

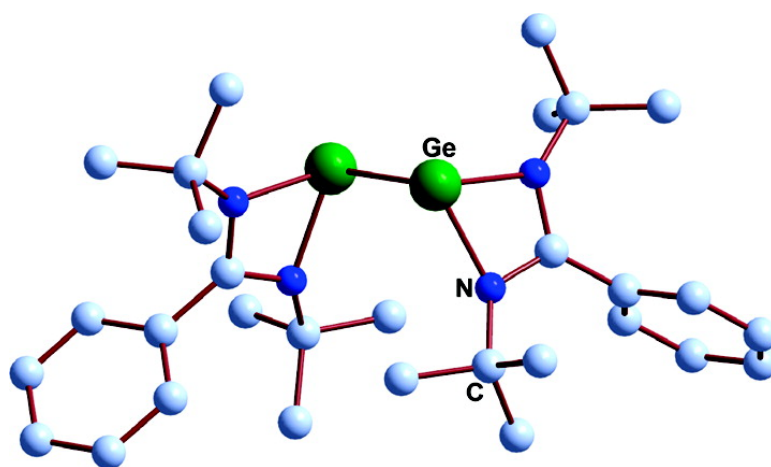
Article

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Selvarajan Nagendran, Sakya S. Sen, Herbert W. Roesky, Debasis Koley, Helmut Grubmu#ller, Aritra Pal, and Regine Herbst-Irmer

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RGe(I)Ge(I)R Compound (R = PhC(*Nt*Bu)₂) with a Ge–Ge Single Bond and a Comparison with the *Gauche* Conformation of Hydrazine[†]

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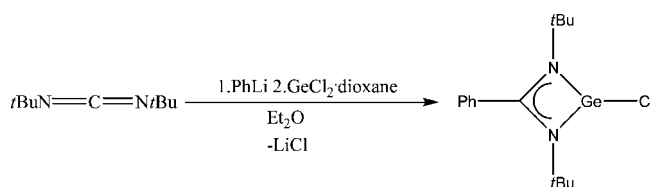
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This article reports the reduction of the chloride [PhC(*Nt*Bu)₂]GeCl with potassium in THF to afford the reddish crystals of [PhC(*Nt*Bu)₂]₂Ge₂ (**2**). The molecule of **2** contains a Ge–Ge bond. The X-ray structure and DFT calculation indicate that the Ge–Ge bond possesses an unusual *gauche*-bent geometry. The Ge–Ge bond length in **2** is 2.570 Å, which is very close to the single Ge–Ge interaction (2.61 Å) but significantly longer than that for typical digermenes, R₂GeGeR₂ (2.21–2.51 Å) and the two structurally characterized digermynes (2.2850 Å and 2.2060 Å), which proves that there is no multiple bond character in **2**.

Introduction

Alkynes (RC≡CR) are compounds with carbon–carbon triple bonds. They contribute largely to the richness and diversity of organic chemistry and portray the simplicity with which carbon forms multiple bonds. Synthesis of similar compounds (RE≡ER) with their heavier congeners (*E* = Si–Pb) was not possible until recently due to the poor overlap of the adjacent p orbitals. Nevertheless, by means of a tailor-made starting material, the first alkyne analogue of a heavier group 14 element, namely, an amber-green diplumbyne (vide infra) [RPbPbR; R = 2,6-Trip₂C₆H₃ (Trip = 2,4,6-*i*Pr₃C₆H₂)] was isolated by Power and co-workers¹ in 2000. Following this, the first carmine red-orange digermine [RGeGeR; R = 2,6-Trip₂C₆H₃ (Trip = 2,4,6-*i*Pr₃C₆H₂)]² and dark blue-green distannyne [RSnSnR; R = 2,6-Dipp₂C₆H₃ (Dipp = 2,4-*i*Pr₂C₆H₃)]³ were also reported by the same group in 2002. The series was complete in 2004 with the first isolation of an emerald-green disilyne [RSiSiR; R = Si(*i*Pr){CH(SiMe₃)₂}]₂ by Sekiguchi and co-workers.⁴ Quite strikingly, all of the heavier alkyne analogues (RE≡ER; *E* = Si–Pb) are *trans*-bent in contrast to the linear geometry of alkynes as indicated by Jurkschat and co-workers.⁵ Also, when the triple bond of HC≡CH has a bond order of 3, the bond order in the case of heavier alkyne analogues decreases as we go down the group from Si to Pb. The calculations show that the bond order has the following trend: disilyne ca. 2.6,

