

# Diaminocarbene homologues: synthesis and crystal structure of the first diaminogermylene LiCl adduct displaying an electrophilic germanium centre

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2-Chloro-3-*tert*-butylaminoquinoxaline **1**, prepared from 2,3-dichloroquinoxaline and *tert*-butylamine under elevated temperatures and pressure, reacts with two equivalents of BuLi and a semimolar amount of GeCl<sub>2</sub>(dioxane) to form a novel cyclic diamino germylene–LiCl adduct **2** solvated in the crystals by dioxane and two molecules of toluene. The bonding of the chloride ion at germanium of the twofold quinoxaline annellated eight-membered N–Ge–N heterocycle, shown by X-ray crystal structure analysis of **2**, indicates electrophilic character and thus *umpolung* of the usually nucleophilic diaminogermylene structural unit by the electron withdrawing annellation and the ambidentate nature of carbenes. The coordination of each quinoxaline ring system by one of its nitrogen atoms to the lithium cation, fixed in a polymer Li<sup>+</sup>–dioxane backbone, amplifies the electron withdrawing effect.

## Introduction

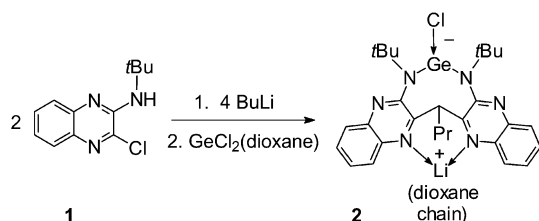
Monomer N-heterocyclic carbenes (NHCs) as well as their higher homologues have attracted recent attention due to fundamental questions concerning the reason for their unexpectedly high stability, their suitability as building blocks in syntheses and, because of their isolobal relation to phosphines and usually nucleophilic properties, as ligands in metal complexes and transition metal catalysed reactions.<sup>1–5</sup> In particular, NHCs have proven their versatility in catalytic reactions often outperforming the customary phosphines and phosphites which they have come to replace in a rapidly growing number of catalytic processes involving phosphorus containing ligands.<sup>5</sup> The striking exceptions are processes involving electron poor phosphines and phosphites. The reason seems obvious. The very concept of NHC stability pivots on the stabilisation of the carbene singlet ground state by donation of electron density from the electron lone pairs of the nitrogen atoms into the empty p-orbital of the carbene carbon. Thus the resulting NHCs are of necessity nucleophilic. Within this concept, the introduction of electron withdrawing substituents on the nitrogen atoms would destabilise the carbenes leading to dimerisation or decomposition. Here we present an example for the synthesis of an electrophilic N-heterocyclic germylene (NHGe) stabilised by LiCl which may serve as a model for conceivable electron deficient NHCs (or Lewis-base adducts thereof) useful to replace electron poor phosphines and phosphites in  $\pi$ -acceptor dependent transition metal catalysts. The change of the electronic properties in the model germylene as compared to usual NHGes is accomplished by appropriate annellation.

Our long standing interest in annellated  $\pi$ -stabilised heterocycles of low-coordinate main-group elements<sup>6</sup> has prompted us to study the influence of annellation on the properties of unsaturated N-heterocyclic silylenes, germynes, stannylenes and also related carbenes.<sup>7–9</sup> A comparison of the structures

and stabilities of benzo and pyrido[2,3] annellated as well as non-annellated five-membered cyclic diaminogermynes, all with neopentyl groups at nitrogen, gave evidence that the annellation destabilises the Ge(II)–N bond in the 1,3,2 $\lambda^2$ -diazagermole ring due to a competition between the organic  $\pi$ -electron system and the germanium for the electron density of the nitrogen lone pairs. In the crystals the differences between benzo and pyrido[2,3] annellation are small.<sup>8</sup> The much lower kinetic stability of pyrido as compared to benzo annellated derivatives was attributed to the  $\pi$ -density distribution in the frontier orbitals.<sup>7a</sup> In order to obtain further evidence for this suggestion and for the effect of electron withdrawal on the stability and reactivity of annellated NHC and their homologues without the unsymmetry factor we started investigations on the syntheses of electron-withdrawing quinoxaline annellated imidazolin-2-ylidenes and their homologues and report here first results on an unusual quinoxaline annellated 1,3,2-diazagermolin-2-ylidene–LiCl(dioxane) adduct.

