

Available online at www.sciencedirect.com



Inorganica Chimica Acta 358 (2005) 1186-1192

Inorganica Chimica Acta

www.elsevier.com/locate/ica

Synthesis and reactivity of the bulky germanium(IV) trisamide complexes BrGe[N(SiMe₃)₂]₃ and LiGe[N(SiMe₃)₂]₃: X-ray crystal structures of BrGe[N(SiMe₃)₂]₃ and [(Me₃Si)₂N]₃Ge(CH₂CH₂CH₂CH₃)

Jennifer L. Walding, Phillip E. Fanwick, Charles S. Weinert *,1

Department of Chemistry, Purdue University, 560 Oval Drive, West Lafayette, IN 47907, USA

Received 21 October 2004; accepted 24 November 2004 Available online 30 December 2004

Dedicated to Professor Duward F. Shriver on the occasion of his 70th birthday

Abstract

The bulky germanium(IV) trisamide complex BrGe[N(SiMe₃)₂]₃ has been prepared and structurally characterized. Reaction of this material with "BuLi resulted in [(Me₃Si)₂N]₃Ge(CH₂CH₂CH₂CH₃), which has also been structurally characterized, but no reaction with lithium metal was observed in the attempted preparation of LiGe[N(SiMe₃)₂]₃. However, analytically pure LiGe[N(SiMe₃)₂]₃was prepared by the reaction of 3 equivalents of LiN(SiMe₃)₂ with GeI₂. Evidence is presented that this germyllithium reagent is a major by-product in the synthesis of Ge[N(SiMe₃)₂]₂ when the latter reagent is obtained from GeCl₂ · (dioxane) prepared by the method of Kolesnikov et al. Reaction of the germyllithium reagent with 2,6-diphenylphenol yields the mixed Ge/Li cage complex [Li(μ_2 -OC₆H₃Ph₂-2,6)₃Ge], which had originally been obtained serendipitously via the reaction of 2,6-diphenylphenol with Ge[N(SiMe₃)]₂.

© 2004 Elsevier B.V. All rights reserved.

Keywords: Germanium; Crystal structure; NMR spectroscopy

1. Introduction

The use of sterically encumbering ligands often allows the stabilization of metal centers with low coordination numbers. In particular, the bulky ligand bis(trimethylsilyl)amido $[-N(SiMe_3)_2]$ [1] has been employed for the preparation of stable bivalent compounds of the group 14 metals Ge and Sn [2,3], the first examples of three-coordinate group 7 metals M[N(SiMe_3)_2]_3 (M = Mn, Co) [4], and trisamide compounds [(Me_3Si)₂N]₃MCl of the group 4 metals Ti, Zr, and Hf [5]. We have employed the germanium bisamide compound Ge[N(SiMe₃)₂]₂ (1) [2,3,6] in reactions with derivatized phenols and resolved binaphthols for the synthesis of germanium(II) aryloxide [7] and chiral binaphthoxide [8] complexes. During the course of this study, we unexpectedly obtained a mixed lithium/germanium species [Li(μ_2 -OC₆H₃Ph₂-2,6)₃Ge] from the reaction of 2,6-diphenylphenol with **1** [9], which had been prepared by reduction of GeCl₄ with Bu₃SnH in the presence of dioxane [10], followed by reaction with 2 equivalents of LiN(SiMe₃)₂ [2,3]. The germanium/lithium complex [Li(μ_2 -OC₆H₃Ph₂-2,6)₃Ge], as well as the entire series of heavier congeners has previously been prepared by the reaction of three equivalents of the alkali metal

^{*} Corresponding author. Tel.: +1 405 7446543; fax: +1 405 7446007. *E-mail address:* weinert@chem.okstate.edu (C.S. Weinert).

¹ Present address: Department of Chemistry, Oklahoma State University, 316 Physical Science, Stillwater OK 740783071, USA.

