′SnSnAr′]$^{2-}$ has a shorter Sn–Sn bond [2.7754(3) Å] than that in [K(THF)$_6$]-[Ar′SnSnAr′]. Theoretical studies show that [Ar′SnSnAr′] has either a multiple-bonded structure [RE$\underset{\cdot\cdot}{\equiv}$ER] (**M**) or single-bonded structure [R$\ddot{E}$–$\ddot{E}$R] (**S**) on the potential energy surface (Chart 1).[5] Although their energy difference is very small (ca. 5 kcal/mol), [Ar′SnSnAr′] has a multiple-bonded structure **M** in solution as in the solid-state structure. Orbital analysis shows that the lowest occupied molecular orbitals of **M** and **S** are different, in which **M** and **S** have small antibonding (slipped $\pi_{in}$*) and large bonding ($\pi_{out}$) character, respectively. In view of experimental data and theoretical studies, the reduction of [Ar′SnSnAr′] can be explained by the fact that the one-electron reduction leads to the formation of the S$^-$ anion instead of the M$^-$ anion. The addition of one more electron to the S$^-$ anion shortens the Sn–Sn bond because the bonding $\pi_{out}$ orbital is doubly occupied.

**Chart 1. Multiple-Bonded M and Single-Bonded S Structures**



**M** **S**

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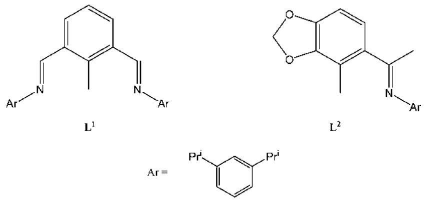
Recently, a series of novel base-stabilized group 14 element(I) dimers [RË–ËR] (E = Si, Ge, Sn) were synthesized.[6] They are comprised of a Ë–Ë single bond and a lone pair of electrons at each E atom. Their structures resemble the single-bonded structure **S** of [Ar′SnSnAr′]. Thus, they are considered as base-stabilized heavier alkyne analogues. The fact that heavier alkyne analogues supported by bulky terphenyl and silyl ligands can be singly or doubly reduced prompted our interest in investigating the reduction of intramolecularly base-stabilized group 14 element(I) dimers. To the best of our knowledge, the reduction of intramolecularly base-stabilized group 14 element(I) dimers is not reported.

Herein, we report the syntheses of digermylenes stabilized by 2,6-diiminophenyl (**L**$^1$; Scheme 1) and 2-imino-5,6-methylenedioxylphenyl (**L**$^2$) ligands. They are comprised of a Ge–Ge single bond and a lone pair of electrons at each Ge atom. Their structures resemble the single-bonded structure **S** of [Ar′SnSnAr′]. We also describe the reduction of the digermylenes with potassium graphite to afford the germylidenide anions.

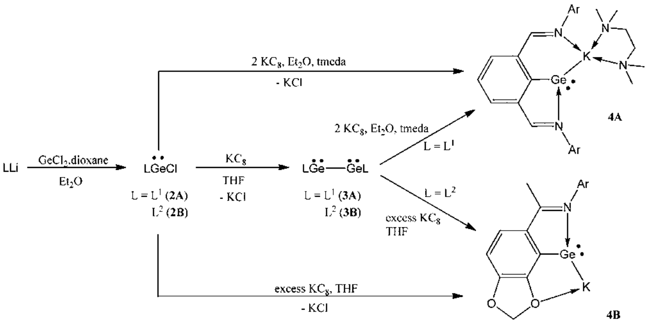
**Scheme 1. 2,6-Diiminophenyl (L$^1$) and 2-Imino-5,6-methylenedioxylphenyl (L$^2$) Ligands**



## ■ RESULTS AND DISCUSSION

**Synthesis of [LGeCl].** The reaction of [L$^1$Br][7] with Bu$^n$Li in THF at −78 °C,[8] followed by treatment with GeCl$_2$·dioxane, afforded [L$^1$GeCl] (**2A**; Scheme 2). Similarly, [L$^2$GeCl] (**2B**) was synthesized by the reaction of [L$^2$Li][9] with GeCl$_2$·dioxane in Et$_2$O. Compounds **2A** and **2B** were isolated as highly air- and moisture-sensitive orange and yellow crystalline solids, respectively. They are soluble in hydrocarbon solvents and have been characterized by NMR spectroscopy. The $^1$H NMR spectrum of **2A** displays one set of signals due to the 2,6-diiminophenyl ligand. In the spectrum, there are two singlets at δ 8.06 and 8.08 ppm, which correspond to two nonequivalent *H*C═N protons. The results indicate that compound **2A** retains its solid-state structure in solution. The $^1$H NMR spectrum of **2B** displays one set of signals due to the 2-imino-5,6-methylenedioxylphenyl ligand. It is worth noting that the −OCH$_2$O− protons are nonequivalent and show two singlets at δ 5.18 and 5.27 ppm in the spectrum. The signal for the *Me*C═N protons (δ 1.68 ppm) shows an upfield shift compared with that of [L$^2$Li] (δ 1.90 ppm).[9]

**Scheme 2. Syntheses of 2–4**



Compounds **2A** and **2B** have been characterized by X-ray crystallography. The molecular structures of **2A** and **2B** are shown in Figures 1 and 2, respectively. In the molecular structure of **2A**, the NAr substituent at the C20 atom and the Ge–Cl moiety are disordered. The disordered substituents are omitted for clarity in Figure 1. In the asymmetric unit of **2B**, there are two independent molecules with slightly different bond lengths and angles (Table 1). Only one of them is discussed here for clarity. The 2,6-diiminophenyl and 2-imino-5,6-methylenedioxylphenyl ligands are bonded in a C,N-chelate fashion to the Ge1 atoms in **2A** and **2B**, respectively. The Ge atoms adopt a distorted trigonal-pyramidal geometry. The sum of the bond angles at the Ge1 atoms (**2A**, 267.40°; **2B**, 268.76°) is comparable with that of the three-coordinated chlorogermylene [(Mamx)GeCl] (270.25°) supported by the 2,4-di-*tert*-butyl-6-[(*N*,*N*-dimethylamino)methyl]phenyl ligand (Mamx).[10] The geometries at the Ge1 atoms in **2A** and **2B** indicate that they are almost nonhybridized and possess lone-pair electrons with high *s* character. In compound **2A**, the Ge1–C19 [2.028(3) Å] and Ge1–N1 [2.247(3) Å] bonds

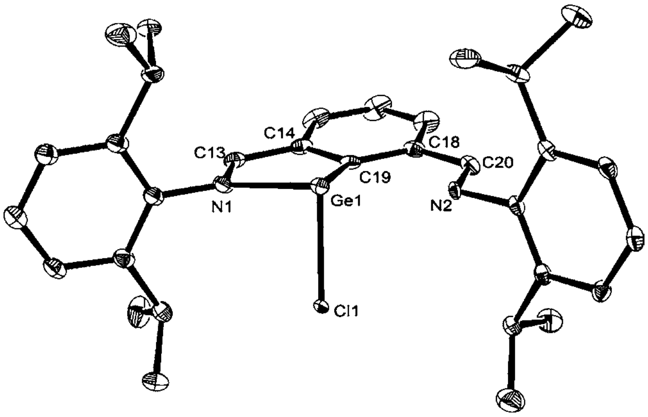


**Figure 1.** Molecular structure of compound **2A** (50% thermal ellipsoids). H atoms, the disordered NAr substituent at the C20 atom, and the disordered Ge1A and Cl1A atoms are omitted for clarity.