## Results and discussion

Quinoxalinedione, readily accessible from *o*-phenylenediamine and oxalic acid, reacts with SOCl<sub>2</sub> to give 2,3-dichloroquinoxaline<sup>10</sup> which is converted by amines according to Hinsberg<sup>11</sup> or Haworth<sup>12</sup> to 2-chloro-3-aminoquinoxaline or 2,3-diaminoquinoxaline, respectively. When we utilised *tert*-butylamine for reasons of steric stabilisation of the target molecules, conversion stopped always at the 2-chloro-3-aminoquinoxaline stage. The resulting 2-chloro-3-*tert*-butylaminoquinoxaline **1** was found to react with less bulky amines to give unsymmetrically substituted diamines, and, what was much more interesting, it allows the synthesis of heterocycles by subsequent reaction at the amino group and substitution of chlorine. The reaction of **1** with two equivalents of *n*BuLi and the semimolar amount of GeCl<sub>2</sub>(dioxane) resulted in a novel eight membered, doubly



Scheme 1

quinoxaline anellated diaminogermylene that is both, a Lewis acid and a Lewis base, and is stabilised as the  $\text{LiCl(dioxane)}$  adduct **2** (Scheme 1). Formation of single crystals of **2**-toluene enabled the determination of its crystal structure.

The  $^1\text{H}$  NMR spectrum of the crystals shows the asymmetrically substituted quinoxaline rings and toluene signals in the aromatic region as well as the dioxane, aromatic methyl, *tert*-butyl, CH and *n*-propyl (not fully resolved) signals. The  $^{13}\text{C}$  NMR spectrum is in accord with the structure of **2**. The EI mass spectrum does not display a  $\text{M}^+$  peak, but shows a characteristic fragmentation pattern of the germylene cleaved from the  $\text{LiCl(dioxane)}$  backbone. Two peaks (457, 358) are distinguished by a high relative intensity of 44 and 45%, respectively, as fragments of high stability. These fragments can be assigned to units that contain a tropylium like  $\text{C}_4\text{NGeN}$  ring system in which stabilisation due to a delocalised  $\pi$ -electron system is possible (Fig. 1).

Unambiguous identification of **2** was accomplished by means of a single crystal structure determination (see Fig. 2). It crystallises in the triclinic crystal system in the space group  $P\bar{1}$  with one molecule in the asymmetric unit and two molecules in the unit cell. Two toluene molecules per unit cell stabilise the crystal. Selected bond lengths and angles are shown in comparison with those of some uncoordinated  $\text{NHGe}$ s in Table 1.

The germanium atom is incorporated in an eight membered ring and coordinated in a distorted trigonal pyramidal fashion by two nitrogen atoms of the quinoxaline fragments [N(5) and N(6)] and a chlorine atom located above the eight membered ring. Whereas the diaminogermylene bond angle [N(5)–Ge(1)–N(6) 105.6(1)°] is relatively close to the tetrahedral angle of 109.5° the N–Ge–Cl bond angles [N(5)–Ge(1)–Cl(1) 96.60(9) and N(6)–Ge(1)–Cl(1) 94.76(8)°] are significantly smaller. The Ge–N bond lengths of 201.6(3) and 203.1(3) pm are in the typical range for single bonds. They are significantly longer than in nucleophilic diaminogermynes (*ca.* 181–187 pm)<sup>3,8</sup> indicating the absence of  $\pi$ -bonds between Ge(1) and N(5) or N(6) as well as the locally anionic character of germanium. The neighbouring N–C bonds [N(5)–C(7) and N(6)–C(15) 137.1(4) pm] are short and comparable to those in the pyrido[2,3] anellated 1,3,2 $\lambda^2$ -diazagermole [137.6(4) pm].<sup>8</sup> The Cl–Ge bond length of 232.6(1) pm is somewhat longer than a Ge–Cl  $\sigma$ -bond in  $\text{GeCl}_2(\text{dioxane})$  [228.13(5) pm]<sup>13</sup> but shorter than the weak Ge–Cl bonds in intramolecular coordinated aminotroponimides [236.8(2) and 237.7(1) pm respectively] recently published by Dias<sup>14</sup> which are related with respect to the  $\text{N}_2\text{Cl}$  surrounding at germanium(II) and an electron-withdrawing (cationic) anellation but distinguished by mixed amido and amino coordination from the chlorodiamide **2**.