phenoxide with GeI₂ and the entire series has been structurally characterized [9]. In our laboratory, the synthesis of 1 was complicated by the formation of a lithium trisamide LiGe[N(SiMe₃)₂]₃ and this product co-distills with the desired germanium(II) bisamide and accounts for the formation of $[Li(\mu_2-OC_6H_3Ph_2-2,6)_3Ge]$ upon reaction of this mixture with 2,6-diphenylphenol. Evidence for this process is the focus of this study. We have characterized the previously reported germanium(IV) trisamide $BrGe[N(SiMe_3)_2]_3$ (2) [11], which reacts with ^{*n*}BuLi to yield the alkylgermanium species [(Me₃Si)₂N]₃- $Ge(CH_2CH_2CH_2CH_3)$ (3). Although 2 could not be converted to the germyllithium complex LiGe[N(SiMe₃)₂]₃ 4, this material was obtained in pure form by the reaction of GeI₂ with 3 equivalents of LiN(SiMe₃)₂. Reaction of 4 with 2,6-diphenylphenol results in the formation of $[Li(\mu_2-OC_6H_3Ph_2-2,6)_3Ge]$ (5). We have obtained X-ray crystal structures of complexes 2 and 3 and have employed ⁷Li NMR spectroscopy to investigate the synthesis of the lithium/germanium complex via both the rational and serendipitous routes.

2. Results and discussion

2.1. Synthesis

The germanium(IV) trisamide BrGe[N(SiMe₃)₂]₃ (2) was obtained in moderate yield via the previously reported synthetic method involving insertion of Ge- $[N(SiMe_3)_2]_2$ (1) into the N–Br bond of BrN(SiMe₃)₂ [11]. Compound 2 is stable with respect to oxygen and moisture due to the presence of three sterically encumbering bis(trimethylsilyl)amido groups. Stirring a suspension of 2 in water in air for 7 days did not result in hydrolysis. Furthermore, protonolysis reactions involving 2 and 2,6-diphenylphenol, which have been useful for the preparation of germanium(II) aryloxides from 1 [9], were unsuccessful and no reaction was observed between 2 and various alcohols or other protic reagents.

Despite the steric bulk of **2**, this species could be converted to the butyl complex $[(Me_3Si)_2N]_3Ge(CH_2-CH_2CH_2CH_3)$ (**3**) by reaction with a slight molar excess of "BuLi in refluxing benzene for 18 h. However, large molar excesses (greater than 1.4 equivalents) of "BuLi not only cause cleavage of the Ge–Br bond but also the Ge–N bonds giving a mixture of products. Because we had unexpectedly obtained $[Li(\mu_2-OC_6H_3Ph_2-2,6)_3-Ge]$ (**5**) by reaction of 2,6-diphenylphenol with **1**, we were interested in obtaining the lithium/germanium amide LiGe[N(SiMe_3)_2]_3 (**4**) from **2** but attempts to convert compound **2** to **4** by reaction of GeI₂ with three equivalents of LiN(SiMe_3)_2 resulted in a pale orange liquid which could be purified by vacuum distillation

(b.p. = 79 °C at 0.05 torr) and the identity of the product was confirmed to be that of **4** by elemental analysis.

The 'Li NMR spectrum of pure 4 contains one resonance at 1.05 ppm, while a ⁷Li NMR spectrum of $Ge[N(SiMe_3)_2]_2$ (1) prepared using the original method of reduction of GeCl₄ [10] for the synthesis of GeCl₂ \cdot (dioxane) contained a resonance at 1.05 ppm as well, indicating the presence of 4 as a contaminant in the product mixture. The formation 4 is likely a result of side products formed in the reduction of GeCl₄ with Et₃SiH during the synthesis of $GeCl_2 \cdot dioxane$. This preparation has been previously proven unreliable and an improved synthetic method has been reported [12], which cleanly gives 1 upon reaction with $LiN(SiMe_3)_2$. Additionally, an alternate preparation of 1 also gives contaminant-free product [6]. Reaction of 2,6-diphenylphenol with compound 1 prepared by either of these methods gives the expected bisaryloxide $Ge(OC_6H_4$ - $Ph_2-2,6)_2$, while reduction of GeCl₄ by the original method and subsequent reaction with $LiN(SiMe_3)_2$ gives a product which contains 4 as a major contaminant and gives the trisaryloxide complex 5 upon reaction with phenol. The similarity in boiling points of 4 and 1 despite the higher molecular weight of 4 renders separation by distillation difficult. Complex 5 was obtained by reaction 4 with 3 equivalents of 2,6-diphenylphenol in 82%vield.