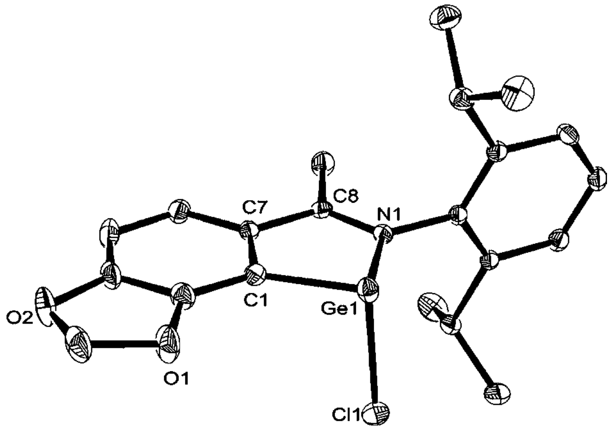


**Figure 2.** Molecular structure of compound **2B** (50% thermal ellipsoids). In the asymmetric unit of **2B**, there are two independent molecules with slightly different bond lengths and angles. Only one of them is shown for clarity. H atoms are omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) of Compounds 2−4

| | | | |
|---|---|---|---|
| **2A** | | | |
| Ge1−C19 | 2.028(3) | C14−C19 | 1.393(5) |
| Ge1−Cl1 | 2.3288(8) | C18−C19 | 1.387(4) |
| Ge1−N1 | 2.247(3) | C18−C20 | 1.461(5) |
| N1−C13 | 1.286(4) | N2−C21 | 1.424(9) |
| C13−C14 | 1.453(5) | | |
| C19−Ge1−Cl1 | 100.61(8) | N1−C13−C14 | 118.2(3) |
| C19−Ge1−N1 | 76.97(12) | C13−C14−C19 | 115.6(3) |
| N1−Ge1−Cl1 | 89.82(7) | C14−C19−Ge1 | 116.0(2) |
| Ge1−N1−C13 | 111.5(2) | | |
| **2B** | | | |
| Ge1−Cl1 | 2.3024(8) | C1−C7 | 1.423(4) |
| Ge1−C1 | 1.992(3) | C7−C8 | 1.460(4) |
| Ge1−N1 | 2.054(2) | N1−C8 | 1.301(3) |
| C1−Ge1−N1 | 80.40(11) | C1−C7−C8 | 114.3(2) |
| C1−Ge1−Cl1 | 93.98(8) | C7−C8−N1 | 115.7(3) |
| N1−Ge1−Cl1 | 94.38(7) | C8−N1−Ge1 | 115.50(18) |
| Ge1−C1−C7 | 113.6(2) | | |
| **3A** | | | |
| Ge1−Ge2 | 2.5059(5) | Ge2−C1 | 1.990(3) |
| Ge1−C33 | 1.967(3) | C1−C6 | 1.413(5) |
| C33−C38 | 1.418(5) | C6−C7 | 1.438(4) |
| C38−C39 | 1.440(5) | C7−N1 | 1.305(4) |
| C39−N3 | 1.300(4) | Ge2−N1 | 2.036(3) |
| Ge1−N3 | 1.986(3) | | |
| N3−Ge1−C33 | 83.21(13) | N1−Ge2−C1 | 81.92(12) |
| N3−Ge1−Ge2 | 102.31(8) | C1−Ge2−Ge1 | 89.10(9) |
| C33−Ge1−Ge2 | 116.11(10) | N1−Ge2−Ge1 | 112.82(8) |
| Ge1−C33−C38 | 110.4(3) | Ge2−C1−C6 | 112.0(2) |
| C33−C38−C39 | 114.9(3) | C1−C6−C7 | 114.6(3) |
| C38−C39−N3 | 116.7(3) | C6−C7−N1 | 117.8(3) |
| C39−N3−Ge1 | 113.4(2) | C7−N1−Ge2 | 112.6(2) |
| **3B** | | | |
| Ge1−Ge2 | 2.5685(5) | Ge2−N2 | 2.017(3) |
| Ge1−N1 | 2.022(3) | Ge2−C22 | 1.954(4) |
| Ge1−C1 | 1.968(4) | C22−C28 | 1.434(5) |
| C1−C7 | 1.436(5) | C28−C29 | 1.447(5) |
| C7−C8 | 1.437(5) | C29−N2 | 1.321(4) |
| C8−N1 | 1.310(5) | | |
| C1−Ge1−N1 | 80.95(14) | C22−Ge2−N2 | 80.87(14) |
| C1−Ge1−Ge2 | 101.50(10) | C22−Ge2−Ge1 | 98.22(11) |
| N1−Ge1−Ge2 | 96.99(8) | N2−Ge2−Ge1 | 99.20(9) |
| Ge1−C1−C7 | 113.2(3) | Ge2−C22−C28 | 114.3(3) |
| C1−C7−C8 | 114.1(3) | C22−C28−C29 | 113.3(3) |
| C7−C8−N1 | 115.5(3) | C28−C29−N2 | 114.9(3) |
| C8−N1−Ge1 | 115.5(2) | C29−N2−Ge2 | 115.5(2) |
| **4A** | | | |
| K1−N2 | 3.179(3) | C6−C7 | 1.396(5) |
| Ge1−C1 | 1.909(4) | C1−C6 | 1.450(5) |
| Ge1−K1 | 3.3560(9) | C1−C2 | 1.423(5) |
| Ge1−N1 | 1.925(3) | C2−C20 | 1.460(5) |
| N1−C7 | 1.361(4) | N2−C20 | 1.281(4) |
| C1−Ge1−K1 | 126.84(11) | C6−C1−Ge1 | 112.6(2) |
| C1−Ge1−N1 | 83.43(13) | Ge1−C1−C2 | 130.2(3) |
| K1−Ge1−N1 | 148.44(9) | C1−C2−C20 | 121.4(3) |
| Ge1−N1−C7 | 115.5(2) | C2−C20−N2 | 124.2(3) |
| N1−C7−C6 | 114.5(3) | C20−N2−K1 | 160.8(2) |
| C7−C6−C1 | 114.0(3) | N2−K1−Ge1 | 55.45(6) |
| **4B** | | | |
| Ge1−K1 | 3.5252(17) | Ge1−N1 | 1.916(5) |
| Ge1−C1 | 1.919(6) | O1−K1 | 2.991(5) |
| C1−C7 | 1.464(9) | O4−K1 | 2.865(5) |
| C7−C8 | 1.375(9) | O6−K1 | 2.723(4) |
| C8−N1 | 1.377(8) | Ge2−K1 | 3.5357(19) |
| N1−Ge1−K1 | 126.69(15) | C1−C7−C8 | 114.1(6) |
| C1−Ge1−K1 | 68.54(18) | C7−C8−N1 | 113.7(6) |
| N1−Ge1−C1 | 82.4(2) | C8−N1−Ge1 | 116.9(4) |
| Ge1−C1−C7 | 112.9(5) | O1−K1−Ge1 | 64.64(9) |

are comparable with those in [$\{2,6\text{-}(CH_2NEt_2)_2C_6H_3\}GeCl$] [Ge−C, 1.941(11) Å; Ge−N, 2.337(11) Å], which comprises an aryl ligand with two *o*-amino donors.[11] The Ge1···N2 distance [2.62(1) Å] in **2A** is significantly longer than the N−Ge dative bonds in N-donor-stabilized chlorogermylenes such as [$\{C_5H_4N\text{-}2\text{-}C(SiMe_3)_2\}GeCl$] [2.082(4) and 2.075(4) Å][12] and [(Mamx)GeCl] [2.0936(13) Å],[10] but it is shorter than the sum of the van der Waals radii (ca. 3.55 Å). The results indicate that the interaction between the Ge1 and N2 atoms is weak. In compound **2B**, the Ge1−C1 [1.992(3) Å] and Ge1−N1 [2.054(2) Å] bonds are comparable with those in [(Mamx)-GeCl] [Ge−C, 2.0156(14) Å; Ge−N, 2.0936(13) Å].[10]

