

Unusual formation of a N-heterocyclic germylene *via* homolytic cleavage of a C–C bond†

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Reaction of the monoanionic radical salt $\text{IP}^{\bullet-}\text{K}^+$ ($\text{IP} = (\text{Py})\text{CH}(\text{=NR})$; $\text{Py} = \text{C}_5\text{H}_4\text{N}$, $\text{R} = 2,6\text{-iPr}_2\text{C}_6\text{H}_3$; α -iminopyridine) with GeCl_2 (dioxane) afforded compound $(\text{IPGeCl})_2$ (**1**) which produced red blocks of IPGe : (**2**), when treated with KC_8 in toluene. **1** is a digermylene formed *via* C–C coupling between two carbon-centered radicals. **2** can be considered as an analogue of a N-heterocyclic carbene, which exhibits a five-membered GeC_2N_2 ring with one C=C double bond. **2** is formed by two-electron reduction of **1** with cleavage of the two Ge–Cl bonds and the central C–C single bond.

The N-heterocyclic germylene (NHGe) with two-coordinate germanium is known as a congener of the corresponding carbene (NHC), which has been of great interest to chemists for decades.¹ The formation of the heterocycles increases the stability of the NHGe compounds (Fig. 1). The strategy for synthesizing germylenes **A–D** mainly involves metathesis reactions with the elimination of small molecules.² In these reactions the ring system functions as an ‘innocent’ ligand. However, molecules containing Ge and non-innocent ligands³ have been rarely reported.

α -Iminopyridine (IP, Scheme 1) as a non-innocent ligand has attracted much attention in radical chemistry. It easily can be converted to the corresponding monoanionic π -radical or to the dianions when treated with alkali or alkaline earth metals.⁴ Although the corresponding chemistry of transition metals and groups 1, 2, and 13 elements has been well documented,^{4b,5} related chemistry of group 14 elements is yet to be explored. Recently, compound $\text{IP}_2\text{Si}(\text{iv})$

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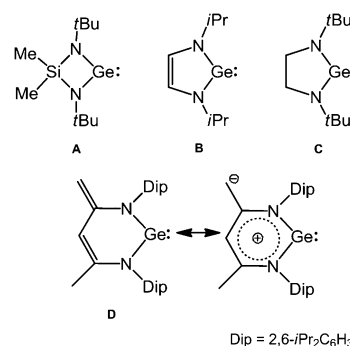
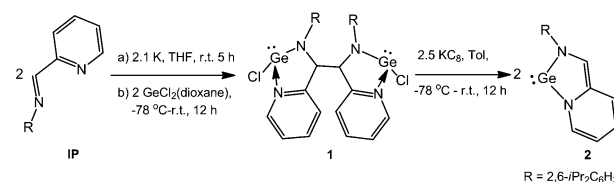


Fig. 1 Representatives of NHGe with a two-coordinate germanium.



Scheme 1 Syntheses of compounds $(\text{IPGeCl})_2$ (**1**) and IPGe : (**2**).

was prepared by the reaction of $\text{IP}^{\bullet-}_2\text{Mg}(\text{THF})$ with SiCl_4 in the presence of Mg metal.^{4b} The corresponding Ge compound has not been reported to date. Very recently, reports on autoionized group 14 compounds were published.^{6a,b} The latter reference describes $(\text{LMCl})^+(\text{MCl}_3)^-$ ($\text{L} = 2\text{-}[\text{C}(\text{Me}) = \text{N}(2,6\text{-iPr}_2\text{-C}_6\text{H}_3)]\text{-6}(\text{MeO})\text{C}_6\text{H}_3\text{N}$; $\text{M} = \text{Ge}(\text{II}), \text{Sn}(\text{II})$) by using a modified IP ligand, which shows spontaneous dissociation of MCl_2 ($\text{M} = \text{Ge}(\text{II})$ and $\text{Sn}(\text{II})$) towards the formation of the cationic GeCl^+ and SnCl^+ species, respectively.⁷ Herein, by employing the IP ligand, we present the synthesis of a NHGe compound *via* an unusual homolytic cleavage of a C–C bond by reduction of its germanium chloride precursor $(\text{IPGeCl})_2$ (**1**).