2.2. Crystallographic studies

Recrystallization of 2 from hot benzene yielded crystals which were suitable for an X-ray structure determination. An ORTEP diagram of 2 is shown in Fig. 1 and selected bond distances and angles are summarized in Table 1. Compound 2 crystallizes in the trigonal space group R3c and has a threefold axis of rotation directed along the Ge–Br bond. The methyl groups of the three – N(SiMe₃)₂ ligands interlock in a gear-like fashion. A comparison of the structure of 2 with that of Ge[N- $(SiMe_3)_2$ (1) [13] reveals that the Ge–N bond lengths of 1.848(3) A in 2 are shorter than those of 1 which have an average value of 1.876(5) Å, while the N-Ge-N angles of $115.52(6)^{\circ}$ in **2** are substantially more obtuse than that of 1 which measures $107.1(2)^{\circ}$. The shorter Ge–N bonds in 2 are likely due to the presence of the higher formal charge on germanium (4+) in 2 versus 1 (2+), while the larger N-Ge-N angles are required to accommodate three bis(trimethylsilyl)amido-ligands rather than two.

The Ge–Br bond distance in **2** of 2.3861(6) Å is significantly shorter than the Sn–Br distance of 2.519(2) Å in BrSn[N(SiMe₃)₂]₃ (6) [11,14], reflecting the smaller covalent radius of Ge (1.22 Å) relative to Sn (1.40 Å) [15]. The Ge–N distance of 1.848(3) Å in **2** is shorter than the Sn–N distance of 2.056(7) Å in **6** and also shorter than the Ti–N bond of 1.940(10) Å in the similar group



Fig. 1. ORTEP plot of $BrGe[N(SiMe_3)_2]_3$ (2). Thermal ellipsoids are drawn at 50% probability.

4 complex CITi[N(SiMe₃)₂]₃ (*d* Ti–N = 1.940(10) Å) [5], which might be expected due to the larger covalent radius of Ti (1.32 Å) [15]. However, when correcting for the difference in covalent radii between germanium and tin (0.18 Å) and germanium and titanium (0.10 Å), all three M–N bond distances are essentially the same. The Ge–N distance in **2** is also very similar to the average Ga–N bond of 1.839(4) Å in ClGa[N-(Si-Me₃)₂]₂[16], where the two elements have very similar covalent radii (r_{cov} = 1.25 Å for Ga). The Ge–N distance in **2** is significantly longer than the average Ge–N bond length of 1.780(4) Å in the mixed aryloxide/amido complex [Ge(OC₆H₃Ph₂-2,6)₂(NMe₂)₂] [17], which is likely a result of the increased steric bulk of the three – N(SiMe₃)₂ ligands relative to that of the –NMe₂ ligands.

The N–Si bonds in **2** have an average value of 1.783(3) Å and are longer than that in the tin congener **6** of 1.758(8) Å [11,14] but are very similar to the average N–Si distances in ClM[N(SiMe₃)₂]₃ of 1.77(1) Å (M = Ti), 1.766(4) Å (M = Zr), and 1.78(1) Å (M =

Table 1 Selected bond lengths (Å) and angles (°) for $[BrGe{N(SiMe_3)_2}_3]$ (1)

beleeted bond lengths (1) and angles () for [Di Ge (1 (bintes)2)3] (1)				
Ge–Br	2.3861(6)	N-Si(1)	1.781(3)	
Ge–N	1.848(3)	N-Si(2)	1.784(3)	
N-Ge-N	115.52(6)	N-Si(1)-C(12)	113.32(1)	
N–Ge–Br	102.39(8)	N-Si(1)-C(13)	111.1(1)	
Ge-N-Si(1)	125.8(2)	N-Si(2)-C(21)	113.5(2)	
Ge-N-Si(2)	118.4(1)	N-Si(2)-C(22)	111.4(1)	
Si(1)-N-Si(2)	115.3(2)	N-Si(2)-C(23)	112.6(2)	
N-Si(1)-C(11)	115.7(1)			



Fig. 2. Space filling drawing of BrGe[N(SiMe₃)₂]₃ (2).

Hf) [5]. Elongation of the N–Si bond is indicative of covalent character in the M–N bond and is most pronounced for **6** while lessened for **2**. Tin is slightly less electropositive than germanium and thus the Sn–N bond is expected to be more covalent in nature than the Ge–N bond. The shortening of the N–Si distances in the group 4 complexes is likely a manifestation of the ability of transition metals to engage in M–L π -interactions, where the M–N bond exhibits some double bond character resulting from donation of electron density from nitrogen to the formally d⁰ metal center. This would make the nitrogen atoms electron deficient, and this deficiency is then alleviated by electron donation from the Me₃Si-groups resulting in a shorter N–Si bond.

A space-filling diagram of 2 is shown in Fig. 2. The bromine atom is significantly encapsulated by the methyl groups of the N(SiMe₃)₂ ligands, while the germanium atom is completely encapsulated by the ligand system. The bulky ligands of 2 render it kinetically inert, which explains the lack of reaction with 2,6-diphenylphenol and various other protic reagents. This also explains the inertness of compound 2 with respect to air and moisture.