Scheme 1



digermine ca. 2, distannyne ca. 2 or 1 depending on the environment, and diplumbyne ca. 1.⁶ Thus, a diplumbyne should be considered as a diplumbylene with a Pb–Pb single bond and a lone pair of electrons on each Pb atom. Analogous to this is the recently reported amidinato and guanidinato germanium (I) dimer by Jones and co-workers in 2006.⁷ These compounds also possess Ge–Ge single bonds with a lone pair of electrons on germanium atoms and exhibit *trans*-bent geometry.

It is explicit from the aforementioned discussion that all of the known heavier group 14 analogues of alkyne and their valence isomers possess a *trans*-bent structure. In view of this, we became interested in assembling a valence isomer of a heavier alkyne with a structure that is different from that of the usual *trans*-bent geometry. Accordingly, we report here the first germanium(I) dimer **2** in a *gauche*-bent geometry stabilized by means of an amidinato ligand with simple *t*Bu substituents on the nitrogen atoms. The dimer **2** was obtained by reducing the amidinato germanium(II) chloride **1** with a slight excess of finely divided potassium metal.

Results and Discussion

The reaction of *tert*-butylcarbodiimide (*t*BuN=C=N*t*Bu) with one equivalent of PhLi in diethyl ether followed by treatment

[†] Dedicated to Professor Edgar Niecke on the occasion of his 70th birthday.

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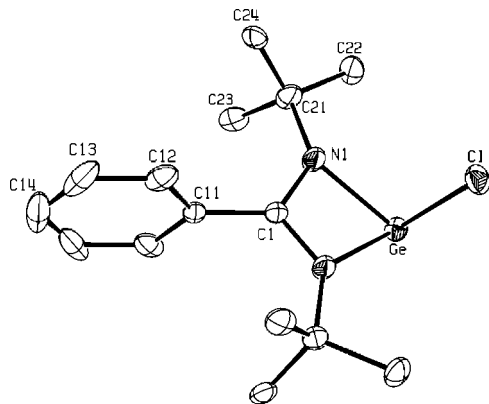


Figure 1. ORTEP view (30% ellipsoid probability) of compound **1**. Hydrogen atoms and disordered atoms have been removed for clarity. Selected bond distances (Å) and bond angles (deg): Ge(1)–Cl(1) 2.2572(13), Ge(1)–N(1) 2.060 ± 0.012(2), N(1)–C(1) 1.330(3), N(1)–C(21) 1.480(3), C(1)–C(11) 1.483(4), N(1)–Ge(1)–N(1) 63.22(11), N(1)–Ge(1)–Cl(1) 92.10(8), N(1)–C(1)–N(1) 108.6(3), N(1)–C(1)–C(11) 125.72(13).

with $\text{GeCl}_2 \cdot \text{dioxane}$ afforded $[\text{PhC}(\text{N}t\text{Bu})_2]\text{GeCl}$ (**1**; Scheme 1). Compound **1** was obtained as a colorless crystalline solid in 75% yield, and its structure was confirmed by NMR spectroscopic, EI mass spectrometric, and elemental analyses.

The ^1H NMR spectrum of compound **1** shows a singlet at 1.08 ppm for the 18 protons of two *t*Bu groups and another multiplet for 5 aromatic protons (7.48–7.56 ppm). The most abundant ion peak in the EI-mass spectrum appeared at m/z 338.5.

Maintaining a toluene solution of **1** overnight at $-32\text{ }^\circ\text{C}$ resulted in colorless single crystals suitable for X-ray structural analysis. Compound **1** crystallizes in the monoclinic space group $C2/c$ (Figure 1). The Ge(II) center exhibits distorted tetrahedral geometry as the sum of the bond angles is 248° , which is significantly smaller than 360° . The two sites of the Ge(II) center are occupied by the N atoms from the amidinato ligand, and the other site is occupied by a chlorine atom. The lone pair of the Ge(II) occupies the remaining coordination site. The structure is very similar to the structures of the recently reported amidinato and guanidinato germanium(II) chlorides.