Compound **1** is isolated as yellow crystals in 60% yield by the reaction of GeCl_2 (dioxane) with $\text{IP}^{\bullet-}\text{K}^+$ in a 1:1 molar ratio (Scheme 1). $\text{IP}^{\bullet-}\text{K}^+$ is prepared *in situ* by treating IP with K metal in THF. The ^1H NMR spectrum of **1** clearly shows two septets

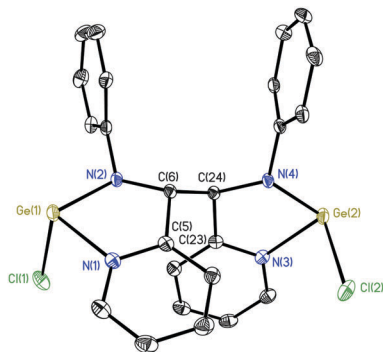


Fig. 2 Molecular structure of **1**. Anisotropic displacement parameters depicted at the 50% probability level. Hydrogen atoms and *i*Pr groups are omitted for clarity. Selected bond lengths [Å] and [°] (only the values for the left backbone are listed): Ge(1)–Cl(1) 2.3604(11), Ge(1)–N(1) 2.0405(14), Ge(1)–N(2) 1.8987(14), N(2)–C(6) 1.4607(19), C(6)–C(24) 1.580(2), C(5)–C(6) 1.512(2), N(1)–C(5) 1.348(2); N(1)–Ge(1)–N(2) 80.65(6), N(1)–Ge(1)–Cl(1) 90.43(5), C(6)–N(2)–Ge(1) 119.23(10), N(2)–C(6)–C(5) 107.45(12), C(5)–C(6)–C(24) 114.80(13), N(2)–C(6)–C(24) 114.43(12), N(1)–C(5)–C(6) 115.42(14).

(4.40 and 2.66 ppm) and four doublets (1.48, 1.10, 1.05 and 0.62 ppm) for four *i*Pr groups of the aryl rings, indicating their asymmetric configuration. The X-ray single crystal structure analysis demonstrated **1** to be a digermylene with a C–C single bond in the center (C(6)–C(24)) (Fig. 2). The distorted tetrahedrally coordinated C(6) and C(24) show all features of sp^3 hybridized carbon atoms. The C(5)–C(6) bond length (1.512(2) Å) indicates a single bond, while the pyridine rings retain the aromatic character. The C(6)–C(24) bond length (1.580(2) Å) is slightly longer than that of a standard $C(sp^3)$ – $C(sp^3)$ (1.54 Å) bond. **1** is possibly formed *via* C–C coupling of two radical intermediates $IP^{\bullet}GeCl$. Such dimerization of π -radicals is also observed in the Al, Ga, Zn, and lanthanide metal (Yb and Sm) derivatives containing redox-active ligands.^{5b,g,8} However, the synthesis of the silicon congener led to a mixture of products ($IPSiCl_3$)₂ (**3**) and $(IPH)(SiCl_3)$ (**4**) when $IP^{\bullet}K^+$ was treated with $SiCl_4$ (see ESI†).

It is worth mentioning that in 2004, Fedushkin *et al.* reported on $(dpp-BIAN^{\bullet})GeCl$ (*dpp-BIAN* = 1,2-bis{(2,6-diisopropylphenyl)-imino}acenaphthene),⁹ a radical germylene compound, which showed for the first time the stabilization of the germanium(II) monochloride with a radical-anionic non-innocent ligand. In 2008, our group reported on the reaction of $[PhC(NtBu)_2]Ge-Cl$ with potassium leading to the formation of the Ge(I)–Ge(I) compound $[PhC(NtBu)_2]_2Ge_2$, which may be generated due to the coupling of two $[PhC(NtBu)_2]Ge^{\bullet}$ intermediates.¹⁰ Such dimerization is prevented by increasing the conjugation and the size of the ring from four-membered CN_2Ge to six-membered C_3N_2Ge . A stable radical $\{[N(Dip)C(tBu)]_2CH\}Ge^{\bullet}$ (*Dip* = 2,6-*i*Pr₂C₆H₃) was prepared by reduction of $\{[N(Dip)C(tBu)]_2CH\}Ge-Cl$ with sodium naphthalenide or $\{[N(Mes)C(Me)_2]CH\}_2Mg_2$ (*Mes* = mesityl), as reported by Jones *et al.*¹¹ It is worth noting that the ligands employed in these compounds show good stabilization properties toward low-valent Ge atoms, involving the metal–ligand electron transfer process. The five-membered C_2N_2Ge ring of **1** is dearomatized due to a lack of conjugation at C(6)–C(24). It is intriguing to study the formation of the final product when **1** was reduced with KC_8 .