The N–M–N bond angles in **2** and **6** and in the group 4 amides are all nearly identical, ranging from 114.1(1)° in ClHf[N(SiMe₃)₂]₃ [5] to 115.52(6)° in **2**. All of these metal complexes can be regarded as isostructural and crystallize in the *R*3*c* space group. They exhibit C_{3v} symmetry and contain a crystallographically imposed C_3 axis directed along the metal–halide bond. The same is not true for compound **3**, however, which exhibits a lower symmetry due to the presence of a butyl group. Crystallization of **3** from hot hexane yielded crystals which were suitable for an X-ray structure determination. An OR-TEP diagram is shown in Fig. 3, and selected bond distances and angles are summarized in Table 2.

The three Ge–N bonds in 3 are longer than those of 2 and measure 1.870(2), 1.891(2), and 1.908(2) Å in



Fig. 3. ORTEP plot of $[(Me_3Si)_2N]_3Ge(CH_2CH_2CH_2CH_3)$ (3). Thermal ellipsoids are drawn at 50% probability.

length, with the Ge-N(3) bond being the longest and the Ge-N(1) bond being the shortest. The Ge-N(1) bond is slightly shorter than those in $Ge[N(SiMe_3)_2]_2$ (1), which measure 1.878(5) and 1.873(5) A [13]. Two of the three N-Ge-N angles measuring 106.23(9)° and 109.99(9)° are substantially more acute in 3 than in 2, but are similar to the N–Ge–N angle in 1 which measures $107.1(2)^{\circ}$ [13]. The third N–Ge–N angle of 116.08(9)° is more obtuse than those of both 2 and 1. Thus, the three bis(trimethylsilyl)amido-ligands are not symmetry related in 3 and the trimethylsilyl groups do not interlock in a gear-like fashion as found in compound 2. The longer Ge–N distances in 3 relative to 2 are a result of the presence of the less electron-withdrawing butyl group compared with the bromine atom in 2, and the shorter Ge–N bonds in 2 indicate that the three amido groups are more tightly held to the germanium metal center than in 3. In addition to the electronic effects, the butyl

Table 2 Selected bond lengths (Å) and angles (°) for $[{(Me_3Si)_2N}_3.Ge(CH_2CH_2CH_2CH_3)]$ (2)

Ge–N(1)	1.870(2)	Ge–N(2)	1.891(2)	
Ge–N(3)	1.908(2)	Ge-C(41)	1.968(3)	
C(41)–C(42)	1.527(4)	C(42)–C(43)	1.514(4)	
C(43)–C(44)	1.518(4)	N(1)-Si(11)	1.769(2)	
N(1)-Si(12)	1.762(2)	N(2)-Si(21)	1.754(2)	
N(2)-Si(22)	1.780(2)	N(3)-Si(31)	1.776(2)	
N(3)–Si(32)	1.768(2)			
N(1)-Ge-N(2)	116.08(9)	N(1)-Ge-N(3)	109.99(9)	
N(2)-Ge-N(3)	106.23(9)	N(1)-Ge-C(41)	105.4(1)	
N(2)–Ge–C(41)	103.0(1)	N(3)-Ge-C(41)	116.4(1)	
Ge-N(1)-Si(11)	120.1(1)	Ge-N(1)-Si(12)	121.7(1)	
Ge-N(2)-Si(21)	131.6(1)	Ge-N(2)-Si(22)	114.3(1)	
Ge-N(3)-Si(31)	118.4(1)	Ge-N(3)-Si(32)	127.2(1)	
Ge-C(41)-C(42)	121.0(2)			

group in 3 is also less sterically encumbering than the bromine atom in 2, since only the α -methylene group affects the steric environment about the germanium atom. This diminished steric environment allows the three amido groups in 3 to adopt more acute bond angles than those of 2.