Treatment of **1** with 1.5 equivalents of finely divided potassium in THF for 48 h afforded a deeply colored solution of germanium dimer $[\text{PhC}(\text{N}t\text{Bu})_2]_2\text{Ge}_2$ (**2**; Scheme 2). Recrystallization of the crude product in toluene gave reddish crystals of the germanium (I) dimer with 35% yield. Compound **2** was isolated as a reddish crystalline solid with good solubility in solvents such as diethyl ether, toluene, and THF. Moreover, it is stable in solution or in the solid state at room temperature in an inert atmosphere. It has been characterized by spectroscopic methods and X-ray crystallography.

The ^1H NMR spectrum of compound **2** shows a singlet at 1.16 ppm for the 36 protons of four *t*Bu groups and another

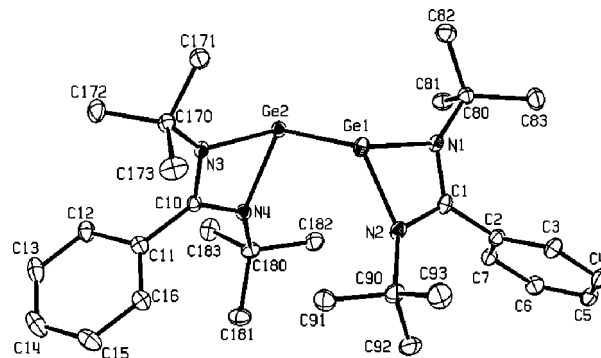


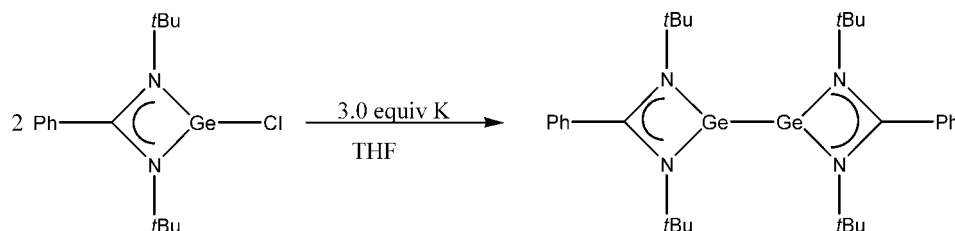
Figure 2. ORTEP view (30% ellipsoid probability) of compound **2**. Hydrogen atoms have been removed for clarity. Selected bond distances (Å) and bond angles (deg): Ge(1)–N(2) 2.005(2), Ge(1)–N(1) 2.026(2), Ge(2)–N(3) 2.020(2), Ge(2)–N(4) 2.014(2), Ge(1)–Ge(2) 2.569(5), C(1)–N(1) 1.326(4), C(1)–N(2) 1.337(4), C(10)–N(3) 1.333(3), C(10)–N(4) 1.338(3), N(1)–C(80) 1.482(4), N(2)–C(90) 1.479(4), N(3)–C(190) 1.481(4), N(4)–C(180) 1.475(4), N(2)–Ge(1)–N(1) 64.65(9), N(2)–Ge(1)–C(1) 32.54(9), N(1)–Ge(1)–C(1) 32.27(9), N(2)–Ge(1)–Ge(2) 103.55(7), N(1)–Ge(1)–Ge(2) 97.84(7), C(1)–Ge(1)–Ge(2) 105.09(6), N(4)–Ge(2)–N(3) 64.85(9), N(4)–Ge(2)–C(10) 32.58(9), N(3)–Ge(2)–C(10) 32.44(9), N(4)–Ge(2)–Ge(1) 104.62(7), N(3)–Ge(2)–Ge(1) 98.17(6), C(10)–Ge(2)–Ge(1) 105.96(6).

multiplet for 10 aromatic protons (7.34–7.39 ppm). Therefore, there is a very small shift in the ^1H NMR spectrum from the starting material. The most abundant ion peak in the EI-mass spectrum appeared at m/z 608.5.

