



Note

Synthesis and characterization of three new thermally stable N-heterocyclic germylenes

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ARTICLE INFO

Article history:

Received 5 December 2008

Received in revised form 17 December 2008

Accepted 18 December 2008

Available online 25 December 2008

Keywords:

Germylene

Germanium

Organogermanium

ABSTRACT

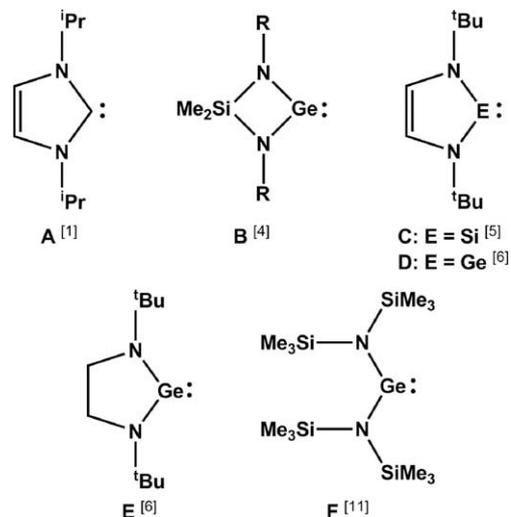
Three new stable germylenes, *rac*-1,3-di-*tert*-butyl-4,5-dimethyl-1,3-diaza-2-germacyclopentane-2-ylide (**1**), 1,3-di-*tert*-butyl-4,4-dimethyl-1,3-diaza-2-germacyclopentane-2-ylide (**2**), and *rac*-1,3,4-tri-*tert*-butyl-1,3-diaza-2-germacyclopentane-2-ylide (**3**) have been synthesized by the reaction of their corresponding germyl dichlorides with elemental lithium. Full synthetic procedures and characterizations are described.

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1. Introduction

The stabilization and isolation of compounds featuring *p*-block elements in unusual or low oxidation states has been a common theme in contemporary main group chemistry. Since their initial disclosure in 1991 [1], the divalent dicoordinate Arduengo-type N-heterocyclic carbenes (NHCs) **A** have dominated this field, primarily on account of their utility as robust ligands for organometallic coordination complexes [2] and, more recently, as organocatalysts [3]. However, the isolation of the first NHGe system by Veith (**B**) actually predates that of the NHC by almost a decade, [4] and Si- and Ge-analogues of Arduengo NHCs (**C–E**) were first described in 1994 and 1992, respectively [5,6]. Since these initial reports, the chemistry of thermally stable N-heterocyclic silylenes and germylenes (NHSi and NHGe respectively) of type **A** has developed apace [7–10].

Most of the five-membered NHGe species reported in the literature are based upon the 1,4-diazabuta-1,3-diene (DAB) framework, and are prepared by salt metathesis reactions of the stable and commercially available Ge(II) source [GeCl₂(dioxane)] with a dimetallated DAB [6]. Germylenes prepared by this procedure typically display increased thermal stability as compared to their saturated analogues. Experimental and theoretical studies suggest that this is due to σ -electron withdrawal/-electron donation by the two nitrogen atoms bound to the germanium atom in combination with electron delocalization in the heterocyclic 6-electron system of the supporting DAB framework [12]. While bulky alkyl groups (such as *tert*-butyl and *neo*-pentyl) have been commonly



employed as substituents at the nitrogen atoms, a number of unsaturated NHGe systems bearing bulky aromatic N-groups have been reported recently [13–16].

Saturated NHGes such as **E** lack stabilization by aromatic electron delocalization but may be stabilized by σ -donation from the nitrogen atom into the vacant *p*-orbital on germanium as well as π -withdrawal of electron density from the germanium to the nitrogen atoms [12]. Synthetic routes to saturated NHGes involve either the transamination of a diamine ligand with the acyclic Ge(II) compound [(Me₃Si)₂N]₂Ge (**F**) [11], or salt metathesis of [GeCl₂ · (diox-

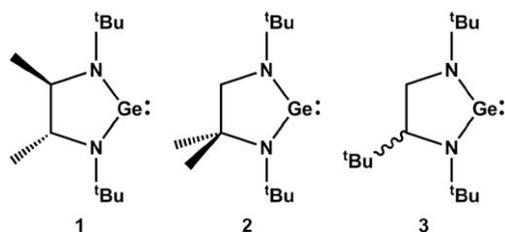
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ane)] with a dilithiated diamine. Hahn et al. recently employed such procedures to prepare the first examples of bidentate chelating benzannulated bis(germylenes) [17,18].