The germanium-nitrogen bond lengths in 2 and 3 fall well within the range for germanium complexes containing one or more -N(SiMe₃)₂ ligands. A oxadiazagermanine carboxalate complex containing two -N(SiMe₃)₂ ligands exhibits short Ge-N bond lengths of 1.785(6) and 1.799(6) A [18], while the germanium(II) complex [Me₃SiNB(^{*t*}Bu)NSiMe₃]Ge[N(SiMe₃)₂] has a long Ge– N distance of 1.910(2) Å [19]. The Ge–N bond in 2 is very similar in length to those in the germanium(IV) complex $[{(Me_3Si)_2N}_2GeS]_2$ which have an average distance of 1.842(4) A [20], and to the Ge-N bond in 1bis(trimethylsilyl)aminogermatrane which measures 1.845(3) Å [21], which also contains a germanium(IV) center. However, the Ge–N(3) bond in 3 is exceptionally long for a germanium(IV) complex containing a bis(trimethylsilylamido) ligand. The aforementioned [Me₃SiNB(^tBu)NSiMe₃]Ge[N(SiMe₃)₂] is formally a complex of germanium(II) and other structurally characterized species containing a -N(SiMe₃)₂ ligand with a Ge–N bond longer than 1.90 Å are germanium(II) species complexed to late transition metals [22,23].

2.3. Variable temperature NMR studies

The steric nature of the three $-N(SiMe_3)_2$ groups in 2 and their ability to interlock in a gear-like fashion result in restricted rotation about the Ge–N bonds in solution and is evident in the ¹H NMR spectrum of 2. The 300 MHz ¹H NMR spectrum of 2 in benzene- d_6 contains two resonances of equal intensity at δ 0.59 and 0.40 ppm. Three of the six trimethylsilyl ligands are proximal to the bromine atom, while three are distal which result in two Si(CH₃)₃ resonances instead of a single resonance in an intensity ratio of 1:1. A single resonance was previously reported for 2 and at δ 0.65 ppm at a lower field strength of 60 MHz [11]. Presumably the two peaks were not resolvable at lower field.

Complex 2 was subjected to a variable-temperature ¹H NMR experiment in toluene- d_8 in order to determine the barrier to rotation about the Ge–N bonds. At -30 °C, the two lines have a linewidth at half height of $\Delta v_{1/2} = 4.13$ Hz and warming the sample to 25 °C results in a broadening of the resonances to $\Delta v_{1/2} = 10.80$ Hz. Upon increasing the temperature to 50 °C, the peaks begin to coalesce and finally become a single broad feature at δ 0.46 ppm at a temperature of 66 °C. This resonance becomes sharper with increasing temperature and has a linewidth of $\Delta v_{1/2} = 6.23$ Hz at 110 °C. The barrier to rotation for the –SiMe₃ groups is calculated to be $\Delta G^{\ddagger} = 16.7 \pm 0.5$ kcal/mol. This value is higher than the values reported for the group 4 metal trisamides ClM[N(SiMe_3)_2]_3 (M = Ti, $\Delta G^{\ddagger} = 15.7 \pm 0.5$ kcal/mol; M = Zr, $\Delta G^{\ddagger} = 14.2 \pm 0.5$ kcal/mol and M = Hf, $\Delta G^{\ddagger} = 14.1 \pm 0.5$ kcal/mol) [5]. The Ge(IV) center has a smaller covalent radius than Ti(IV) and therefore rotation about the M–N bonds in **2** is higher than that of the titanium complex due to steric reasons.

The ¹H NMR spectrum of the alkylgermanium complex 3 at room temperature exhibits a sharp resonance at 0.45 ppm corresponding to the 54 protons of the bis(trimethylsilyl)amido groups. The single butyl group of 2 results in two triplets at 0.96 (CH₃) and 1.70 (Ge– CH_2), as well as a multiplet resulting in the overlap of signals for the β - and γ -methylene groups centered at 1.41 ppm. In contrast to the ¹H NMR spectrum of 2, the -SiMe₃ protons of **3** are all equivalent at room temperature and thus give only one signal. This single resonance splits into two resolved features at 0.53 and 0.48 ppm at -60 °C as shown by variable temperature NMR spectroscopy. Thus, the barrier to rotation about the Ge–N bonds in 3 has a value of $\Delta G^{\ddagger} = 11.0 \pm 0.5$ kcal/mol, which is less than that for compound 2 and for the group 4 compounds $CIM[N(SiMe_3)_2]_3$ (M = Ti, Zr, Hf) [5]. The shorter Ge–N bonds in the solid-state structure of 2 indicate that the three amido groups are more tightly held to the germanium metal center than in 3, which accounts for the larger barrier to rotation of these ligands in 2 versus 3.