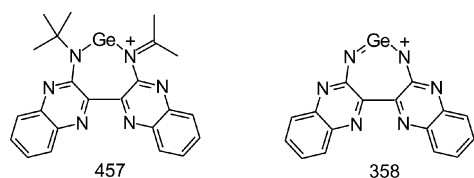


Fig. 1 Possible structures of high intensity cations formed in the EI-MS induced fragmentation of **2**.

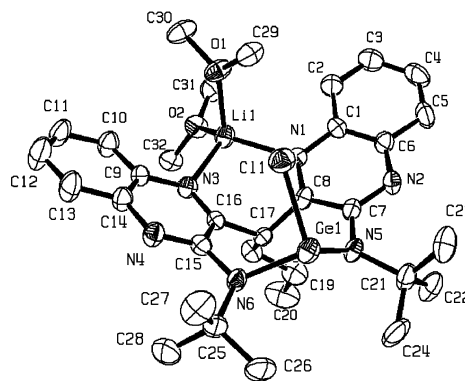


Fig. 2 Molecular structure of **2**-2 toluene (monomer unit with two half dioxane ligands). Hydrogen atoms and the cocrystallised toluene molecules have been omitted for clarity. Thermal ellipsoids are drawn at 50% probability.

The eight membered ring of **2** contains two planar  $\text{C}_2\text{N}$  groups of the quinoxaline rings [C(7), C(8), N(5) and C(15), C(16), N(6)] and a carbon atom [C(17)] of the former *n*-butyl group besides the germanium atom in a distorted chair conformation. The two quinoxaline units and the C(17) atom are arranged in a six membered ring that is completed by the lithium atom and displays half chair conformation. The dioxane molecules bridge the lithium atoms of neighbouring molecules and thus form a one dimensional chain in which neighbouring molecules show opposite orientation (Fig. 3). The coordination of the lithium atoms on the nitrogen atoms of the pyrazine rings results in a small but noticeable shortening of the already very short C–N bonds within the pyrazine rings [N(1)–C(8) 131.7(4), N(2)–C(7) 133.2(4), N(3)–C(16) 130.8(4) and N(4)–C(15) 132.8(4) pm]. This points to an amplification of the electron withdrawing character. The elongation of the C–C bridge bonds [C(7)–C(8) 145.1(5) and C(15)–C(16) 146.2(5) pm] typical for anellated  $\text{NHGe}$ s<sup>8</sup> is particularly pronounced and together with the short C–N distances refers to a diazadiene character of the N(1)–C(8)–C(7)–N(2) and N(3)–C(16)–C(15)–N(4) fragments, respectively.

