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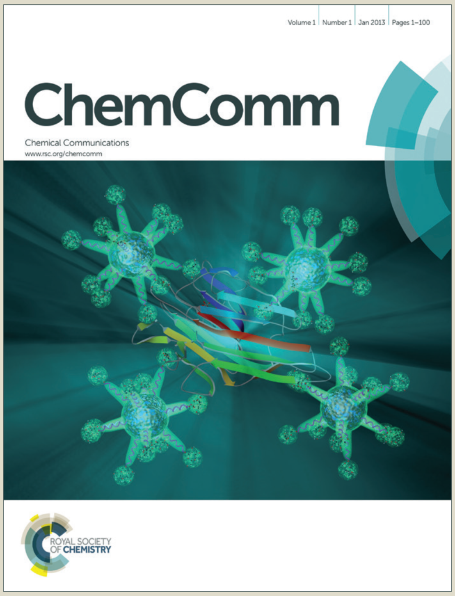

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Unusual Formation of a N-heterocyclic Germylene via Homolytic Cleavage of a C-C Bond

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Reaction of the monoanionic radical salt $IP^{\cdot-}K^+$ (IP = (Py)CH(=NR); Py= C_5H_4N, R = 2,6-$i$$Pr_2C_6H_3$; α-iminopyridine) with $GeCl_2$(dioxane) afforded compound $(IPGeCl)_2$ (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 altering single and double bonds. 2 is formed under 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** is mainly due to metathesis reactions under the elimination of small molecules.[2] In these reactions the ring system functions as an 'innocent' ligand. However, molecules containing Ge and non-innocent ligands[3] have been rarely reported.

α-Iminopyridine (IP, Scheme 1) as a non-innocent ligand has attracted much attention in radical chemistry. It can be easily activated 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 still premature. Recently, compound $IP_2Si(IV)$ was prepared by the reaction of $IP^{\cdot}_2Mg(THF)$ with $SiCl_4$ in the presence of Mg metal.[4b] The corresponding Ge compound is not reported till now. Very recently reports on autoionized Group 14 compounds were published.[6a,b] The latter reference describes $(LMCl)^+(MCl_3)^-$ (L = 2-[C(Me)=N(2,6-$i$$Pr_2$-$C_6H_3$)]-6-(MeO)$C_6H_3$N; M= Ge(II), Sn(II)) by using a modified IP ligand, which shows spontaneous dissociation of MCl_2 (M = Ge(II), Sn(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 under reduction of its germanium chloride precursor $(IPGeCl)_2$ (**1**).

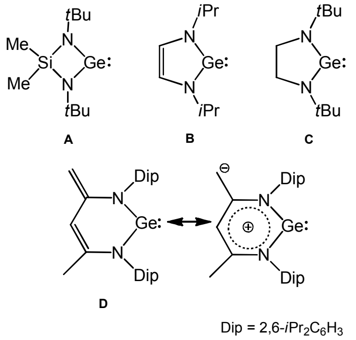
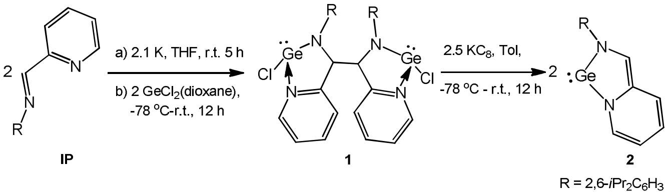


Fig. 1 Representatives of NHGe with two-coordinate germanium.



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

Compound **1** is isolated as yellow crystals in 60% yield by the reaction of $GeCl_2$(dioxane) with $IP^{\cdot-}K^+$ in a 1:1 molar ratio (Scheme 1). $IP^{\cdot-}K^+$ is prepared *in situ* by treating IP with K metal in THF. The ^1H NMR spectrum of **1** clearly shows two septets (4.40 and 2.66 ppm) as well as four doublets (1.48, 1.10, 1.05 and 0.62 ppm) for four iPr groups of the aryl rings, indicating its 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(6)-C(5) 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$^{\cdot}$GeCl. Such dimerization of π-radicals is also observed in the Al, Ga, Zn, and lanthanide metals (Yb, Sm) derivatives containing redox-active ligands.[5b,5g,8] However, the synthesis of its silicon congener led to a mixture of products (IPSiCl$_3$)$_2$ (**3**) and (IPH)(SiCl$_3$) (**4**) when IP$^{\cdot-}$K$^+$ was treated with SiCl$_4$ (See ESI†).

It is worth to mention that in 2004 Fedushkin *et al*. reported on (dpp-BIAN$^{\cdot}$)GeCl (dpp-BIAN= 1,2-bis{(2,6-diisopropylphenyl) imino}acenaphthene)[9] a radical germylene compound which shows 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(N*t*Bu)$_2$]Ge-Cl with potassium leading to the formation of the Ge(I)-Ge(I) compound [PhC(N*t*Bu)$_2$]$_2$Ge$_2$, which may be generated from the coupling of two [PhC(N*t*Bu)$_2$]Ge· intermediates.[10] Such dimerization is prevented by increasing the conjugation and size of the ring from four-membered CN$_2$Ge to six-membered C$_3$N$_2$Ge. Stable radical {[N(Dip)C(*t*Bu)]$_2$CH}Ge$^{\cdot}$ (Dip = 2,6-*i*Pr$_2$C$_6$H$_3$) was prepared by reduction of {[N(Dip)C(*t*Bu)]$_2$CH}Ge-Cl with sodium naphthalenide or {[N(Mes)C(Me)$_2$]CH}$_2$Mg$_2$ (Mes = mesityl) by Jones *et al.*[11] It is worth to note 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$_2$N$_2$Ge ring of **1** is dearomatized due to 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$_8$.