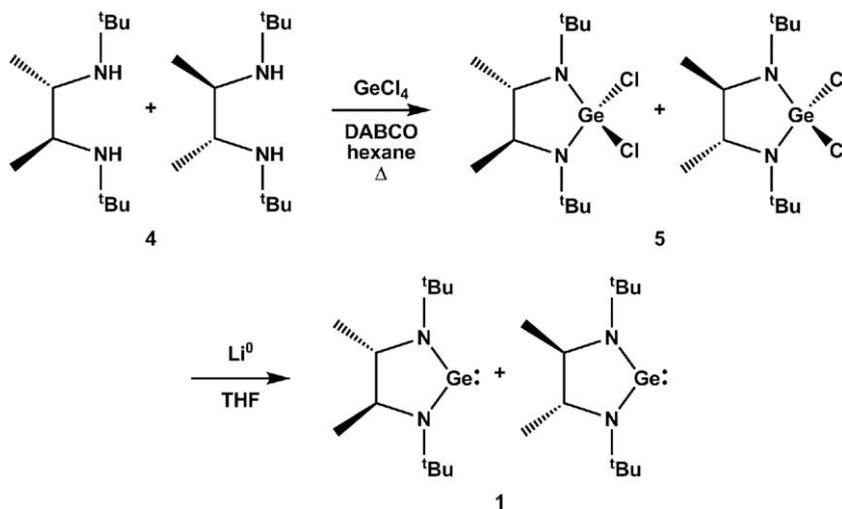
2. Results and discussion

Herein we report the synthesis and characterization of rare examples of saturated N-heterocyclic germylenes derived from simple diamines: compound **1** (as a racemic mixture), the germanium analogue of the previously reported racemic N-heterocyclic silylene $\text{Me}_2[\text{NN}]\text{Si}$, [19] and compounds **2** and **3**, the latter also a racemic mixture. The structures of **1**, **2**, and **3** are similar to that of **E** but with substitution of alkyl groups at the backbone carbon atoms. Germylenes **1**, **2**, and **3** are monomeric and isolated as pale yellow liquids. All compounds were characterized by ^1H , and $^{13}\text{C}\{^1\text{H}\}$ NMR, high-resolution mass spectrometry, and elemental analysis.



The new germylenes **1**, **2**, and **3**. The S,S isomer of **1** is not shown.

The racemic germylene **1** was prepared by the reduction of the dichlorogermene compound **5** with lithium metal in THF at room temperature as shown in Scheme 1. First *N,N'*-di-*tert*-butylethylenediamine, obtained by the reaction of glyoxal with *tert*-butylamine, was treated with methyllithium to produce a racemic mixture of the diamine compound **4** in 94% yield [20]. No meso diamine compound was observed in this reaction, as the second nucleophilic addition of CH_3^- to a $\text{C}=\text{N}$ double bond is evidently highly stereoselective. The diamine **4** was then converted to the corresponding dichlorogermene **5** after reaction with germanium tetrachloride in the presence of 1,8-diazabicyclo [2.2.2] octane (DABCO). When **5** was reduced with metallic lithium in THF at room temperature the racemic germylene **1** was produced in 71% yield. Germylene **1** was purified by short-path Kugelrohr distillation at 80°C (0.1 Torr).



Scheme 1. The synthesis of germylene **1**. Compounds **4**, **5**, and **1** are shown as pairs of enantiomers.

Germylene **2** is substituted with two methyl groups on the same backbone carbon. Compound **2** was prepared by reducing its corresponding dichlorogermene **10** with elemental lithium as shown in Scheme 2. First, α -bromoisobutyryl bromide **6** was treated with *tert*-butylamine to give the bromo amide **7** in 96% yield [21,22]. The tertiary bromide position was substituted with *tert*-butylamine during a subsequent step in the presence of powdered NaOH in 85% yield to give the amido amine **8** [23]. Finally the diamine ligand **9** was obtained by reducing **8** with LiAlH_4 in 2-methyltetrahydrofuran in 87% yield [23]. The diamine was then converted to the dichlorogermene **10** after reaction with germanium tetrachloride in the presence of triethylamine in 67% yield. The dichlorogermene was reduced with elemental lithium at room temperature and the germylene **2** was produced in 76% yield. The germylene was purified by short-path distillation at 90°C (0.1 Torr).

Germylene **3** has one *tert*-butyl group in the backbone. It is synthesized by the same general method as **1** and **2** as shown in Scheme 3. *N,N'*-di-*tert*-butylethylenediamine **11** was treated with *tert*-butyllithium to produce the iminoamine **12** in 97% yield [20] which was then reduced to the diamine **13** with $\text{AlH}_3 \cdot \text{NME}_3$ in 96% yield [24]. The diamine was then converted to the dichlorogermene **14** by reaction with germanium tetrachloride in the presence of triethylamine in 65% yield. When the dichlorogermene was reduced with elemental lithium at room temperature, the germylene **3** was obtained in 75% yield. The germylene was purified by distillation at 85°C (0.1 Torr).