The molecular structure of **2** is shown in Figure 2. Compound **2** crystallizes in the orthorhombic space group $Pbca$. The coordination environment of one of the Ge(I) atoms exhibits a distorted tetrahedral geometry (Figure 2). The coordination sites of the Ge(I) centers are each occupied by the N atoms of the amidinato ligand and by the other Ge(I) atom. The lone pair of the Ge(I) occupies the remaining coordination site of the tetrahedron. The Ge–Ge bond length in **2** is 2.570 Å, which is very close to the single Ge–Ge interaction (2.61 Å) but significantly longer than that for typical digermenes, R_2GeGeR_2 (2.21–2.51 Å⁸) and the two structurally characterized digermynes (2.2850 Å² and 2.2060 Å⁹), which proves that there is no multiple bond character in **2**.

In order to elucidate the nature of the Ge–Ge interaction, we performed DFT calculations on the isolated gauche species **2**. Calculations were performed at both B3LYP/6–31G** and BP86/6–31G** levels of theory. Structures and energies are reported in the B3LYP level unless otherwise mentioned. The DFT optimized geometry **3** shows a close resemblance with the geometry of **2** (Figures 2 and 3), though the Ge–Ge bond length is overestimated (2.702 Å in **3** vs 2.570 Å in **2**), and there are subtle differences in average Ge–N distances (2.091 Å in **3** vs 2.015 Å in **2**). Moreover, the C1–Ge1–Ge2'–C10'

Scheme 2



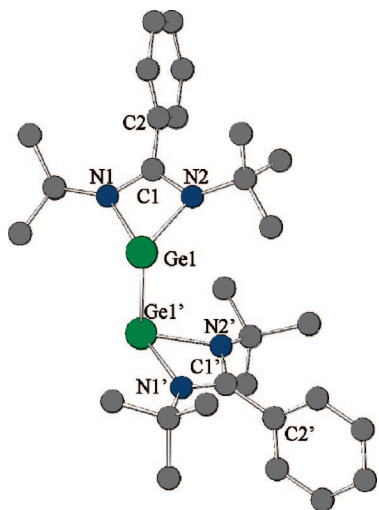


Figure 3. B3LYP/6-31G** optimized structure **3** (hydrogens are omitted for clarity) with selected bond lengths (in Å) and angles (in deg). Ge1–Ge1' 2.702, Ge1–N1 (Ge1'–N1') 2.094, Ge1–N2 (Ge1'–N2') 2.091, N1–C1 (N1'–C1') 1.335, N2–C1 (N2'–C1') 1.345, C2–Ge1–Ge1' 106.5, C2'–Ge1'–Ge1 106.5, C1–Ge1–Ge1'–C1' 113.0.

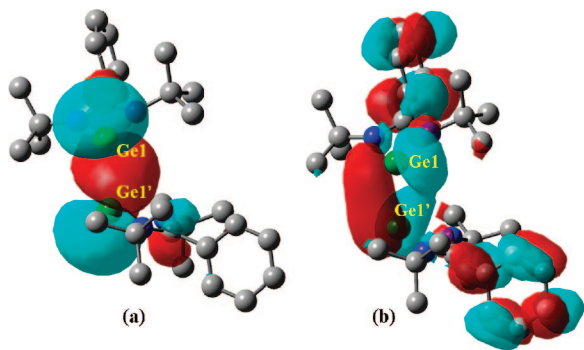


Figure 4. Frontier orbitals of **3** (isodensity value = 0.002 electron/bohr³). (a) KS-HOMO (−3.564 eV). (b) KS-LUMO (−0.598 eV).

dihedral angle has increased by 8.1° (113.0° in **3** vs 104.9° in **2**) during the course of the optimization.

In Figure 4, (a) shows the Kohn–Sham (KS) HOMO of the optimized structure of **3**, which is largely composed of σ -bonding interaction between the Ge p-orbitals, whereas in KS-LUMO (b), there is a strong Ge–Ge π_y bonding overlap with an additional Ge–N π^* interaction (Figure 4). Similar types of frontier orbitals are reported by Jones and co-workers in their theoretical investigations of *trans*-bent Ge(I) dimers. Weinhold's NBO analysis indicates a strong Ge–Ge bonding interaction in **3**, with high p-character (s-character 14.4%; p-character 85.3%) and a Wiberg bond index of 0.915. The Ge–N bonds are highly polarized (NPA charges, Ge; 0.524 *e* and N (mean); −0.713 *e*) with an average bond order of 0.431.