Surprisingly, the reaction of **1** with 2.5 equivalents of KC_8 in toluene at -78 °C resulted in a novel $NHGe$ species which was isolated as red blocks in 48% yield (Scheme 1). The utilization of toluene as a solvent is crucial and advantageous over THF and *n*-hexane since the reduction in the latter two solvents was not successful. The C(24) resonance of **2** (120.3 ppm) in the ¹³C NMR spectrum is remarkably downfield shifted when compared with that of **1** (76.1 ppm), which exhibits the sp^2 orbital hybridization of C(24). The UV-visible spectrum shows a strong absorption band at 425 nm which is comparable to those found for **D** (266, 360, and 460 nm).¹² **2** is highly soluble in organic solvents such as THF, toluene, and *n*-hexane as well as sensitive to oxygen and moisture. The one-pot reaction of the IP ligand, $GeCl_2$ (dioxane), and KC_8 in a molar ratio of 1 : 1 : 2 resulted in a brown oily mixture. We also tried the reaction of the dianionic salt $(IP)_2Na_4(Et_2O)_4$ (ref. 4a) with $GeCl_2$ (dioxane), but only **1** was obtained instead of the expected **2**.

The X-ray single crystal structure¹³ of **2** is shown in Fig. 3, which shows a five-membered GeC_2N_2 ring with a two-coordinate Ge atom. The Ge atom is perfectly located in the N(1)–C(23)–C(24)–N(2) plane to which the 2,6-substituted aryl ring is perpendicularly arranged. The Ge(1)–N(1) (1.907(2) Å) and Ge(1)–N(2) (1.860(2) Å) bond lengths are shorter than those of **1** (2.0405(14) Å and 1.8987(14) Å) while comparable to those of **D** (1.8658(17) Å and 1.8650(18) Å) (see ESI†). The N(2)–C(24) distance in **2** is 1.372(3) Å, which is much shorter than that in **1** (1.4607(19) Å). Moreover, the C(23)–C(24) distance (1.369(3) Å) in **2** is shorter by *ca.* 0.14 Å when compared with that in **1** (1.512(2) Å), but still longer than a common C–C double bond (1.34 Å). In addition, the pyridinyl ring in **1** is more uniform than that of **2**. All these changes show that the bond lengths of **2** are averaged, which indicates a conjugated system. The altering bond lengths of compounds **1**, **2**, and heterofulvene-like **D** are shown in Scheme S3 (see ESI†).

To obtain a better view of the bicyclic heteroatom containing unsaturated ring, theoretical calculations are carried out. The calculated current strength susceptibilities for selected bonds of compound **2** are reported together with the obtained current pathways as shown in Fig. S8 (see ESI†). Diatropic currents are assumed to circle clockwise, while paratropic ones circle anti-clockwise. For the five-membered Ge containing GeC_2N_2 ring, the current strength lies at 10.8 nA T^{-1} , which is only 1 nA T^{-1} weaker than the one obtained for