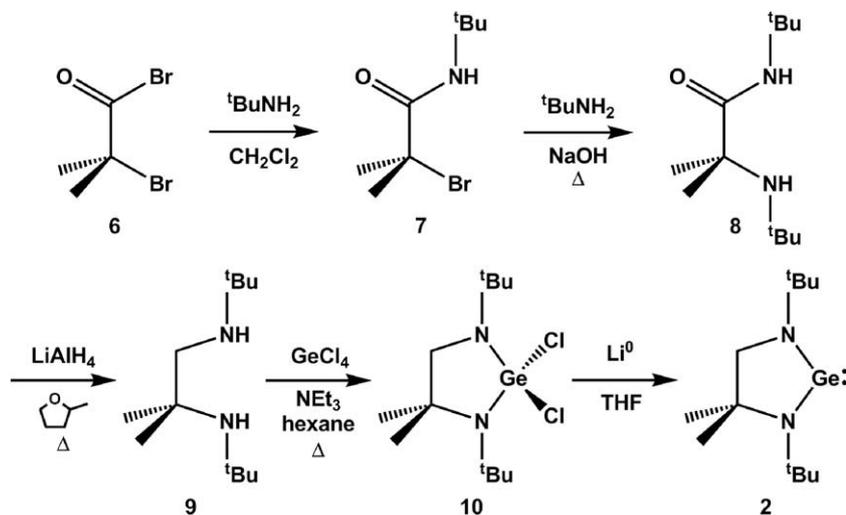
In conclusion, three new N-heterocyclic saturated germylenes, **1**, **2**, and **3** have been synthesized. It appears that the divalent Ge atom is quite tolerant to various backbone ligands and its +2 oxidation state is stabilized by the nitrogen atoms in the backbone. These compounds may lead to new N-heterocyclic ligands (or chiral ligands) for metal complex catalysis.

3. Experimental

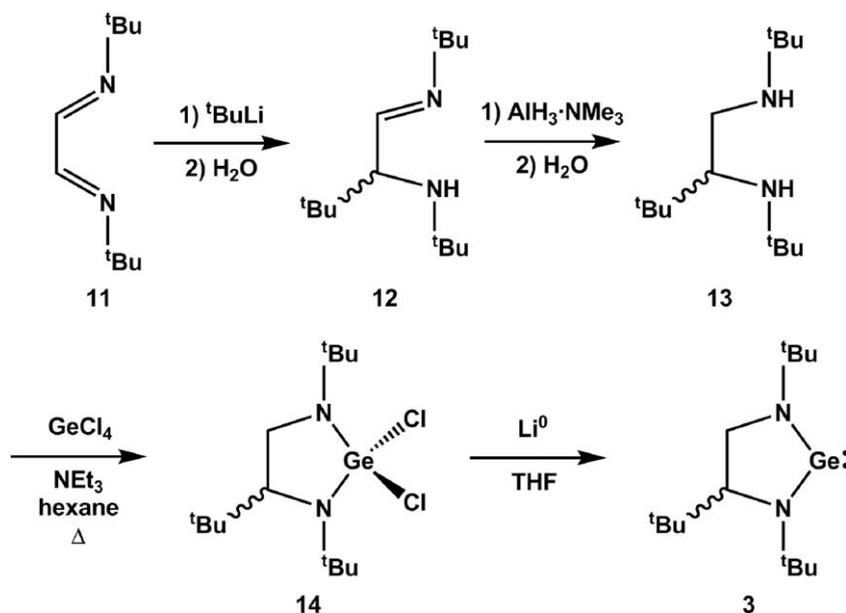
3.1. General

3.1.1. Chemicals and reagents

All reactions and manipulations were conducted under a dry argon atmosphere using standard Schlenk techniques. DABCO, *tert*-butylamine, α -bromoisobutyryl bromide, sodium hydroxide, lithium aluminum hydride, and *tert*-butyllithium were obtained from Sigma Aldrich and used as received. $\text{AlH}_3 \cdot \text{NME}_3$ [25] and *N,N'*-di-



Scheme 2. The synthesis of germylene 2.



Scheme 3. The synthesis of germylene 3.

tert-butylethylenediimine [26] were prepared via literature methods. Germanium tetrachloride was obtained from Gelest Inc. and distilled and degassed immediately before use. Lithium metal was purchased in mineral oil and washed with pentane prior to use. All solvents were dried using either sodium/potassium alloy or sodium benzophenone radical.