**Synthesis of [LGe−GeL].** The reaction of [LGeCl] with $KC_8$ in THF at room temperature afforded the digermylenes [LGe−GeL] [L = $\mathbf{L^1}$ (**3A**), $\mathbf{L^2}$ (**3B**)], which are the first examples of diaryldigermylenes stabilized by *o*-imino donor(s). Other examples of digermylenes stabilized by amidinate ligands were reported by research groups of Roesky and Jones.[6b,d,i] Recently, the $Ge^I$ radical [$HC\{C(Bu^t)NAr\}_2Ge^{\bullet}$] was synthesized by the reduction of the corresponding chlorogermylene with $Na(C_{10}H_8)$ in THF.[13] The results imply that digermylenes are formed via the dimerization of $Ge^I$ radical intermediates. Compounds **3A** and **3B** were isolated as highly air- and moisture-sensitive purple and red crystalline solids, respectively. They are soluble in hydrocarbon solvents and have been characterized by NMR spectroscopy. The $^1H$ NMR spectrum of **3A** at room temperature displays one doublet at δ 0.87 ppm and one broad singlet at δ 2.74 ppm for the $Pr^i$ substituents. The results are not consistent with the solid-state structure, suggesting that the imino substituents are fluxional in solution at room temperature. In this regard, the $^1H$ NMR spectra of **3A** was acquired at −100 °C, whereupon a multiplet at δ 0.28−1.40 ppm for the $CH\mathit{Me}_2$ protons and seven broad singlets at δ 2.04−3.74 ppm for the $\mathit{C}HMe_2$ protons were resolved. The IR spectrum of **3A** also shows two N=C stretching modes of the nonequivalent imino substituents at ν 1587 and 1624 $cm^{-1}$. The $^1H$ NMR spectrum of **3B** shows one set of signals due to the 2-imino-5,6-methylenedioxylphenyl ligand. The signal for the *Me*C=N protons (δ 1.97 ppm) shows a downfield shift compared with that of **2B**. The UV−vis spectrum of **3A** in toluene shows three absorption bands at 438, 586, and 702 nm in the visible-light region, which shows a bathochromic shift compared with that of the tin congener (425, 457, and 561 nm) reported by Roesky and co-workers.[6j] The shift is comparable with that observed in the electronic spectra of the amidinate-stabilized group 14 element(I) dimers [{$R^1C(NAr)_2$}$\ddot{E}$]$_2$ [$R^1 = C_6H_4$-4-Bu$^t$; Ar = $C_6H_3$-2,6-Pr$^i_2$; E = Si (629 nm), Ge (502 nm), Sn (388 nm)].[6i] Moreover, this is opposite to the electronic spectra of multiple-bonded heavier group 14 alkyne analogues, in which there is a hypsochromic shift upon descending the group.[2j] These imply that the Ge−Ge bond in **3A** has little $\pi$ character. Similarly, the UV−vis spectrum of **3B** in THF shows three absorption bands at 475, 506, and 659 nm in the visible-light region.

Compounds **3A** and **3B** have been characterized by X-ray crystallography. Their molecular structures are shown in Figures 3 and 4, respectively. They are comprised of gauche-bent structures similar to the amidinate-stabilized digermylene [PhC(NBu$^t$)$_2$Ge]$_2$.[6d] In contrast, their structures are different from the more sterically hindered digermylene [Bu$^t$C(NAr)$_2$Ge]$_2$,[6b] which shows a trans-bent structure. The Ge atoms in **3A** and **3B** adopt a distorted trigonal-pyramidal geometry, which indicates that there is a lone pair of electrons on each Ge atom. The Ge−Ge bonds [**3A**, 2.5059(5) Å; **3B**, 2.5685(5) Å] are comparable with that in [PhC(NBu$^t$)$_2$Ge]$_2$ [2.569(5) Å] and [Bu$^t$C(NAr)$_2$Ge]$_2$ [2.6380(8) Å].[6b,d] The results imply that the Ge−Ge bonds do not have any multiple-bond character. The Ge−C and Ge−N bonds in compounds **3A** and **3B** are slightly shorter than those in **2A** and **2B**, respectively.

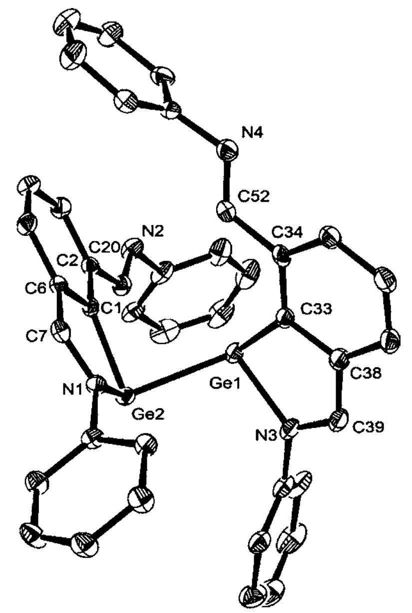


**Figure 3.** Molecular structure of compound **3A** (50% thermal ellipsoids). H atoms and Pr$^i$ substituents are omitted for clarity.

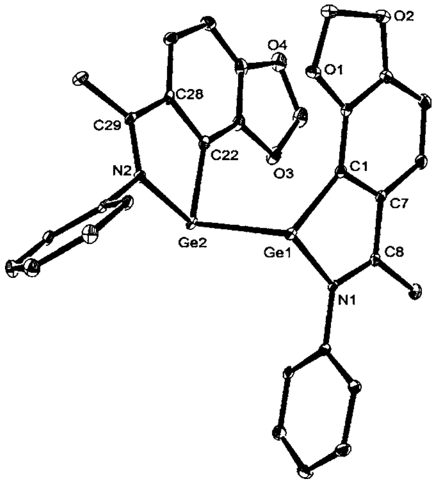
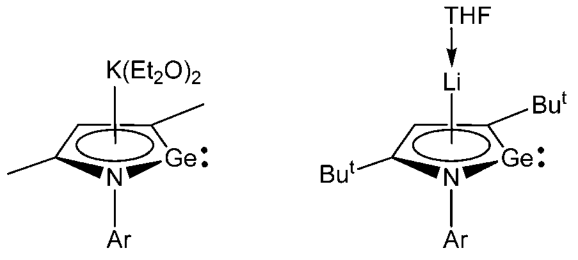


**Figure 4.** Molecular structure of compound **3B** (50% thermal ellipsoids). H atoms and Pr$^i$ substituents are omitted for clarity.