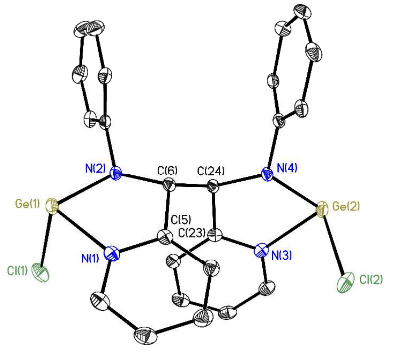


Fig. 2 Molecular structure of **1**. Anisotropic displacement parameters depicted at the 50 % probability level. Hydrogen atoms and *i*Pr groups are omitted for clarity. Selected bond lengths [Å] and [°] (only the values for left backbone are listed): Ge(1)-Cl(1) 2.3604(11), Ge(1)-N(1) 2.0405(14), Ge(1)-N(2) 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).

Surprisingly, the reaction of **1** with 2.5 equivalents of KC$_8$ in toluene at -78 ^{o}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 ^{13}C 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 and 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)$_2$Na$_4$(Et$_2$O)$_4$[4a] with GeCl$_2$(dioxane) but only **1** was obtained instead of expected **2**.

The X-ray single crystal structure[13] of **2** is shown in Fig. 3 which shows a five-membered GeC$_2$N$_2$ ring with a two-coordinate Ge atom. The Ge atom is perfectly located in the N1-C23-C24-N2 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 shortened 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†).

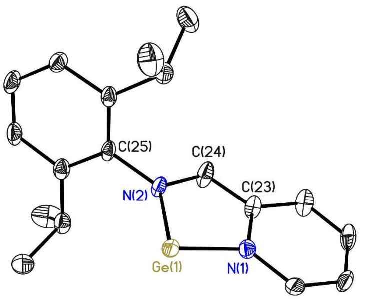
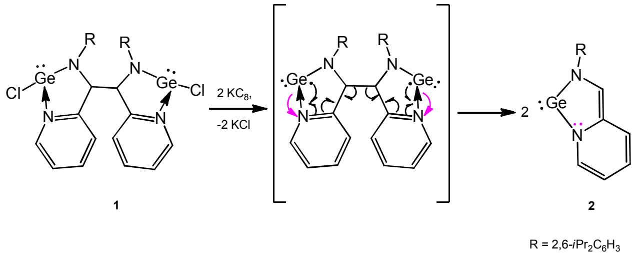


Fig. 3 Molecular structure of **2**. Anisotropic displacement parameters depicted at the 50 % probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and [°]: Ge(1)-N(1) 1.907(2), Ge(1)-N(2) 1.860(2), N(2)-C(25) 1.436(3), N(2)-C(24) 1.372(3), C(23)-C(24) 1.369(3), N(1)-C(23)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

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 for compound **2** are given together with the obtained current pathways in Figure S8 (see ESI†). Diatropic currents are assumed to circle clockwise, paratropic ones anti-clockwise. For the five-membered Ge containing C$_2$N$_2$Ge ring the current strength lies at 10.8 nA/T, which is only 1 nA/T weaker than the one obtained for benzene (11.8 nA/T). The current strength (3.5 nA/T) for the six-membered pyridinyl ring however is smaller, but still indicates a weak aromaticity. At the C-N bond fusing the two ring currents are flowing in opposite directions and thus partly counterbalance each other. Therefore the obtained current strength susceptibility lies at 6.8 nA/T. 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 nonaromatic, NICS(1) and NICS(1)zz correctly predict it to be weakly aromatic. All calculated NICS values agree that the remaining molecular rings are all 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 kJ/mol, which is much weaker than the binding energy of ethane (382.8 kJ/mol) 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 for the bond breaking. Several DFT functionals have been tested (see details in ESI†). The mechanism for the formation of **2** is still unclear. A two-electron transfer process of **1** may initially occur under the treatment with KC_8. The two Ge-Cl bonds and the central C-C single bond are homolytically cleaved, under releasing of two electrons (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 ($(Py\text{-}CHNSiRR')_2Sn$ (R, R' = *i*Pr, *t*Bu, 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]



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

In summary, we have shown an unusual formation of a NHGe derived from compound $(IPGeCl)_2$ (**1**) as a precursor. The implemented radical property 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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Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental section, details of crystal refinement and high resolution ICP-MS spectrometry, and computational details. CCDC 953613-953616 (**1**-**4**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c000000x/

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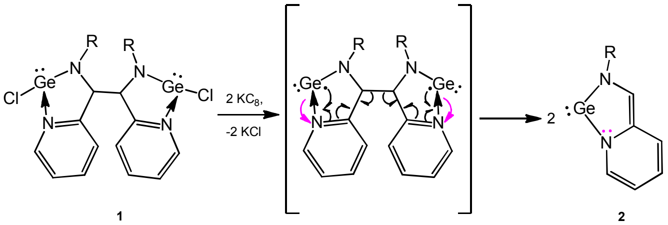
13 Some unusual residual electron density can be observed around Ge on one of the molecules in the lattice, which may be due to the influence of some unknown impurity. However, supported by various methods of characterization including the high resolution ICP-MS spectrometry, the existence of compound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

TOC



1

2

R = 2,6-$i\text{Pr}_2C_6H_3$

A N-heterocyclic germylene has been synthesized via an unusual homolytic cleavage of a C-C bond under reductive condition.