

Reactivity of germanium(II) hydride with nitrous oxide, trimethylsilyl azide, ketones, and alkynes and the reaction of a methyl analogue with trimethylsilyl diazomethane†

Anukul Jana,^a Herbert W. Roesky^{*a} and Carola Schulzke^b

Received 15th July 2009, Accepted 11th September 2009

First published as an Advance Article on the web 5th October 2009

DOI: 10.1039/b914164b

The reactions of stable β -diketiminate germanium(II) hydride LGeH (**1**) [$L = \text{HC}(\text{CMeNAr})_2$, $\text{Ar} = 2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3$] with nitrous oxide, trimethylsilyl azide, ketones, and alkynes are described. **1** reacts with nitrous oxide to yield the germanium(II) hydroxide LGeOH (**2**), and with trimethylsilyl azide affords in toluene at room temperature the germanium(II) azide LGeN₃ (**3**), and also the germanium(IV) diamide $L'\text{Ge}(\text{NHSiMe}_3)_2$ ($L' = \text{CH}\{(\text{C}=\text{CH}_2)(\text{CMe})(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3\text{N}_2)\}$) (**4**). Ketones (PhCOCF_3 , $2\text{-C}_4\text{H}_3\text{SCOCF}_3$) and **1** generated the germanium(II) alkoxides (**5–6**) in high yield. The activated terminal alkyne ($\text{HC}\equiv\text{CCO}_2\text{Me}$) and disubstituted alkyne ($\text{EtO}_2\text{CC}\equiv\text{CCO}_2\text{Et}$) react with **1** to form the germanium(II) substituted alkenes (vinyl germylene) (**7–8**). Further reaction of the methylgermanium(II) compound LGeMe (**9**) with trimethylsilyl diazomethane resulted in the formation of germanium(IV) amide $L'\text{Ge}(\text{Me})\text{NHN}=\text{CHSiMe}_3$ (**10**). Compounds **2–8**, and **10** were characterized by microanalysis and multi-nuclear NMR spectroscopy. Furthermore compounds **3–6**, and **8** are confirmed by X-ray structural analysis.

Introduction

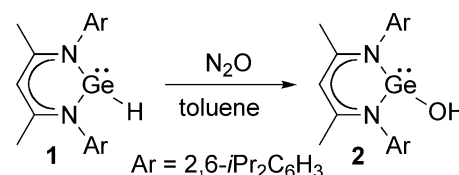
The chemistry of divalent germanium compounds has received considerable attention due to their carbene like properties.¹ Such compounds are generally reactive and tend to oligomerize or polymerize. However, Ge(II) compounds can be stabilized kinetically by sterically demanding ligands and/or thermodynamically by inter- and intramolecular coordination. Compounds of divalent germanium bonded to small substituents (such as H, Me, Et, and *n*Bu) are highly reactive and therefore exist only as intermediates. Organometallics hydrides of group 14 play an important role in various metathesis reactions and therefore the reactivity of hydrides like R_3SiH , R_3GeH , and R_3SnH is well studied.² To overcome these difficulties our group reported the syntheses and structures of LGeR ($\text{R} = \text{H, Me, and } n\text{Bu}$; $L = \text{HC}(\text{CMeNAr})_2$, $\text{Ar} = 2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3$).^{3,4} More recently we also communicated the reactivity of LGeH with some unsaturated compounds including carbon dioxide and trimethylsilyl diazomethane.^{5,6} Herein we report the reactivity of LGeH (**1**) with nitrous oxide, trimethylsilyl azide, ketones, and alkynes. Furthermore, we also describe the reactivity of LGeMe with trimethylsilyl diazomethane.

Results and discussion

Syntheses and characterization

It is well known that nitrous oxide acts as a mono oxygen source. It can supply the oxygen to the low valent metal center or to

the metal–metal bond to generate metal oxygen compounds.⁷ However there is no reaction known of group 14 metal hydride with nitrous oxide to form the metal hydroxide. Herein we are reporting the reaction of LGeH with nitrous oxide under the formation of LGeOH (**2**) in almost quantitative yield (Scheme 1). Compound **2** was previously reported by our group by the reaction of LGeCl with water in the presence of 1,3-di(2,4,6- $\text{Me}_3\text{C}_6\text{H}_2$)-2-ylidene⁸ or alternatively by the reaction of $L'\text{Ge}$ ($L' = \text{CH}\{(\text{C}=\text{CH}_2)(\text{CMe})(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3\text{N}_2)\}$) with water.⁹



Scheme 1 Preparation of compound **2**

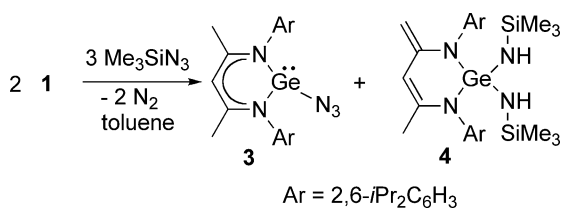
Recently we reported on the reactivity of **1** with diazoalkane by formation of germanium(II) substituted hydrazone derivatives.⁶ Subsequently we became interested in studying the reactivity of **1** with trimethylsilyl azide. In 2005 our group communicated the first end-on azide insertion into an Al–C bond of an aluminacyclopentene and the formation of aluminaazacyclobutene.¹⁰ Trimethylsilyl diazomethane and trimethylsilyl azide are isoelectronic and both exhibit 1,3-dipolar properties. Therefore we expected that the azide might also insert end-on into the germanium–hydrogen bond of **1**. However the reaction of **1** with trimethylsilyl azide at room temperature afforded two products in a ratio of 1:1 (Scheme 2).