3.1.2. Instrumentation

^1H NMR and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded at room temperature on a Bruker AC-300 spectrometer and were referenced to internal TMS or residual solvent resonances. Mass spectral analyses were performed using a Shimadzu QP 5000. Elemental analyses were performed by Robertson Microlit Laboratories Madison, NJ, USA and Chemisar Laboratories Inc. Guelph, ON, Canada.

3.2. *rac*-1,3-Di-*tert*-butyl-2,2-dichloro-4,5-dimethyl-1,3,2-diazagermolidine, 5

A solution of the diamine (**4**) (8.60 g, 42.9 mmol), 1,8-diazabicyclo[2.2.2]octane (DABCO) (9.65 g, 86.0 mmol), and hexane

(125 mL) was stirred at 0 °C. GeCl_4 (11.0 g, 51.3 mmol) in 25 mL of hexane was added dropwise to the cooled solution. The reaction mixture was then fitted with a reflux condenser and refluxed overnight after which it was cooled, filtered, and the solvent removed. The crude yellow oil was distilled in a Kugelrohr oven (80 °C, 0.1 Torr) to give a viscous pale yellow oil (11.28 g, 76.9%).

^1H NMR (C_6D_6): δ 1.07 (d, 6H, $J = 6.3$ Hz); 1.22 (s, 18H); 2.73 (q, 2H, $J = 6.3$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 25.27; 31.60; 54.55; 58.07. High resolution mass spectrometry: calculated for $[\text{C}_{12}\text{H}_{26}\text{N}_2\text{GeCl}_2]^+$ 338.0711, found 338.0715. Anal. Calc. for $\text{C}_{12}\text{H}_{26}\text{N}_2\text{GeCl}_2$: C, 42.16; H, 7.67; N, 8.19. Found: C, 42.43; H, 7.69; N, 8.22%.

3.3. *rac*-1,3-Di-*tert*-butyl-4,5-dimethyl-1,3-diaza-2-germacyclopentane-2-ylide, 1

To a 200 mL Schlenk flask was added lithium wire cut into small pieces (0.35 g, 50.6 mmol) and THF (100 mL). Then, *rac*-1,3-di-*tert*-butyl-2,2-dichloro-4,5-dimethyl-1,3,2-diazagermolidine (**5**) (8.05 g, 23.6 mmol) dissolved in 15 mL THF was added via cannula. The reaction was monitored by ^1H NMR until all the starting

material disappeared (~1 h). The reaction mixture was filtered and the solvent removed resulting in a dark brown oil. The oil was vacuum distilled (80 °C, 0.1 Torr) to give a very pale yellow liquid (4.55 g, 71.2%).

^1H NMR (C_6D_6): δ 1.11 (d, 6H, $J = 6.0$ Hz); 1.28 (s, 18H); 3.02 (q, 2H, $J = 6.0$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 27.44; 33.87; 55.02; 63.02. High resolution mass spectrometry: calculated for $[\text{C}_{12}\text{H}_{26}\text{N}_2\text{Ge}]^+$ 268.1333, found 268.1335. Anal. Calc. for $\text{C}_{12}\text{H}_{26}\text{N}_2\text{Ge}$: C, 53.19; H, 9.67; N, 10.34. Found: C, 52.92; H, 9.86; N, 10.45%.

3.4. 1,3-Di-*tert*-butyl-2,2-dichloro-4,4-dimethyl-1,3,2-diazagermolidine, **10**

A solution of the diamine (**9**) (6.17 g, 30.8 mmol), triethylamine (12 mL), and hexane (125 mL) was stirred at 0 °C. GeCl_4 (7.26 g, 33.9 mmol) in 25 mL of hexane was added dropwise to the cooled solution. The reaction mixture was then fitted with a reflux condenser and refluxed overnight after which it was cooled, filtered, and the solvent removed. The crude yellow oil was distilled in a Kugelrohr oven (105 °C, 0.1 Torr) to give a pale yellow oil (7.00 g, 67.1%).

^1H NMR (C_6D_6): δ 1.21 (s, 6H); 1.22 (s, 9H); 1.36 (s, 9H); 2.59 (s, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 29.63; 29.73; 34.15; 54.13; 56.79; 60.17; 61.24. High resolution mass spectrometry: calculated for $[\text{C}_{12}\text{H}_{26}\text{N}_2\text{GeCl}_2]^+$ 338.0711, found 338.0723. Anal. Calc. for $\text{C}_{12}\text{H}_{26}\text{N}_2\text{GeCl}_2$: C, 42.16; H, 7.67; N, 8.19. Found: C, 41.82; H, 8.06; N, 8.42%.