Unlike the previous studies, which investigated both the structural and electronic features of *trans*-bent group 14 elements, herein we report a similar theoretical characterization of a *gauche*-bent Ge(I) dimer **3**. We were curious to understand the relative stability of the optimized *gauche*-bent structure with respect to its *trans*-variant. To this end, we performed a relaxed potential energy scan of the C1–Ge1–Ge1'–C1' dihedral angle from **3**. Figure 5 shows the energy profile along with the concomitant change in dihedral angles and Ge1–Ge1' distances.

The drastic increase in the Ge1–Ge1' distance occurs with the increase of the dihedral angle from roughly 153° to 166°.

The end structure of the scan with *trans* oriented amidinate ligands (C1–Ge1–Ge1'–C1' 180°) was fully optimized. Interestingly, the unconstrained optimization furnished the *gauche*-bent structure **3**. In fact, all similar attempts to optimize the *trans* configured geometry failed. This prompted us to conclude the absence of any *trans*-variant of conformer **2**.

Though previous theoretical investigations have pointed out the stability of the planar-*trans* conformation for the Ge, Sn, and Pb species,¹⁰ they have also emphasized the effect of the bulky ligands in destabilizing the *gauche* conformer on steric grounds and experimentally utilizing this strategy to isolate the *trans*-bent conformer.

After the confirmation of the *gauche*-bent structure of the germanium dimer **2**, we were very interested to compare it with the *gauche* structure of hydrazine. The number of electrons around one Ge(I) center is the same as that of one nitrogen atom in hydrazine. A selection of the structural data for **2**, **3**, and hydrazine¹¹ are shown in Figure 6.

Each nitrogen atom in hydrazine shows a distorted tetrahedral geometry with no multiple bond character just like what Ge(I) exhibits in **2**. From the above results, we can argue that the bonding and the geometry of Ge(I) is very similar to the isoelectronic neutral neighboring group 15 element derivative.

In conclusion, we have prepared a germanium(I) dimer, which is stabilized by bulky amidinate ligands. Theoretical studies confirm that the dimer exhibits a *gauche*-bent geometry, and the Ge–Ge bond shows no multiple bond character. We are currently exploring the further chemistry of the Ge(I) dimer **2**.

Experimental Section

All manipulations were carried out in an inert atmosphere of dinitrogen using standard Schlenk techniques and in a dinitrogen filled glovebox. Solvents were dried and distilled prior to use. The NMR spectra were recorded in THF-*d*₈. The chemical shifts δ were relative to SiMe₄. EI mass spectra were obtained using a Finnigan MAT 8230 instrument. Elemental analyses were performed by the Institut für Anorganische Chemie, Universität Göttingen. Melting points were measured in a sealed glass tube on a Büchi B-450 melting point apparatus and were uncorrected.

Preparation of Compound 1. PhLi (6.86 mL, 13.72 mmol, 1.8 M in diethyl ether) was added to a solution of *t*BuN=C=N*t*Bu (2.12 g, 13.72 mmol) in diethyl ether (80 mL) at −78 °C. The solution was raised to ambient temperature and stirred for 4 h. The solution was added drop by drop to a stirred suspension of GeCl₂·dioxane (3.18 g, 13.72 mmol) in diethyl ether (20 mL) at −78 °C. The reaction mixture was warmed to room temperature and was stirred for 24 h. The precipitate was filtered, and after the removal of all volatiles, the residue was extracted with toluene (20 mL). Storage of the extract at −32 °C in a freezer for 1 day afforded colorless crystals of **1**. Mp: 145–150 °C. Elemental analysis (%) calculated for C₁₅H₂₃ClGeN₂ (339.45): C 53.18; H 6.77; N 8.27; found: C, 52.66; H, 6.63; N, 8.06. ¹H NMR (200 MHz, THF-*d*₈, 25 °C): δ = 1.08 ppm (s, 18H, *t*Bu), 7.41–7.48 ppm (m, 5H, Ph); ¹³C{¹H}NMR (500 MHz, THF-*d*₈, 25 °C): δ = 31.8 (CMe₃), 54.2

(8) As determined by the survey of the Cambridge Crystallographic Database.