**Reaction of [LGe−GeL] with KC$_8$.** The reaction of the digermylene **3A** with 2 equiv of KC$_8$ in Et$_2$O, followed by the addition of excess tetramethylethylenediamine (TMEDA), results in cleavage of the Ge$^I$−Ge$^I$ bond to afford the germylidenide anion [**L$^1$**GeK·TMEDA] (**4A**).[14] Similarly, the reaction of **3B** with excess KC$_8$ (2.7 equiv) in THF for 2 days afforded the germylidenide anion [L$^2$GeK] (**4B**). The results are in contrast with the reduction of the heavier alkyne analogue [Ar′SnSnAr′] with potassium, by which the doubly reduced species K$_2$[Ar′SnSnAr′] was formed.[2g] Moreover, the reduction of the amidinate-stabilized digermylene [Bu$^t$C(NAr)$_2$Ge]$_2$ leads to decomposition to give elemental germanium and [Bu$^t$C(NAr)$_2$K].[6b]

Power et al. showed that the radical anions [REER]$^{\bullet-}$ and the doubly reduced species [REER]$^{2-}$ (E = Ge, Sn; R = terphenyl substituent) were synthesized by the reaction of the corresponding heavier chlorocarbene analogues [RECl] with excess alkali metal.[15] In this regard, the reaction of compound **2A** with 2 equiv of KC$_8$ in Et$_2$O was performed to afford compound **4A**. The reaction appears to proceed through the formation of compound **3A**, which then reacts with two molecules of KC$_8$ to form **4A**. Similarly, the reaction of compound **2B** with excess KC$_8$ (3.5 equiv) afforded compound **4B**. The X-ray crystal structures of compounds **4A** and **4B** show that the K atoms are $\eta^1$-coordinated with the low-valent Ge atoms (see below). Their crystallographic data also suggest that the negative charges at the Ge atoms are stabilized by electron delocalization in the GeCCCN five-membered rings. Recently, research groups of Driess and Jones reported the synthesis of the N-heterocyclic germylidenide complexes **I** and **II** by the reaction of [HC{C(R)N(Ar)}GeCl] (R = Me, Bu$^t$) with 2 equiv of alkali metal (Scheme 3).[16] It is worth noting that the mechanism for the formation of **I** and **II** is suggested to proceed through several reductive processes and ring contraction, which is different from that for **4A** and **4B**.

**Scheme 3. Germylidenides I and II**



**I** **II**

Compound **4A** was isolated as a highly air- and moisture-sensitive green crystalline solid, which is stable in solution and the solid state at room temperature in an inert atmosphere. The $^1$H NMR spectrum of **4A** displays one doublet at $\delta$ 1.18 ppm and one septet at $\delta$ 3.23 ppm for the Pr$^i$ substituents. The results indicate that compound **4A** has $C_{2v}$ symmetry in solution and the imino substituents may be equivalently coordinated to the Ge atom. The $^1$H NMR signal for the

*H*C═N proton ($\delta$ 8.15 ppm) shows a downfield shift compared with that of **2A**, suggesting that the negative charge at the Ge atom is stabilized by electron delocalization in the GeCCCN five-membered ring. The electronic delocalization is also supported by the bond lengths of the GeCCCN five-membered ring (see below).

Compound **4B** was isolated as a highly air- and moisture-sensitive red crystalline solid. Compound **4B** shows different color compared with green **4A** and pale-yellow **I**, which implies the noninnocence of the ligands.[16a] Moreover, the molecular structures of compounds **4A** and **4B** are different from that of **I**, which comprises a $\eta^5$-coordinated K atom.

Compound **4B** is stable in ethereal solvents and the solid state. However, it decomposes in toluene and benzene, which was confirmed by NMR spectroscopy. The identification of the decomposed compound is still in progress. Thus, spectroscopic analysis of **4B** can only be performed in THF-$d_8$. The $^1$H NMR spectrum shows one set of signals due to the 2-imino-5,6-methylenedioxylphenyl ligand. The signal for the *Me*C═N protons ($\delta$ 2.12 ppm) shows a downfield shift compared with that of **2B**, indicating that there is electron delocalization in the GeCCCN five-membered ring.

Compounds **4A** and **4B** have been characterized by X-ray crystallography. Compound **4A** has a polymeric structure by the interaction of the K1 atoms with the C4 atoms of the adjacent germylidenide molecules (Figure 5b). In the monomeric unit of compound **4A** (Figure 5a), the K1 atom is $\eta^1$-coordinated with the Ge1 atom of the GeCCCN ring, which is different from **I** and **II** comprising a $\eta^5$-coordinated alkali-metal center.[16] The K1 atom is also coordinated with the N2−4 atoms of the imino substituent and TMEDA (average K−N bond length: 2.961 Å). The coordination sphere on the K1 atom is further supplemented by an interaction with the *ipso*-C atom of a Ar substituent [K1···C21, 3.314(4) Å]. The GeCCCN five-membered ring in **4A** is planar, whereas those in **2A** and **3A** are puckered. The Ge1−K1 bond [3.3560(9) Å] is comparable with the tris(trimethylgermyl)germanide complex [$(\mathrm{Me_3Ge})_3\mathrm{GeK}$(18-crown-6)] [3.4213(11) Å][17] and the germylidenide complex **I** [3.449(1) and 3.573(1) Å].[16a] In addition, the Ge1−N1 [1.925(3) Å], N1−C7 [1.361(4) Å], C6−C7 [1.396(5) Å], C1−C6 [1.450(5) Å], and Ge1−C1 [1.909(4) Å] bond lengths suggest that there is an appreciable electron delocalization in the GeCCCN five-membered ring compared with those in compounds **2A** and **I** [Ge−N, 1.944(2) Å; N−C, 1.382(3) Å; C−C, 1.371(3) and 1.411(3) Å; Ge−C, 1.887(2) Å].[16a]

In the monomeric form of compound **4B** (Figure 6a), the K1 atom is $\eta^1$-coordinated with the Ge1 atom of the GeCCCN ring. The coordination sphere on the K1 atom is further supplemented by an $\eta^2$-interaction of the phenyl ring, the O1 atom of the $-\mathrm{OCH_2O}-$ substituent, and the O3 atom of the disordered $\mathrm{Et_2O}$ molecule. This leads to the K1 atom displacing from the GeCCCN plane by 2.358 Å. The Ge1−K1 bond [3.5252(17) Å] and the bond lengths of the GeCCCN ring [Ge1−N1, 1.916(5) Å; C8−N1, 1.377(8) Å; C7−C8, 1.375(9) Å; C1−C7, 1.464(9) Å; Ge1−C1, 1.919(6) Å] are comparable with those in **4A**. In addition, the electrostatic interaction of the K1 atom with the O4 and O6 atoms and the Ge2 atom of the adjacent germylidenide molecules leads to a polymeric form (Figure 6b). In the asymmetric unit (Figure S1 in the Supporting Information), there is solvent disordering at the K atoms. The K2 and K4 atoms are coordinated with either a THF or a $\mathrm{Et_2O}$ molecule.[18]