3.5. 1,3-Di-*tert*-butyl-4,4-dimethyl-1,3-diaza-2-germacyclopentane-2-ylide, **2**

To a 100 mL Schlenk flask was added lithium wire cut into small pieces (0.17 g, 24.3 mmol) and THF (40 mL). Then, 1,3-di-*tert*-butyl-2,2-dichloro-4,4-dimethyl-1,3,2-diazagermolidine (**10**) (4.06 g, 11.9 mmol) dissolved in 15 mL THF was added dropwise. The reaction was monitored by ^1H NMR until all the starting material disappeared (~3 h). The reaction mixture was filtered and the solvent removed resulting in a dark yellow oil. The yellow oil was vacuum distilled (90 °C, 0.1 Torr) to give a very pale yellow oil (2.44 g, 75.8%).

^1H NMR (C_6D_6): δ 1.27 (s, 9H); 1.33 (s, 6H); 1.44 (s, 9H); 3.13 (s, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 30.60; 32.01; 36.69; 54.35; 57.01; 65.04; 67.98. High resolution mass spectrometry: calculated for $[\text{C}_{12}\text{H}_{26}\text{N}_2\text{Ge}]^+$ 268.1333, found 268.1329. Anal. Calc. for $\text{C}_{12}\text{H}_{26}\text{N}_2\text{Ge}$: C, 53.19; H, 9.67; N, 10.34. Found: C, 52.83; H, 9.93; N, 10.60%.

3.6. *rac*-1,3,4-Tri-*tert*-butyl-2,2-dichloro-1,3,2-diazagermolidine, **14**

A solution of the diamine (**13**) (10.0 g, 43.8 mmol), triethylamine (20 mL), and hexane (125 mL) was stirred at 0 °C. GeCl_4 (9.38 g, 43.8 mmol) in 25 mL of hexane was added dropwise to the cooled solution. The reaction mixture was then fitted with a reflux condenser and refluxed overnight after which it was cooled, filtered, and the solvent removed. The crude yellow oil was distilled in a Kugelrohr oven (105 °C, 0.1 Torr) to give a very viscous yellow oil (10.45 g, 64.5%).

^1H NMR (C_6D_6): δ 0.98 (s, 9H); 1.23 (s, 9H); 1.25 (s, 9H); 2.7–3.0 (m, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 29.43; 29.66; 31.58; 36.61; 46.94; 54.58; 56.78; 63.23. High resolution mass spectrometry: calculated for $[\text{C}_{14}\text{H}_{30}\text{N}_2\text{GeCl}_2\text{-CH}_3]^+$ 351.0789, found 351.0789. Anal. Calc. for

$\text{C}_{14}\text{H}_{30}\text{N}_2\text{GeCl}_2$: C, 45.45; H, 8.17; N, 7.57. Found: C, 45.77; H, 8.45; N, 7.58%.

3.7. *rac*-1,3,4-Tri-*tert*-butyl-1,3-diaza-2-germacyclopentane-2-ylide, **3**

In a 100 mL Schlenk flask was placed lithium wire cut into pieces (0.20 g, 28.8 mmol). To this flask 40 mL THF was added. Then, *rac*-1,3,4-tri-*tert*-butyl-2,2-dichloro-1,3,2-diazagermolidine (**14**) (5.18 g, 14.0 mmol) dissolved in 20 mL THF was added via cannula. The reaction was monitored by ^1H NMR until all the starting material disappeared (~1 h). The reaction mixture was filtered and the solvent removed resulting in a pale yellow oil. The yellow oil was vacuum distilled (85 °C, 0.1 Torr) to give a pale yellow liquid (3.14 g, 75.1%).

^1H NMR (C_6D_6): δ 0.92 (s, 9H); 1.28 (s, 9H); 1.34 (s, 9H); 3.2–3.4 (m, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 29.15; 32.34; 35.04; 35.60; 52.34; 55.60; 56.99; 69.11. High resolution mass spectrometry: calculated for $[\text{C}_{14}\text{H}_{30}\text{N}_2\text{Ge-C}_4\text{H}_9]^+$ 239.0942, found 239.0952. Anal. Calc. for $\text{C}_{14}\text{H}_{30}\text{N}_2\text{Ge}$: C, 56.23; H, 10.11; N, 9.37. Found: C, 55.88; H, 9.93; N, 9.04%.

Acknowledgements

We thank the National Science Foundation for support of this research (Grant No. CHE-0451536).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.12.042.

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