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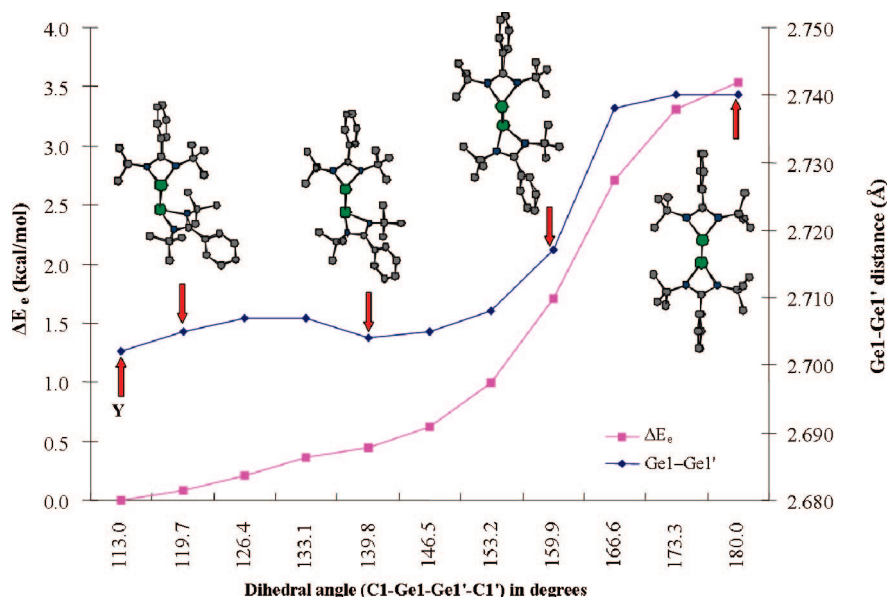


Figure 5. Potential energy scan for the isomerization of **3** with respect to the C1–Ge1–Ge1'–C1' dihedral angle changes at the B3LYP/6–31G** level of theory (refer to the text).

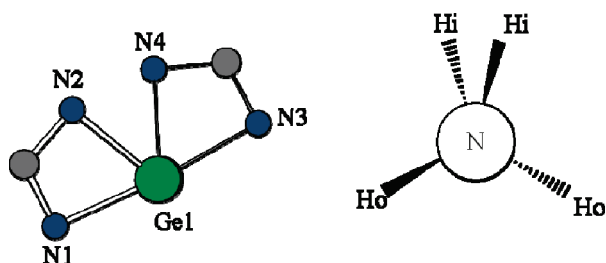


Figure 6. Structural features between isoelectronic hydrazine (gauche) and the *gauche*-Ge(I) skeleton of **2** and **3**. For complete labeling, please refer to Figure 3. Ge–Ge–N1 96.4 (97.8), Ge–Ge–N3 96.4 (98.2), Ge–Ge–N2 103.8 (103.6), Ge–Ge–N4 103.8 (104.6), N1–Ge1–N2 64.0 (64.6), and N4–Ge2–N3 63.0 (64.8). N–N–Ho 107.8 (106 ± 2), N–N–Hi 112.2 (112 ± 2), H–N–N–H (91 ± 2); Hi (inner angles) and Ho (outer angles). The values within parenthesis refer to experimental observables.

(CMe₃), 128.6, 128.9, 129.1, 129.9, 130.6, 135.6 (Ph), 173.3 ppm (NCN); EI-MS: *m/z*(%): 338.5[M⁺], (100).