3. Conclusions

In summary, we have structurally characterized the germanium(IV) trisamide BrGe[N(SiMe₃)₂]₃ 2 and converted this species to the alkylgermanium compound [(Me₃Si)₂N]₃Ge(CH₂CH₂CH₂CH₃)] **3** by reaction with one equivalent of "BuLi. Although the germyllithium complex LiGe[N(SiMe₃)₂]₃ 4 could not be prepared from 2 by reaction with lithium metal, 4 was accessible by the reaction of GeI2 with three equivalents of LiN-(SiMe₃)₂. As shown by ⁷Li NMR spectroscopy, compound 4 was found to be present as a product in the synthesis of $Ge[N(SiMe_3)_2]_2$ from $GeCl_2 \cdot (dioxane)$ and LiN(SiMe₃)₂ when the germanium(II) chloride complex was prepared by the originally reported reduction of GeCl₄ with Bu₃SnH [10]. Compound 4 was subsequently employed for the preparation of [Li(OC₆H₃Ph₂-2,6)₃Ge] 5 and explains the formation of 5 in our attempts to prepare $[Ge(OC_6H_3Ph_2-2,6)_2]$ using $Ge[N(SiMe_3)_2]_2$ [9].

The previously reported 2 [11] has been further characterized by X-ray crystallography and variable temperature NMR spectroscopy, which serves to investigate the barrier to rotation about the Ge–N bonds of 2. Despite the kinetic inertness of 2, this species could be converted to the germanium(IV) alkyl amido complex 3 which was also characterized by VT NMR spectroscopy and a solid-state structure determination. Compound 3 contains a less sterically encumbered germanium metal center relative to 2 and therefore exhibits a lower barrier to rotation about the Ge–N bonds than compound 2.

4. Experimental

All manipulations were carried out using standard Schlenk line, glovebox, and syringe techniques [24]. The compounds Ge[N(SiMe₃)₂]₂ [2,3,6], BrN(SiMe₃)₂ [25], and HOC₆H₃Ph₂-2,6 [26] were prepared according to the literature procedures. Solvents were purified using an Innovative Technologies solvent purification system. ¹H NMR spectra were recorded at 300 MHz and referenced to residual protic solvent. ⁷Li NMR spectra were recorded at 194.3 MHz and referenced to a 1.0 M solution of LiCl in D₂O. Elemental analyses were carried out in-house at Purdue University.

4.1. Synthesis of $BrGe[N(SiMe_3)_2]_3$ (2)

Compound **2** was prepared by a slight variation of the published procedure [11]. To a solution of Ge- $[N(SiMe_3)_2]_2$ (4.52 g, 11.5 mmol) in hexane (10 mL) was added a solution of $[BrN(SiMe_3)_2]$ (3.04 g, 12.6 mmol) in hexane (10 mL). The reaction mixture became colorless, then dark brown. The solution was stirred overnight followed by removal of the volatiles in vacuo, yielding a brown solid. The solid was washed with hexane (3 × 5 mL), yielding a white solid which was recrystallized from hot benzene to give **2** as colorless needles. Yield: 4.17 g (58%). ¹H NMR (C₆D₆): δ 0.59 (s, 27 H), 0.40 (s, 27 H). Anal. Calc. for C₁₈H₅₄BrGeN₃Si₆: C, 34.12; H, 8.59; N, 6.63; Br, 12.61. Found: C, 33.65; H, 8.39; N, 6.24; Br, 12.39.

4.2. Synthesis of [(Me₃Si)₂N]₃Ge(CH₂CH₂CH₂CH₃) (3)

A solution of "BuLi (2.5 M in hexanes, 0.80 mL, 2.0 mmol) was added to a suspension of **2** (1.04 g, 1.64 mmol) in benzene (20 mL). The reaction mixture was refluxed under a N₂ atmosphere for 18 h and was then allowed to come to room temperature. The volatiles were removed in vacuo to yield a white solid. Hexane (2 mL) was added and the mixture was warmed until all of the material dissolved. Slow cooling of the solution yielded **3** as colorless crystals. Yield: 0.24 g (70%). ¹H NMR (C₆D₆): δ 1.70 (q, 2H, Ge–CH₂CH₂–), 1.52–1.30 (m, 4H, Ge–CH₂CH ₂CH₂CH₃), 0.96 (t, 3H, CH₃–), 0.45 (s, 54H, -Si(CH₃)₃) ppm. Anal. Calc. for C₂₂H₆₃GeN₃Si₆: C, 62.87; H, 15.11; N, 6.88. Found: C, 63.02; H, 15.04; N, 6.94.