Compounds of this type that constitute a new way to simultaneously coordinate both anions and cations onto element organic molecules and enable the conversion of nucleophilic into electrophilic diaminocarbenes or their heavier homologues by suitable anellation are not known to us from the literature. It was reported, however, that very strong donors like NHC can form adducts with  $\text{NHSi}$  and  $\text{NHGe}$ , in which the heavier homologue acts as the electrophile showing that the ambident character is not lost by weak  $\pi$ -interactions.<sup>15</sup> The electrophilicity is strongly increased for the heaviest homologues  $\text{NHSn}$  and  $\text{NHPb}$ , which not only form NHC adducts,<sup>15</sup> but, as shown for  $\text{NHSn}$ , also exist as dimers in the crystal and are solvated by TMEDA<sup>16</sup> or THF.<sup>7</sup> Carbene adducts are known furthermore in the case of acyclic diaryl-, dihalo- and bis(trimethylsilyl)amino-germylenes, stannylenes and plumbylenes<sup>17</sup> which due to the absence of electron-donating substituents or to the competition with electron-withdrawing N–Si interactions are in general more electrophilic. In the parent quinoxaline anellated  $\text{NHGe}$  of the adduct **2** the N–Ge  $\pi$ -stabilisation is negated by the electron withdrawing effect of the anellated rings. With respect to electron withdrawal by *N*-substituents there is some relationship to  $\text{Ge}[\text{N}(\text{SiMe}_3)_2]_2$ ,<sup>18</sup> and as compared to the usual nucleophilic behaviour of *N,N'*-diorgano-diaminogermynes there is an *umpolung* to electrophilic properties. Considering the ambidentate nature of carbenes, it may also be regarded as shift from the dominance of Lewis base to Lewis acid character.

To establish the potential and mechanism of this novel one-pot multi-step cyclisation reaction further investigations are

**Table 1** Selected bond lengths (pm) and angles (°) of **2**·2 toluene and some N-heterocyclic germylenes

NHGe: <sup>a</sup>	<b>2</b> ·2toluene	C <sub>6</sub> H <sub>4</sub> (Nnp) <sub>2</sub> Ge <sup>8</sup>	C <sub>5</sub> H <sub>3</sub> N(Nnp) <sub>2</sub> Ge <sup>8</sup>	C <sub>2</sub> H <sub>2</sub> (Nnp) <sub>2</sub> Ge <sup>8</sup>	C <sub>6</sub> H <sub>4</sub> (NSiMe <sub>3</sub> ) <sub>2</sub> Ge <sup>3c</sup>
N–Ge	201.6(3) 203.1(3)	186.1(3) 186.6(3)	186.0(3) 186.6(3)	180.8(1)	186.6(9) 186.1(8)
N–C <sub>ring</sub>	137.1(4)	139.3(5) 139.1(5)	137.6(4) 137.6(4)	143.7(3)	138.8(2) 138.4(2)
N–C <sub>chain</sub>	151.3(4)	145.9(5)	146.6(4)	145.4(2)	—
C=C	152.2(8) 145.1(5) 146.2(5)	145.5(5) 141.9(5)	146.8(4) 142.9(5)	138.6(7)	not given
C–C <sub>ring</sub>	150.7(5) 151.2(5)				
N–Ge–N	105.6(1)	84.9(1)	84.6(1)	87.75(6)	87.2(4)

<sup>a</sup> np neopentyl.

needed that exceed the scope of the present study. An orientating experiment of monolithiation of **1** and subsequent reaction with Ph<sub>2</sub>PCl gave evidence for preference of metalation on nitrogen and subsequent LiCl metathesis.<sup>19</sup> No interference by the chlorine atom in position 2 was observed. For the succeeding steps in the formation of **2** from **1** according to Scheme 1 two routes seem possible. The first comprises coupling of the primary 2-chloroquinoxalineamide with *n*BuLi followed by its  $\alpha$ -lithiation with a further equivalent of *n*BuLi and coupling with a second molecule of 2-chloroquinoxaline-1-amide to a diamide which undergoes the final cyclisation upon addition of GeCl<sub>2</sub>(dioxane). As such a diamide could not be identified, it should be mentioned that the coupling reactions could also occur after addition of GeCl<sub>2</sub>(dioxane) and formation of the Ge–N bonds. The higher polarity of N–Li as compared to C–Li bonds and the relatively low reactivity of Ge–N bonds towards RLi should allow the formation of Ge–N bonds in the presence of remaining *n*BuLi, and the coupling of two quinoxaline residues *via* germanium should further support the cyclisation to the eight-membered ring. If the N<sub>2</sub>Cl species is formed by attack of amide to an intermediate N–Ge–Cl species without chloride elimination or by coordination of chloride to a N–Ge–N substructure remains unresolved. However, this does not affect the importance of **2** as an isolable adduct of an electrophilic diaminogermylene to LiCl(dioxane). Several sterically protected acyclic diaminogermynes as well as non-aromatic four, five and six membered cyclic diaminogermynes, like **2** also synthesised from diamides and GeCl<sub>2</sub>(dioxane), are monomeric and are uncoordinated by Lewis bases due to electronic stabilisation by the electron lone pairs of the nitrogen atoms. The same holds true for 1,3,2 $\lambda^2$ -diazagermoles and the respective benzo and pyrido[2,3] anellated