Preparation of Compound 2. THF (50 mL) was added to a mixture of **1** (1.42 g, 4.18 mmol) and finely divided potassium (0.25 g, 6.25 mmol) at ambient temperature. The resulting red mixture was stirred for 2 days. The solvent was then removed *in vacuo*, and the residue was extracted with toluene (50 mL). The insoluble precipitate was filtered off, and the red filtrate was concentrated to yield crystals of **2** (0.89 g, 35%). Mp: 220–225 °C. Elemental analysis (%) calcd for C₃₀H₄₆Ge₂N₄ (607.99): C 59.26; H 7.63; N 9.22; found, C, 57.52; H, 7.47; N, 8.54. Due to the sensitivity of the crystals the analytical values show some deviation from the calcd one. ¹H NMR (200 MHz, THF-*d*₈, 25 °C): δ = 1.16 ppm (s, 36H, *t*Bu), 7.34–7.39 ppm (m, 10H, Ph); ¹³C{¹H}NMR (500 MHz, THF-*d*₈, 25 °C): δ = 31.9 (CMe₃), 32.1 (CMe₃), 53.5 (CMe₃), 55.0 (CMe₃), 123.0, 126.9, 127.8, 128.1, 128.3, 128.9, 129.1, 129.4, 129.9, 130.5, 131.5, 138.0 (Ph), 154.5 (NCN), 164.3 ppm (NCN); EI-MS: *m/z*(%): 608.5[M⁺] (100).

Crystal Structure Determination. The data of both structures were collected on a Bruker three-circle diffractometer equipped with a SMART 6000 CCD detector and a mirror-system-monochromated Cu Kα source. The data were integrated with SAINT, and an

empirical absorption correction with SADABS was applied.^{12,13} The structure was solved by the Patterson method (SHELXS-97)¹⁴ and refined against all data by the full-matrix least-squares methods on *F*² (SHELXL-97).¹⁵ All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically on calculated positions using a riding model with their *U*_{iso} values constrained to 1.5 *U*_{eq} of their pivot atoms for terminal sp³ carbon atoms and 1.2 times for all other carbon atoms.

Crystal Data for Compound 1. C₁₅H₂₃ClGeN₂, *M*_r = 339.39, monoclinic space group *C2/c*, *a* = 14.037(3) Å, *b* = 11.109(2) Å, *c* = 11.847(2) Å, β = 115.20(3)° *V* = 1671.6(5) Å³, *Z* = 4, ρ_{calcd} = 1.349 Mg m⁻³, *F*(000) = 704, *T* = 100(2) K, μ (Cu Kα) = 3.862 mm⁻¹.

Of the 8223 measured reflections, 1192 were independent (*R*_{int} = 0.0346). The final refinement converged to *R*₁ = 0.0290 for *I* > 2σ(*I*), *wR*₂ = 0.0675 for all data. The final difference Fourier synthesis gave a min/max residual electron density of −0.204/+0.214 e[−] Å^{−3}.

Crystal Data for Compound 2. C₃₀H₄₆Ge₂N₄, *M*_r = 607.89, orthorhombic space group *P*_{bca}, *a* = 20.379(3) Å, *b* = 14.120(2) Å, *c* = 21.943(3) Å, *V* = 6319.7(16) Å³.

Of the 56663 measured reflections, 4494 were independent (*R*_{int} = 0.0686). The final refinement converged to *R*₁ = 0.0299 for *I* > 2σ(*I*), *wR*₂ = 0.0743 for all data. The final difference Fourier synthesis gave a min/max residual electron density of −0.458/+0.415 e[−] Å^{−3}.

In structure **1**, the Ge and Cl atoms are disordered along the 2-fold axis. A similar disorder also appears in the recently reported germanium(II) halides. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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Computational Details. All calculations were performed with the Gaussian 03 program package.¹⁶ The geometry of complex **2** was optimized at the BP86¹⁷ and B3LYP¹⁸ level using a quasi-relativistic Stuttgart-Dresden ECP¹⁹ with a corresponding valence basis set (31/31/1) for Ge, (augmented by a d-type polarization function with an exponent of 0.246) and 6-31G* basis sets for C and N, and an extra polarization function was added to H.²⁰ Geometry optimizations were carried out without any symmetry restriction. Harmonic force constants were computed at the optimized geometries to characterize the stationary points as minima. Weinhold's NBO approach was used to calculate the NPA

charges, orbital populations and other bonding analyses.²¹ The constrained potential energy scan of the dihedral angle (C1–Ge1–Ge1'–C1') was performed at the B3LYP level. The molecular orbital plots were made using the GaussView program package.²²

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Supporting Information Available: Crystal data (CIF) for **1** and **2**, Cartesian coordinates of the optimized structure **3** in both levels of theory, and the full list of authors of ref 16. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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