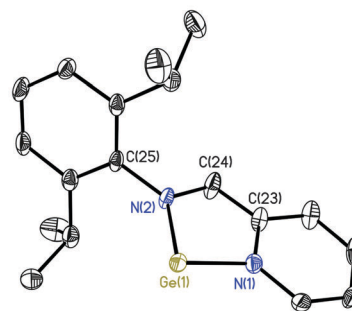
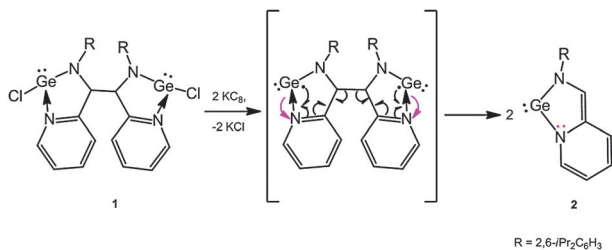


Fig. 3 Molecular structure of **2**. Anisotropic displacement parameters depicted at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and [°]: Ge(1)–N(1) 1.907(2), Ge(1)–N(2) 1.860(2), N(2)–C(25) 1.436(3), N(2)–C(24) 1.372(3), C(23)–C(24) 1.369(3), N(1)–C(23) 1.393(3); N(2)–Ge(1)–N(1) 82.93(9), C(24)–N(2)–Ge(1) 115.11(16), C(23)–C(24)–N(2) 115.2(2) and C(24)–C(23)–N(1) 112.8(2).



Scheme 2 Proposed mechanism for the formation of **2** (the pink arrows demonstrate the switch of the lone pair on the N_{pyridinyl} atom).

benzene (11.8 nA T^{-1}). The current strength (3.5 nA T^{-1}) for the six-membered pyridinyl ring however is weaker, but still indicates weak aromaticity. At the C–N bond fusing the two rings, the currents flow in opposite directions and thus partly cancel each other. Therefore the obtained current strength susceptibility lies at 6.8 nA T^{-1} . The currents circling around the phenyl ring, perpendicular to the molecular plane of the two connected rings, are not found to influence the current strength and pathways of the fused rings. Thus, according to the magnetic criterion, molecule **2** is considered to be aromatic. We also performed NICS(0) as well as NICS(1)zz calculations (see ESI[†]). While NICS(0) predicts the pyridinyl ring to be non-aromatic, NICS(1) and NICS(1)zz correctly predict it to be weakly aromatic. All calculated NICS values agree that the remaining molecular rings are aromatic. The calculated NICS values are in agreement with the current density calculations. Both methods show **2** to be aromatic according to the magnetic criterion.

The elongation of the central C–C bond of **1** implies a relatively weak covalent interaction between the two IP fragments. The bond dissociation energy of **1** to **2** was calculated to be $107.5 \text{ kJ mol}^{-1}$, which is much weaker than the binding energy of ethane ($382.8 \text{ kJ mol}^{-1}$) at the same level of theory. However, the investigation of the C(6)–C(24) bond cleavage of **1** is not trivial, due to the determination of the transition state being responsible for the bond breaking. Several DFT functionals have been tested (see details in the ESI[†]). The mechanism for the formation of **2** is still unclear. A two-electron transfer process of **1** may initially occur by the treatment with KC_8 . The two Ge–Cl bonds and the central C–C single bond are homolytically cleaved (Scheme 2). During this process, a series of single and double bond transformations are spontaneously triggered. Two equivalents of **2** are finally generated as a stable product in this reaction. IPSn , the analogue of **2** is hitherto unknown, while a coupled species $(\text{Py-CHNSiRR}')_2\text{Sn}$ ($\text{R}, \text{R}' = \text{iPr}, \text{tBu}, \text{or Me}$) is documented.^{8b} To the best of our knowledge, the synthesis of **2** is the first example of this type of heavier N-heterocyclic carbene analogue.¹

In summary, we have shown an unusual formation of a NHGe derived from its precursor $(\text{IPGeCl})_2$ (**1**). The implemented radical properties of IP in its Ge derivative cannot be retained, instead radical coupling and cleavage of bonds accompanied with electron transfer occurred. This finding provides a new view of the chemistry of carbene analogues.

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- Some unusual residual electron density can be observed around Ge on one of the molecules in the lattice, which may be due to the influence of some unknown impurity. However, supported by various methods of characterization including the high resolution ICP-MS spectrometry, the existence of compound **2** is definitely confirmed (see ESI[†]).