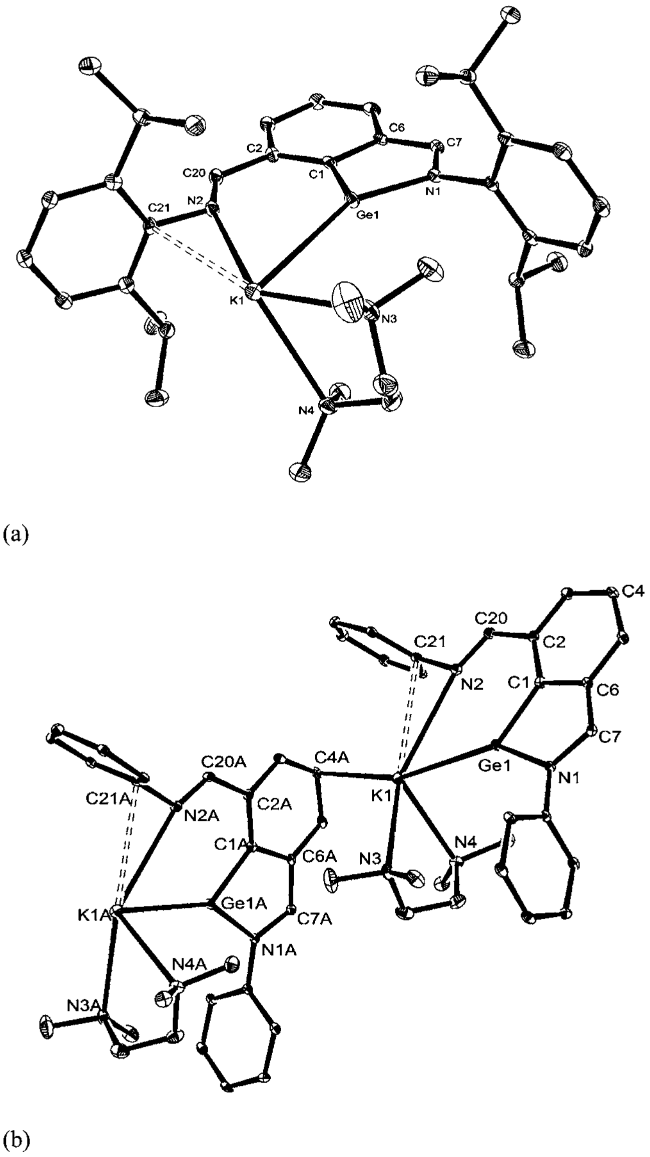


**Figure 5.** Molecular structure of compound **4A** (20% thermal ellipsoids): (a) perspective view of the molecule; (b) its polymeric form. H atoms (a and b) and $\mathrm{Pr^i}$ substituents (b) are omitted for clarity.

In conclusion, the digermylenes [LGe−GeL] [L = $\mathbf{L^1}$ (**3A**), $\mathbf{L^2}$ (**3B**)], which are supported by 2,6-diiminophenyl ($\mathbf{L^1}$) and 2-imino-5,6-methylenedioxylphenyl ligands ($\mathbf{L^2}$), were synthesized by the reaction of the chlorogermylenes [LGeCl] [L = $\mathbf{L^1}$ (**2A**), $\mathbf{L^2}$ (**2B**)] with 1 equiv of $\mathrm{KC_8}$. The germylidenide anion **4A** was synthesized by the reaction of **3A** with 2 equiv of $\mathrm{KC_8}$ and excess TMEDA. Similarly, the germylidenide anion [$\mathbf{L^2}$GeK] (**4B**) was synthesized by the reaction of **3B** with excess $\mathrm{KC_8}$. The crystallographic and spectroscopic data of compounds **4A** and **4B** show that the K atoms are $\eta^1$-coordinated with the low-valent Ge atoms. Moreover, the negative charges at the Ge atoms in compounds **4A** and **4B** are stabilized by electron delocalization in the germanium heterocycles.

## ■ EXPERIMENTAL SECTION

**General Procedure.** All manipulations were carried out under an inert atmosphere of argon gas using standard Schlenk techniques. Solvents were dried over and distilled over Na/K alloy prior to use. $\mathbf{L^1}$Br and $\mathbf{L^2}$Li were prepared as described in the literature.[7,9] The $^1$H and $^{13}$C NMR spectra were recorded on a JEOL ECA 400

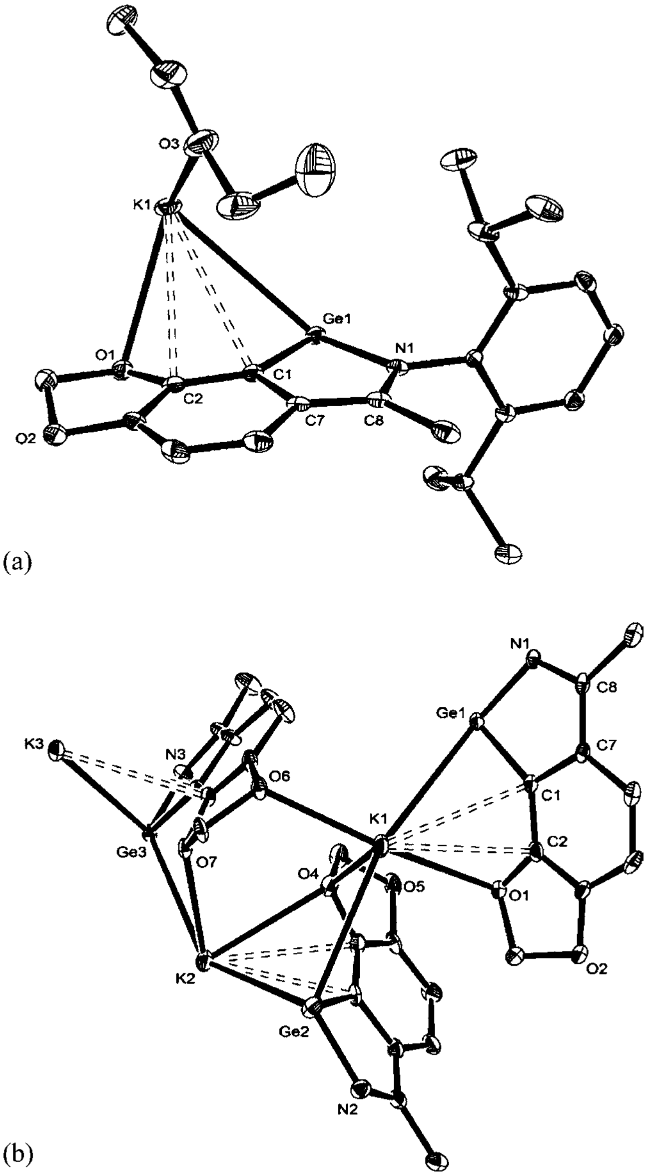


**Figure 6.** Molecular structure of compound **4B** (20% thermal ellipsoids): (a) perspective view of the molecule; (b) its polymeric form. H atoms and disordered solvent molecule(s) are omitted for clarity in parts a and b. Ar substituents are also omitted for clarity in part b.

spectrometer. The chemical shifts δ are relative to $SiMe_4$ for $^1H$ and $^{13}C$ NMR. Elemental analyses were performed by the Division of Chemistry and Biological Chemistry, Nanyang Technological University. Melting points were measured in sealed glass tubes and were not corrected.

**[$L^1$GeCl] (2A).** $Bu^nLi$ (2.0 M in cyclohexane, 3.0 mL, 6.00 mmol) was added dropwise to a THF solution (50 mL) of $L^1Br$ (2.66 g, 5.00 mmol) at −78 °C, and the reaction mixture was stirred for 1 h. It was warmed to −40 °C and stirred for another 2 h. A THF solution (10 mL) of $GeCl_2\cdot$dioxane (1.27 g, 5.50 mmol) was then added to the reaction mixture at −78 °C. The resulting red solution was warmed to room temperature gradually and stirred for 12 h. Solvent was removed under vacuum, and the residue was extracted with toluene. LiCl was then filtered off, and the red filtrate was concentrated to afford **2A** as orange crystals. Yield: 2.24 g (80.0%). Mp: 245 °C. Elem anal. Calcd for $C_{32}H_{39}ClGeN_2$: C, 68.64; H, 7.03; N, 5.01. Found: C, 68.31; H, 6.91; N, 4.85. $^1H$ NMR (395.9 MHz, $C_6D_6$, 25 °C): δ 1.14–1.26 (m of overlapping d, $J_{H-H}$ = 6.37 Hz, 24H, $CH(CH_3)_2$), 3.37 (br s, 4H, $CH(CH_3)_2$), 7.00–7.05 (m, 2H, Ph), 7.14–7.18 (m, 7H, Ph), 8.06 (s, 1H, CH=N), 8.08 (s, 1H, CH=N). $^{13}C\{^1H\}$ NMR (100.5 MHz, $C_6D_6$, 25 °C): δ 24.44 ($CH(CH_3)_2$), 24.56 ($CH(CH_3)_2$), 24.99 ($CH(CH_3)_2$), 25.16 ($CH(CH_3)_2$), 28.63 ($CH(CH_3)_2$), 28.69 ($CH(CH_3)_2$), 123.96, 126.61, 128.93, 132.29 (*Ph*Ge), 140.41, 140.56, 145.06, 145.24 165.48, 165.59 (N*Ar*), 171.69, 171.93 (*C*=NAr). UV–vis (toluene): $\lambda_{max}$ (ε) 218 (15 538), 245 (18 501), 336 (1786), 407 nm (932 $dm^3\ mol^{-1}\ cm^{-1}$). IR (Nujol, $cm^{-1}$): 2955s, 2924s, 2853s, 1628w, 1609w, 1551w, 1458m, 1377m, 1364w, 1323w, 1260w, 1175w, 1167w, 1096w, 1049w, 799m, 750w, 721w.