Ge(II) heterocycles stabilised by cyclic delocalisation.<sup>3,8</sup> The crystal structure analysis of this pyrido anellated NHGe does not show any interaction between the basic pyridine nitrogen atoms and germanium, and during synthesis no evidence was obtained for the coordination of LiCl formed.<sup>8</sup> Thus, the incomplete elimination of LiCl and formation of **2** is due to changed electronic properties of the parent diaminogermylene. The Lewis acid properties of the germanium atom in **2** stabilising the germanium–chloride bond are attributed to the strongly electron withdrawing effect of the quinoxaline rings that extinguishes the usually nucleophilic character of diaminogermynes. The cationic lithium is coordinated by the strongly basic nitrogen atoms of the pyrazine rings [N(1) and N(3)] and thus increases the electron pull of the anellated heterocycles. Whether single quinoxaline anellation at the diazagermole ring is sufficient for loss of the usual nucleophilic properties on germanium (of diaminogermylene moieties) and salt addition remains to be determined by further experiments.

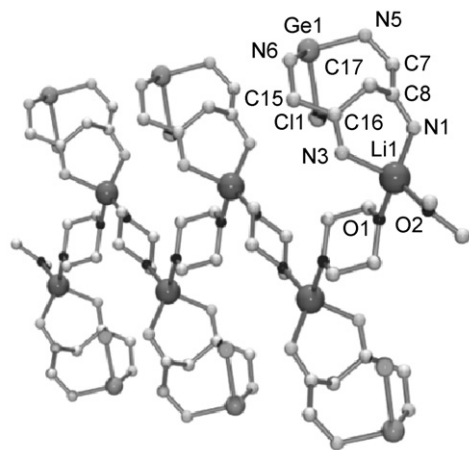
## Conclusion

By reaction of 2-chloro-3-*tert*-butylaminoquinoxaline **1** with two equivalents of *n*BuLi and the semimolar amount of GeCl<sub>2</sub>(dioxane) a new type of N-heterocyclic germylene is accessible which is stabilised by addition of LiCl(dioxane). The parent diaminogermylene in the adduct **2** does not stabilise the germanium(II) centre in the known way by  $\pi$ -bond interaction to the neighbouring electron lone pairs of nitrogen, but acts as a Lewis acid towards the chloride ion of LiCl. This behaviour is presumably a consequence of the strong electron withdrawal by the anellated quinoxaline rings and delocalisation of the electron lone pairs on nitrogen into their unsaturated electron systems inducing an *umpolung* of the usual nucleophilic to electrophilic properties of diaminogermynes. Thus, **2** is the first example of an electrophilic NHGe stabilised by a Lewis base. It can serve as a model compound for the synthesis of their NHC analogues. Change of the electronic properties induced by suitable anellation is conceivable. This first example of an electrophilic N-heterocyclic germylene might well start off a search for electron deficient NHCs as replacement for their phosphorus counterparts in catalysis.