4.3. Synthesis of $LiGe[N(SiMe_3)_2]_3$ (4)

To a suspension of GeI₂ (0.750 g, 2.30 mmol) in ether (10 mL) was added a solution of LiN(SiMe₃)₂ (1.23 g, 7.35 mmol) in ether (75 mL) via cannula. The reaction mixture was stirred for 4 h resulting in a yellow solution. The volatiles were removed in vacuo and the resulting material was suspended in hexane. The suspension was filtered through Celite and the residue was washed with hexane (3 × 5 mL). The hexane was removed in vacuo and the resulting oil was vacuum distilled (b.p. = 79 °C at 0.050 torr), yielding a yellow/orange oil. Yield: 0.67 g (52%). ¹H NMR (C₆D₆): δ 0.32 (s) ppm. ⁷Li NMR (C₆D₆): δ 1.05 (s) ppm. *Anal*. Calc. for C₁₈H₅₄GeLiN₃-Si₆: C, 38.56; H, 9.71; N, 7.49. Found: C, 38.23; H, 9.90; N, 7.74.

4.4. Synthesis of $[Li(\mu_2 - OC_6H_3Ph_2 - 2, 6)_3Ge]$ (5)

To a solution of **4** (0.34 g, 0.61 mmol) in benzene (10 mL) was added a solution of 2,6-diphenylphenol (0.48 g, 1.9 mmol) in benzene (5 mL). The solution was stirred for 18 h. The volatiles were removed in vacuo and the resulting solid was recrystallized from 10 mL of benzene/hexane (1:1, v/v) to yield **5** as colorless crystals. Yield: 0.40 g (82%). *Anal.* Calc. for $C_{54}H_{39}GeLiO_3$: C, 79.53; H, 4.82. Found: C, 79.82; H, 5.22.

4.5. X-ray structure determination

Crystal data and data collection parameters are contained in Table 3. A suitable crystal was mounted on a glass fiber in a random orientation under a cold stream of dry nitrogen. Preliminary examination and final data collection were performed with Mo K α radiation ($\lambda = 0.71073$ Å) on a Nonius KappaCCD. Lorentz and polarization corrections were applied to the

2

Table 3	
Crystallographic data	for compounds 1 and

	1	2
Formula	C ₁₈ H ₅₄ BrGeN ₃ Si ₆	C22H63GeN3Si6
Space group	<i>R</i> 3 <i>c</i> (# 161)	$P2_1/n$ (#14)
Unit cell dimensions		
a (Å)	17.8668(4)	11.7654(4)
b (Å)	17.8668(4)	17.9616(6)
c (Å)	16.926(1)	16.8366(8)
α (°)	90	90
β (°)	90	103.33(2)
γ (°)	120	90
$V(Å^3)$	4679.3(3)	3462.1(2)
Z	6	4
$\rho_{\rm calc} ({\rm g}{\rm cm}^{-3})$	1.349	1.172
Temperature (K)	150	150
Radiation	Μο Κα	Μο Κα
Wavelength (Å)	0.71073	0.71073
R	0.030	0.043
R_w	0.065	0.093

data [27]. An empirical absorption correction using SCALEPACK was applied [28]. Intensities of equivalent reflections were averaged. The structure was solved using the structure solution program PATTY in DIR-DIF92 [29]. The remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were included in the refinement but restrained to ride on the atom to which they are bonded. The structure was refined in full-matrix least-squares where the function minimized was $\Sigma w (|F_o|^2 - |F_c|^2)^2$ and the weight *w* is defined as $w = 1/{\{\sigma^2(F_o^2) + (0.0585P)^2 + 1.4064P\}}$, where $P = (F_o^2 + 2F_c^2)/3$. Scattering factors were taken from the "International Tables for Crystallography" [30]. Refinement was performed on a AlphaServer 2100 using shelx97 [31]. Crystallographic drawings were done using programs ORTEP3 [32]. See http:// www.rsc.org for crystallographic data in CIF or other electronic format.

5. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Center, deposition numbers CCDC 218741 (2) and CCDC 236920 (3). Copies of this information may be obtained from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1233 336033; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

C.S.W. gratefully acknowledges Professor Ian P. Rothwell for helpful discussions. This work was funded by a grant from the National Science Foundation (Grant No. CHE-0078405).