**[$L^2$GeCl] (2B).** A solution of $L^2Li$ (0.68 g, 2.06 mmol) in $Et_2O$ (57 mL) was added dropwise to a stirred suspension of $GeCl_2\cdot$dioxane (0.48 g, 2.06 mmol) in $Et_2O$ (4.7 mL) at 0 °C. The reaction mixture was raised to ambient temperature and stirred additionally for 15 h. The precipitate was filtered, and the filtrate was concentrated to afford yellow crystals of **2B**. Yield: 0.50 g (56.4%). Mp: 207 °C. Elem anal. Calcd for $C_{21}H_{24}ClGeNO_2$: C, 58.59; H, 5.62; N, 3.25. Found: C, 58.21; H, 5.43; N, 3.19. $^1H$ NMR (395.9 MHz, $C_6D_6$, 23.3 °C): δ 0.84 (d, $^3J_{HH}$ = 6.8 Hz, 3H, $CH(CH_3)_2$), 0.91 (d, $^3J_{HH}$ = 7.2 Hz, 3H, $CH(CH_3)_2$), 1.15 (d, $^3J_{HH}$ = 6.8 Hz, 3H, $CH(CH_3)_2$), 1.43 (d, $^3J_{HH}$ = 6.3 Hz, 3H, $CH(CH_3)_2$), 1.68 (s, 3H, $CH_3$), 2.64 (sept, $^3J_{HH}$ = 6.8 Hz, 1H, $CH(CH_3)_2$), 3.21 (sept, $^3J_{HH}$ = 6.8 Hz, 1H, $CH(CH_3)_2$), 5.18 (s, 1H, $OCH_2O$), 5.27 (s, 1H, $OCH_2O$), 6.53 (d, $^3J_{HH}$ = 8.2 Hz, 1H, Ph), 6.83 (d, $^3J_{HH}$ = 8.2 Hz, 1H, Ph), 6.99–7.01 (m, 1H, Ph), 7.10–7.13 (m, 2H, Ph). $^{13}C\{^1H\}$ NMR (100.6 MHz, $C_6D_6$, 24.0 °C): δ 17.18, 24.08, 24.22, 25.23 ($CH(CH_3)_2$), 28.24, 29.15 ($CH(CH_3)_2$), 101.33, 107.48, 124.03, 124.81, 125.23, 135.36, 138.08, 141.12, 143.15, 145.22 (Ar/Ph), 150.73 ($CH_3$), 151.11 ($OCH_2O$), 178.88 (*C*=NAr). UV–vis (THF): $\lambda_{max}$ (ε) 217 (7326), 254 (2297), 260 (1809), 348 nm (2409 $dm^3\ mol^{-1}\ cm^{-1}$). IR (Nujol, $cm^{-1}$): 2953s, 2922s, 2853s, 1549m, 1445m, 1435m, 1377w, 1362w, 1316m, 1256m, 1152w, 1128w, 1096w, 1043m, 935w, 887w, 802w, 777w.

**[$L^1$Ge–Ge$L^1$] (3A).** THF (20 mL) was added to a mixture of **2A** (1.12 g, 2.00 mmol) and $KC_8$ (0.28 g, 2.07 mmol) at room temperature. The resulting blue mixture was stirred for 1 day. The insoluble precipitate was then filtered off, and volatiles were removed under vacuum. The residue was extracted with hexane and then filtered. The blue filtrate was concentrated to afford **3A** as purple crystals. Yield: 0.56 g (53.4%). Mp: 250 °C. Elem anal. Calcd for $C_{64}H_{78}Ge_2N_4$: C, 73.25; H, 7.44; N, 5.34. Found: C, 73.11; H, 7.25; N, 5.21. $^1H$ NMR (399.5 MHz, THF-$d_8$, 25 °C): δ 0.87 (br d, 48H, $CH(CH_3)_2$), 2.74 (br s, 8H, $CH(CH_3)_2$), 6.93 (br s, 2H, Ph), 7.00–7.12 (m, 13H, Ph), 7.75–7.77 (br m, 3H, Ph), 8.03 (br s, 4H, CH=N). $^1H$ NMR (399.5 MHz, THF-$d_8$, −100 °C): δ 0.28–1.40 (m, 48H, $CH(CH_3)_2$), 2.04 (br s, 1H, $CH(CH_3)_2$), 2.14 (br s, 2H, $CH(CH_3)_2$), 2.56 (br s, 1H, $CH(CH_3)_2$), 2.78 (br s, 1H, $CH(CH_3)_2$), 3.05 (br s, 1H, $CH(CH_3)_2$), 3.20 (br s, 1H, $CH(CH_3)_2$), 3.74 (br s, 1H, $CH(CH_3)_2$), 6.52–7.37 (m, 15H, Ph), 7.51 (s, 1H, CH=N), 7.53 (s, 1H, CH=N), 8.03–8.14 (m, 2H, Ph), 8.39 (s, 1H, Ph), 8.61 (s, 1H, CH=N), 8.70 (s, 1H, CH=N). $^{13}C\{^1H\}$ NMR (100.5 MHz, $C_6D_6$, 25 °C): δ 24.78 (br s, $CH(CH_3)_2$), 28.47 ($CH(CH_3)_2$), 123.43, 124.55, 125.88, 138.48 (*Ph*Ge), 140.60 (br, N*Ar*), 146.96 (br, N*Ar*), 161.25 (br, N*Ar*), 179.19 (br, *C*=NAr). UV–vis (toluene): $\lambda_{max}$ (ε) 284 (12 453), 438 (1373), 586 (1693), 702 nm (6516 $dm^3\ mol^{-1}\ cm^{-1}$). IR (Nujol, $cm^{-1}$): 2955s, 2924s, 2853s, 1624m, 1587w, 1549w, 1489w, 1460m, 1381m, 1360w, 1337w, 1304m, 1260w, 1211w, 1175w, 1159w, 1090w, 1057w, 1020w, 995w, 924w, 887w, 880w, 799w, 758w, 716w.