## Experimental

### General

All experiments were carried out under purified dry argon using standard Schlenk techniques. Solvents were dried with sodium and freshly distilled under argon. NMR spectra were measured with ARX 300 (Bruker), standard was trace amounts of protonated solvent. The mass spectra were recorded with a single focussing sector field mass spectrometer

**Fig. 3** Schematic packing of **2**·2toluene (anellation and *tert*-butyl groups omitted).

AMD40 (Intectra). Elemental analyses were carried out with an elemental analyser LECO Model CHNS-932 with standard combustion conditions and handling of the samples in air. Melting points were determined in sealed capillaries under argon and are uncorrected. 2,3-Dichloroquinoxaline and GeCl<sub>2</sub>(dioxane) were prepared according to the literature. Other materials were used as purchased unless stated otherwise.

### Preparation of 2-chloro-3-*tert*-butylaminoquinoxaline (1)

An 75 mL autoclave was charged with 2,3-dichloroquinoxaline (7.57 g, 38 mmol) and *t*BuNH<sub>2</sub> (30 mL, 286 mmol). The apparatus was heated to 120 °C for 2 h. After opening a soft yellow solid was transferred to a beaker and suspended in hexane. A white solid (*t*BuNH<sub>2</sub>·HCl) was filtered off and washed with hexane. The solution was concentrated and 8.2 g (92%) of off-white precipitate collected, mp 107 °C. Anal. for C<sub>12</sub>H<sub>14</sub>ClN<sub>3</sub> (235.72). Calcd. (found): C, 60.87 (61.26); H, 6.16 (6.00); N, 17.34 (17.86). <sup>1</sup>H NMR (300.1 MHz, CDCl<sub>3</sub>, 298 K): δ 7.52 (dd, <sup>3</sup>J = 8.2, <sup>4</sup>J = 1.5 Hz, 1 H, H<sub>a</sub>), 7.41 (dd, <sup>3</sup>J = 8.3, <sup>4</sup>J = 1.3 Hz, 1 H, H<sub>b</sub>), 4.99 (s, 1 H, NH), 1.04 (s, 9 H, CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (75.5 MHz): 148.3, 142.2, 139.1, 137.4, 130.7, 129.0, 127.2, 125.7, 52.9 (CMe<sub>3</sub>), 29.0 (CH<sub>3</sub>). EI-MS (70 eV): *m/z* (%) = 235 (99) [M<sup>+</sup>(<sup>35</sup>Cl)], 220 (99), 181 (100) [M<sup>+</sup> – C<sub>4</sub>H<sub>7</sub>], 144 (99) [M<sup>+</sup> – Bu<sup>t</sup> – Cl] and fragments thereof.