References

- M.F. Lappert, P.P. Power, A.R. Sanger, R.C. Srivastava, Metal and Metalloid Amides, Ellis Horwood, Chichester, UK, 1980.
- [2] D.H. Harris, M.F. Lappert, J. Chem. Soc., Chem. Commun. (1974) 895.
- [3] M.J.S. Gynane, D.H. Harris, M.F. Lappert, P.P. Power, P. Rivière, M. Rivière-Baudet, J. Chem. Soc., Dalton Trans. (1977) 2004.
- [4] J.J. Ellison, P.P. Power, S.C. Shoner, J. Am. Chem. Soc. 111 (1989) 8044–8046.
- [5] C. Airoldi, D.C. Bradley, H. Chudzynska, M.B. Hursthouse, K.M.A. Malik, P.R. Raithby, J. Chem. Soc., Dalton Trans. (1980) 2010.
- [6] Q. Zhu, K.L. Ford, E.J. Roskamp, Heteroatm Chem. 3 (1992) 647.
- [7] C.S. Weinert, A.E. Fenwick, P.E. Fanwick, I.P. Rothwell, J. Chem. Soc., Dalton Trans. (2003) 532.

- [8] C.S. Weinert, P.E. Fanwick, I.P. Rothwell, J. Chem. Soc., Dalton Trans. (2002) 2948.
- [9] C.S. Weinert, P.E. Fanwick, I.P. Rothwell, J. Chem. Soc., Dalton Trans. (2003) 1795.
- [10] S.P. Kolesnikov, I.S. Rogozhin, O.M. Nefedov, Izv. Akad. Nauk SSSR, Ser. Khim. (1974) 2379.
- [11] M.F. Lappert, M.C. Misra, M. Onyszchuk, R.S. Rowe, P.P. Power, M.J. Slade, J. Organomet. Chem. 330 (1987) 31.
- [12] T. Fjeldberg, A. Haaland, B.E.R. Schilling, M.F. Lappert, A.J. Thorne, J. Chem. Soc., Dalton Trans. (1986) 1551.
- [13] R.W. Chorley, P.B. Hitchcock, M.F. Lappert, W.-P. Leung, P.P. Power, M.M. Olmstead, Inorg. Chim. Acta 198–200 (1992) 203.
- [14] R.D. Rogers, J.L. Atwood, J. Cryst. Spectrosc. Res 13 (1983) 1.
- [15] J. Emsley, The Elements, Oxford University Press, Oxford, 1991.
- [16] P.J. Brothers, R.J. Wehmschulte, M.M. Olmstead, K. Ruhlandt-Senge, S.R. Parkin, P.P. Power, Organometallics 13 (1994) 2792.
- [17] G.D. Smith, P.E. Fanwick, I.P. Rothwell, Inorg. Chem. 29 (1990) 3221.
- [18] G. Ossig, A. Meller, O. Müller, R. Herbst-Irmer, Organometallics 15 (1996) 5060.
- [19] S.R. Foley, Y. Zhou, G.P.A. Yap, D.S. Richeson, Inorg. Chem. 39 (2000) 924.
- [20] G.L. Wegner, A. Jockisch, A. Schier, H. Schmidbaur, Z. Naturforsch. B 55 (2000) 347.

- [21] S.N. Nikolaeva, K. Megges, J. Lorbeth, V.S. Petrosyan, Z. Naturforsch. B 53 (1998) 973.
- [22] K.E. Litz, K. Henderson, R.W. Gourley, M.M. Banaszak Holl, Organometallics 14 (1995) 5008.
- [23] K.E. Litz, J.W. Kampf, M.M. Banaszak Holl, J. Am. Chem. Soc. 120 (1998) 7484.
- [24] D.F. Shriver, M.A. Drezdzon, The Manipulation of Air Sensitive Comounds, Wiley, New York, 1986.
- [25] N. Wiberg, F. Raschig, J. Organomet. Chem. 10 (1967) 15.
- [26] D.E. Dana, A.S. Hay, Synthesis (1982) 164.
- [27] P.C. McArdle, J. Appl. Cryst. 29 (1996) 306.
- [28] Z. Otwinowski, W. Minor, Methods Enzymol. (1996) 276.
- [29] P.T. Beurskens, G. Admirall, G. Beurskens, W.P. Bosman, S. Garcia-Granda, R.O. Gould, J.M.M. Smits, C. Smykalla, The DIRDIF92 Program System, Technical Report, Crystallography Laboratory, University of Nijmegen, The Netherlands, 1992.
- [30] International Tables for Crystallography, vol. C, Kluwer Academic Publishers, Dordrecht, The Netherlands, 1992, Tables 4.2.6.8 and 6.1.1.4.
- [31] G.M. Sheldrick, SHELXS97. A Program for Crystal Structure Refinement, University of Gottingen, Germany, 1997.
- [32] L.J. Farrugia, J. Appl. Cryst. 30 (1997) 565.