**[$L^2$Ge–Ge$L^2$] (3B).** THF (14.2 mL) was added to a mixture of **2B** (0.91 g, 2.12 mmol) and $KC_8$ (0.32 g, 2.37 mmol) at ambient temperature. The resulting green reaction mixture was stirred overnight. The solvent was then removed in vacuo, and the residue was extracted with diethyl ether (50 mL). The insoluble precipitate was filtered off, and the green filtrate was concentrated to yield red crystals of **3B**. Yield: 0.59 g (70.5%). Mp: 243 °C. Elem anal. Calcd for $C_{42}H_{48}Ge_2N_2O_4$: C, 63.83; H, 6.13; N, 3.55. Found: C, 63.67; H, 5.92; N, 3.31. $^1H$ NMR (395.9 MHz, $C_6D_6$, 23.3 °C): δ 0.89 (br s, 6H, $CH(CH_3)_2$), 1.12 (br s, 6H, $CH(CH_3)_2$), 1.22 (br s, 6H, $CH(CH_3)_2$), 1.47 (br s, 6H, $CH(CH_3)_2$), 1.97 (s, 6H, $CH_3$), 2.60 (br s, 2H, $CH(CH_3)_2$), 3.41 (br s, 2H, $CH(CH_3)_2$), 5.17 (br s, 2H, $OCH_2O$), 5.28 (br s, 2H, $OCH_2O$), 6.67 (d, $^3J_{HH}$ = 8.2 Hz, 2H, Ph), 7.09 (br s,

Table 2. Crystallographic Data for Compounds 2–4

| | 2A | 2B | 3A |
|---|---|---|---|
| formula | $C_{32}H_{39}ClGeN_2$ | $C_{21}H_{24}ClGeNO_2$ | $C_{64}H_{78}Ge_2N_4$ |
| $M$ | 559.69 | 430.45 | 1048.48 |
| color | orange | yellow | purple |
| cryst syst | monoclinic | monoclinic | monoclinic |
| space group | $P2(1)/c$ | $P2(1)/c$ | $P2(1)/c$ |
| $a$/Å | 9.0808(2) | 14.9469(3) | 13.8962(6) |
| $b$/Å | 26.5379(5) | 15.6737(3) | 20.0041(9) |
| $c$/Å | 14.0952(2) | 18.6069(4) | 23.8699(10) |
| $\alpha$/deg | 90 | 90 | 90 |
| $\beta$/deg | 118.933(1) | 112.2490(10) | 120.555(3) |
| $\gamma$/deg | 90 | 90 | 90 |
| $V$/Å$^3$ | 2972.78(10) | 4034.55(14) | 5714.0(4) |
| $Z$ | 4 | 8 | 4 |
| $d_{calcd}$/g cm$^{-3}$ | 1.251 | 1.417 | 1.219 |
| $\mu$/mm$^{-1}$ | 1.142 | 1.665 | 1.094 |
| $F$(000) | 1176 | 1776 | 2216 |
| cryst size/mm | 0.20 × 0.20 × 0.06 | 0.12 × 0.10 × 0.04 | 0.16 × 0.08 × 0.06 |
| index range | $-12 \leq h \leq 12$ | $-20 \leq h \leq 20$ | $-17 \leq h \leq 17$ |
| | $-37 \leq k \leq 37$ | $-21 \leq k \leq 21$ | $-25 \leq k \leq 25$ |
| | $-20 \leq l \leq 20$ | $-25 \leq l \leq 26$ | $-29 \leq l \leq 29$ |
| no. of rflns collected | 73 916 | 57 560 | 79 103 |
| $R1$, $wR2$ [$I > 2\sigma(I)$] | 0.0572, 0.1605 | 0.0432, 0.1042 | 0.0440, 0.1032 |
| $R1$, $wR2$ (all data) | 0.0952, 0.1840 | 0.0836, 0.1305 | 0.0835, 0.1309 |
| GOF, $F^2$ | 1.087 | 1.078 | 1.031 |
| no. of data/restraints/param | 9068/380/474 | 11 670/0/479 | 11 671/38/668 |
| largest diff peak, hole/e Å$^{-3}$ | 1.651, −0.926 | 1.552, −0.800 | 0.499, −0.594 |

| | 3B | 4A | 4B |
|---|---|---|---|
| formula | $C_{42}H_{48}Ge_2N_2O_4$ | $C_{38}H_{55}GeKN_4$ | $C_{100}H_{134.45}Ge_4K_4N_4O_{12}$ |
| $M$ | 790.00 | 679.55 | 2031.33 |
| color | red | green | red |
| cryst syst | monoclinic | monoclinic | monoclinic |
| space group | $P2(1)/c$ | $P2(1)/c$ | $P2(1)/n$ |
| $a$/Å | 12.1121(4) | 12.0702(6) | 15.8408(6) |
| $b$/Å | 15.1482(6) | 19.1886(10) | 26.3835(8) |
| $c$/Å | 22.2158(9) | 16.1095(7) | 25.1989(9) |
| $\alpha$/deg | 90 | 90 | 90 |
| $\beta$/deg | 110.586(2) | 95.285(3) | 95.867(2) |
| $\gamma$/deg | 90 | 90 | 90 |
| $V$/Å$^3$ | 3815.8(3) | 3715.3(3) | 10476.4(6) |
| $Z$ | 4 | 4 | 4 |
| $d_{calcd}$/g cm$^{-3}$ | 1.375 | 1.215 | 1.288 |
| $\mu$/mm$^{-1}$ | 1.619 | 0.967 | 1.352 |
| $F$(000) | 1640 | 1448 | 4250 |
| cryst size/mm | 0.26 × 0.14 × 0.12 | 0.40 × 0.20 × 0.12 | 0.40 × 0.04 × 0.04 |
| index range | $-14 \leq h \leq 15$ | $-18 \leq h \leq 17$ | $-19 \leq h \leq 19$ |
| | $-18 \leq k \leq 18$ | $0 \leq k \leq 28$ | $-31 \leq k \leq 31$ |
| | $-27 \leq l \leq 27$ | $0 \leq l \leq 23$ | $-29 \leq l \leq 30$ |
| no. of rflns collected | 48 879 | 12 818 | 129 898 |
| $R1$, $wR2$ [$I > 2\sigma(I)$] | 0.0417, 0.1024 | 0.0749, 0.1558 | 0.0585, 0.1374 |
| $R1$, $wR2$ (all data) | 0.0751, 0.1283 | 0.1812, 0.1866 | 0.1615, 0.1975 |
| GOF, $F^2$ | 1.103 | 0.916 | 1.036 |
| no. of data/restraints/param | 7786/0/461 | 12 818/0/409 | 19 228/630/1333 |
| largest diff peak, hole/e Å$^{-3}$ | 0.507, −0.944 | 0.622, −0.798 | 0.758, −0.698 |

3H, Ph), 7.18–7.21 (m, 5H, Ph). $^{13}C\{^1H\}$ NMR (100.5 MHz, $C_6D_6$, 23.0 °C): $\delta$ 17.55, 23.90, 25.14, 25.48 ($CH(CH_3)_2$), 28.31 ($CH(CH_3)_2$), 100.26, 105.47, 123.75, 124.06, 134.09, 140.97, 142.96, 144.61 (Ar/Ph), 148.95 ($CH_3$), 160.00 ($OCH_2O$), 166.90 ($C{=}NAr$). UV–vis (THF): $\lambda_{max}$ ($\varepsilon$) 217 (14 210), 253 (6816), 259 (6681), 261 (6370), 295 (5136), 347 (4280), 475 (477), 506 (756), 659 nm (4357 dm$^3$ mol$^{-1}$ cm$^{-1}$). IR (Nujol, cm$^{-1}$): 2953s, 2922s, 2853s, 1607w, 1493w, 1456s, 1377s, 1337w, 1319w, 1304w, 1258m, 1192w, 1177w, 1142w, 1113m, 1094m, 1043m, 1018m, 986w, 935w, 874w, 849w, 800m, 777w, 737w, 721w, 704w, 642w.