### Preparation of 2-toluene (2)

Compound **1** (3.02 g, 11.10 mmol) was stirred in 40 mL of toluene, and 15.9 mL of 1.4 M BuLi solution was added dropwise at ambient temperature. After stirring for 3 h, 1.29 g (5.50 mmol) of GeCl<sub>2</sub>(dioxane) was added. The resulting mixture was stirred for 12 h, LiCl was filtered off, and the filtrate was concentrated to 5 mL. Orange crystals of **2**-toluene, formed overnight, were separated for X-ray crystal structure analysis. 30 mL of hexane was added to the mother liquor, and the precipitate was filtered off, overall yield 3.43 g (73%). Anal. for C<sub>46</sub>H<sub>58</sub>ClGeLiN<sub>6</sub>O<sub>2</sub> (841.99). Calcd. (found): C, 65.56 (incomplete combustion); H, 6.95 (6.94); N, 10.21 (9.98). <sup>1</sup>H NMR (300.1 MHz, CDCl<sub>3</sub>, 298 K): δ 7.99 (dd, <sup>3</sup>J = 8.1, <sup>4</sup>J = 1.4 Hz, 2 H, Ar), 7.79 (dd, <sup>3</sup>J = 8.3, <sup>4</sup>J = 1.1 Hz, 2 H, Ar), 7.31 (m, <sup>3</sup>J = 7.0, 8.4, <sup>4</sup>J = 1.5 Hz, 2 H, Ar), 7.18 (m, <sup>3</sup>J = 7.0, 8.2, <sup>4</sup>J = 1.4 Hz, 2 H, Ar), 7.00–7.14 (s, m, toluene), 3.35 (s, 8 H, dioxane), 2.47 (m, 1 H, CH), 1.46 (s, 18 H, CMe<sub>3</sub>), 1.13 (m, 2 H, CH<sub>2</sub>), 0.88 (m, 2 H, CH<sub>2</sub>), 0.80 (t, 3 H, <sup>3</sup>J = 7.3 Hz, CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (75.5 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C; alkyl range: [D8]Toluol, 135-DEPT, –40 °C): 151.9, 146.2, 142.9, 136.7, 130.5, 130.0, 127.7, 125.1 (quinoxaline); 66.9 (dioxane), 52.8 (CH), 52.2 (CMe<sub>3</sub>), 52.0 (CMe<sub>3</sub>), 51.6 (CH), 32.9 (CH<sub>2</sub>), 30.4 (CH<sub>2</sub>), 28.6 (CMe<sub>3</sub>), 28.5 (CMe<sub>3</sub>), 22.9 (CH<sub>2</sub>), 21.5 (CH<sub>2</sub>), 21.4 (C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>), 14.0 and 14.4 (CH<sub>3</sub>). EI-MS (70 eV): *m/z* (%) = 513 (1) [M<sup>+</sup> – LiCl – Me], 498 (0.5) [M<sup>+</sup> – LiCl – 2Me], 471 (1) [M<sup>+</sup> – LiCl – Bu], 457 (44) [M<sup>+</sup> – LiCl – Bu – Me], 442 (22) [M<sup>+</sup> – LiCl – Bu – 2Me], 427 (3) [M<sup>+</sup> – LiCl – Bu – 3Me], 414 (18) [M<sup>+</sup> – LiCl – 2Bu], 399 (24) [M<sup>+</sup> – LiCl – 2Bu – Me], 386 (30) [M<sup>+</sup> – LiCl – 2Bu – 2Me], 358 (45) [(C<sub>8</sub>H<sub>4</sub>N<sub>3</sub>)<sub>2</sub>Ge<sup>+</sup>] and fragments thereof.

### Crystal data and structure determination for 2-toluene

C<sub>46</sub>H<sub>58</sub>ClGeLiN<sub>6</sub>O<sub>2</sub>, *M<sub>r</sub>* = 841.96, triclinic, space group *P* $\bar{1}$  (no. 2), *a* = 1060.0(1), *b* = 1339.7(1), *c* = 1743.5(2) pm,  $\alpha$  = 71.240(2),  $\beta$  = 72.668(2),  $\gamma$  = 89.640(2)°, *V* = 2.2269(4) mm<sup>3</sup>, *Z* = 2,  $\mu$  = 0.791 mm<sup>–1</sup>,  $\rho_{\text{calcd}}$  = 1.256 Mg mm<sup>–3</sup>,  $\lambda$  = 71.073 pm. A set of data for a crystal with the dimensions 0.20 × 0.10 × 0.05 mm<sup>3</sup> was measured at 218(2) K on a Siemens CCD (SMART) diffractometer. 13 411 (8959 independent) reflections were collected for 1.30 <  $\theta$  < 26.37°. *R*<sub>1</sub> = 0.0530 (for 8959 reflections with *I* > 2 $\sigma$ (*I*)).

*wR*<sub>2</sub> = 0.1123 (all data). Absorption correction was performed using SADABS.<sup>20</sup> The positions of all atoms except hydrogen were determined with direct methods (SHELXTL PLUS)<sup>21</sup> and refined. Idealised positions for the hydrogen atoms were calculated.

CCDC reference number 166031. See <http://www.rsc.org/suppdata/nj/b2/b205902a/> for crystallographic data in CIF or other electronic format.

### Acknowledgements

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