**[L$^1$GeK·TMEDA] (4A).** *Method A.* $Et_2O$ (20 mL) was added to a mixture of **3A** (0.54 g, 0.52 mmol) and $KC_8$ (0.14 g, 1.03 mmol) at room temperature. The resulting green mixture was stirred for 1 day. The insoluble precipitate was then filtered off, and TMEDA (0.90 mL, 6.04 mmol) was added at 0 °C. The resulting green solution was stirred at room temperature for 3 h. The solution was filtered and concentrated to afford **4A** as green crystals. Yield: 0.53 g (75.7%).

*Method B.* $Et_2O$ (20 mL) was added to a mixture of **2A** (1.12 g, 2.00 mmol) and $KC_8$ (0.56 g, 4.15 mmol) at room temperature. The resulting green mixture was stirred for 1 day. The insoluble precipitate was then filtered off, and TMEDA (0.90 mL, 6.04 mmol) was added at 0 °C. The resulting green solution was stirred at room temperature for 3 h. The solution was filtered and concentrated to afford **4A** as green crystals. Yield: 0.76 g (55.9%).

*Mp:* 155 °C. Elem anal. Calcd for $C_{38}H_{55}GeKN_4$: C, 67.14; H, 8.16; N, 8.25. Found: C, 66.21; H, 7.13; N, 7.51. Attempts to obtain acceptable elemental analysis data for compound **4A** failed because of its extreme air sensitivity. $^1$H NMR (399.5 MHz, $C_6D_6$, 25 °C): $\delta$ 1.18 (d, $^3J_{H-H}$ = 6.87 Hz, 24H, $CH(CH_3)_2$), 1.87 (s, 12H, $NCH_3$), 2.00 (s, 4H, $NCH_2$), 3.23 (sept, $^3J_{H-H}$ = 6.87 Hz, 4H, $CH(CH_3)_2$), 6.85 (t, $^3J_{H-H}$ = 7.31 Hz, 1H, Ph), 7.09−7.18 (m, 6H, Ph), 7.36 (d, $^3J_{H-H}$ = 7.31 Hz, 2H, Ph), 8.15 (s, 2H, CH═N). $^{13}C\{^1H\}$ NMR (100.5 MHz, $C_6D_6$, 25 °C): $\delta$ 25.27 ($CH(CH_3)_2$) 28.05 ($CH(CH_3)_2$), 45.45 ($NCH_3$), 57.59 ($NCH_2$), 118.01, 123.30, 125.20, 128.88 (*Ph*Ge), 137.27, 141.87, 149.37, 149.96 (N*Ar*), 167.43 (*C*═NAr). UV−vis (THF): $\lambda_{max}$ ($\varepsilon$) 224 (6987), 236 (6218), 241 (6092), 246 (6059), 252 (5950), 258 (5875), 267 (6000), 278 (6107), 292 (6168), 395 (2170), 433 (2020), 703 nm (739 dm$^3$ mol$^{-1}$ cm$^{-1}$). IR (Nujol cm$^{-1}$): 2955s, 2922s, 2853s, 1601m, 1584w, 1547w, 1504w, 1462m, 1433m, 1414w, 1391w, 1377w, 1358w, 1335w, 1315m, 1290w, 1258w, 1190w, 1175w, 1155w, 1136w, 1098w, 1080w, 1034w, 1011w, 962w, 949w, 932w, 845w, 802w, 789w, 779w, 756w, 682w.

**[L$^2$GeK] (4B).** *Method A.* THF (20 mL) was added to a mixture of **3B** (0.59 g, 0.75 mmol) and excess $KC_8$ (0.27 g, 2.02 mmol) at ambient temperature. The resulting red reaction mixture was stirred for 2 days. The insoluble precipitate was filtered off. Volatiles of the filtrate were removed in vacuo. The residue was extracted with $Et_2O$ (30 mL). After filtration and concentration of the filtrate, **4B** was afforded as red crystals. Yield: 0.16 g (21.0%).

*Method B.* THF (31 mL) was added to a mixture of **2B** (1.30 g, 3.03 mmol) and excess $KC_8$ (1.43 g, 10.6 mmol) at ambient temperature. The resulting red reaction mixture was stirred overnight. The insoluble precipitate was filtered off. Volatiles of the filtrate were removed in vacuo. The residue was extracted with $Et_2O$ (50 mL). After filtration and concentration of the filtrate, **4B** was afforded as red crystals. Yield: 0.67 g (43.5%).

*Mp:* 380 °C. Elem anal. Calcd for $C_{21}H_{24}GeKNO_2$: C, 58.08; H, 5.57; N, 3.23. Found: C, 56.86; H, 4.13; N, 2.52. Attempts to obtain acceptable elemental analysis data for compound **4B** failed because of its extreme air sensitivity. $^1$H NMR (400.1 MHz, THF-$d_8$, 23.3 °C): $\delta$ 1.03 (d, $^3J_{HH}$ = 6.8 Hz, 6H, $CH(CH_3)_2$), 1.12 (d, $^3J_{HH}$ = 7.0 Hz, 6H, $CH(CH_3)_2$), 2.12 (s, 3H, $CH_3$), 2.65 (sept, $^3J_{HH}$ = 6.8 Hz, 2H, $CH(CH_3)_2$), 5.72 (s, 2H, $OCH_2O$), 6.31 (d, $^3J_{HH}$ = 8.7 Hz, 1H, Ph), 7.04−7.07 (m, 4H, Ph). $^{13}C\{^1H\}$ NMR (100.6 MHz, THF-$d_8$, 23.3 °C): $\delta$ 15.71, 23.83 ($CH(CH_3)_2$), 27.05, 27.86 ($CH(CH_3)_2$), 98.18, 104.07, 119.73, 122.50, 125.25, 128.24, 128.55, 130.18, 145.41 (Ph/Ar), 147.49 ($CH_3$), 148.06 ($OCH_2O$), 155.93 (*C*═NAr). UV−vis (THF): $\lambda_{max}$ ($\varepsilon$) 220 (2591), 252 (1945), 254 (1955), 261 (1800), 268 (1663), 297 (1227), 328 (1174), 505 (120), 662 nm (510 dm$^3$ mol$^{-1}$ cm$^{-1}$). IR (Nujol, cm$^{-1}$): 2940s, 2909s, 2855s, 1609w, 1460s, 1377m, 1339w, 1246w, 1196w, 1096w, 1026w, 926w, 777w, 721w.

**X-ray Data Collection and Structural Refinement.** Intensity data for compounds **2**−**4** were collected using a Bruker APEX II diffractometer. The crystals of **2**−**4** were measured at 103(2) K. The structures were solved by direct phase determination (*SHELXS-97*) and refined for all data by full-matrix least-squares methods on $F^2$.[19] All non-H atoms were subjected to anisotropic refinement. The H atoms were generated geometrically and allowed to ride in their respective parents atoms; they were assigned appropriate isotopic thermal parameters and included in the structure-factor calculations. Selected X-ray crystallography data of **2**−**4** are summarized in Table 2.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

CIF files giving X-ray data for **2**−**4** and the asymmetric unit of compound **4B**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) Compound **4B** can only be synthesized in THF. The volatiles of the reaction mixture were removed in vacuo. The $^1$H NMR spectrum of the crude product shows the presence of two THF molecules, which could coordinate to the K atom. Compound **4B** can only be crystallized in $Et_2O$. As a result, THF and $Et_2O$ molecules compete the coordination sphere of K atoms, which lead to the solvent disordering in the asymmetric unit.

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