One is the germanium(II) azide (**3**), and the other is the germanium(IV) diamide (**4**). Compound **3** was formed by metathesis reaction of **1** with Me_3SiN_3 under elimination of Me_3SiH . In

^aInstitut für Anorganische Chemie, Universität Göttingen, Tammannstrasse 4, 37077, Göttingen, Germany. E-mail: hroesky@gwdg.de; Fax: +49-551-393373

^bSchool of Chemistry, Trinity College Dublin, Dublin 2, Ireland

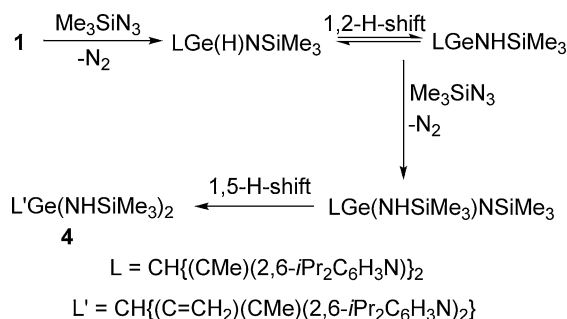
† CCDC reference numbers 713790, 715866, 730408, 738339, and 730403 for **3**, **4**, **5**, **6**, and **8** respectively. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b914164b



Scheme 2 Preparation of compounds 3 and 4

the literature only two germanium(II) azides are reported by nucleophilic substitution reaction using NaN₃ and germanium(II) chloride precursors,¹¹ whereas compound **4** was generated by elimination of dinitrogen from azide, with the resulting nitrene inserting into the germanium–hydrogen bond. The final oxidative addition of another nitrene is followed by simultaneous hydrogen transfer from one methyl group, which is attached to the heterocyclic ring backbone. A few reactions of group 14 compounds with divalent elements and organic azides have been reported.¹² The initial dinitrogen elimination from Me₃SiN₃ is generally accepted, and supported by experimental observations.¹³

The formation of the imide LGe(F)NSiMe₃ was observed by elimination of dinitrogen from Me₃SiN₃ followed by oxidative addition to the germanium(II) center of LGeF,¹⁴ whereas LGeMe reacted with Me₃SiN₃ under dinitrogen elimination, oxidative addition, followed by intramolecular hydrogen transfer from one methyl group of the ring backbone to yield L'Ge(Me)NHSiMe₃.⁴ Subsequently we propose a reasonable pathway for the formation of **4** (Scheme 3).



Scheme 3 Proposed pathway for the formation of 4

Compound **3** crystallizes in the triclinic space group *P*-1 from *n*-hexane at room temperature. There are three independent molecules in the unit cell (Fig. 1). The IR spectrum of **3** exhibits a band at 2068 cm⁻¹, which is assigned to the N₃ stretching frequency.

4 is a colorless solid soluble in benzene, THF, *n*-hexane, and *n*-pentane respectively and shows no decomposition on exposure to dry air. **4** was characterized by ¹H and ²⁹Si NMR spectroscopy, EI mass spectrometry, elemental analysis, and X-ray structural analysis. The ¹H NMR spectrum of **4** shows a singlet (δ 0.01 ppm), which can be assigned to the Si(CH₃)₃ protons.

Maintaining a *n*-hexane solution of **4** for two days at -32 °C resulted in colorless single crystals suitable for X-ray structural analysis. **4** crystallizes in the monoclinic space group *P*2₁/*n*, with one molecule of **4** in the asymmetric unit. **4** exists as a monomer in the solid state (Fig. 2). There are no intermolecular hydrogen bonds observed in the crystal lattice. The coordination polyhedron around the germanium atom comprises four nitrogen atoms, two

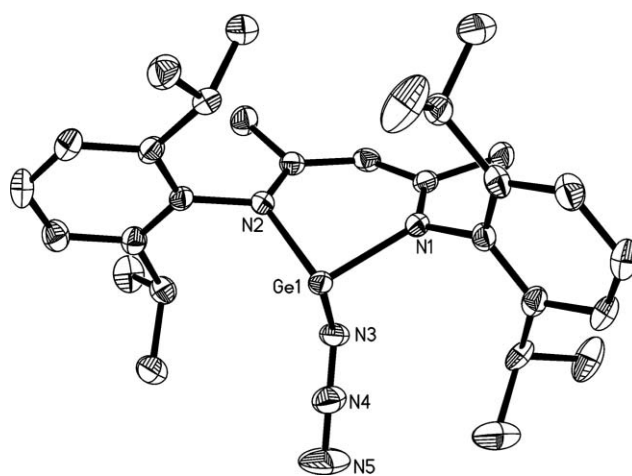


Fig. 1 Molecular structure of **3**. Thermal ellipsoids are shown at 50% probability. H atoms are omitted for clarity reasons. Selected bond lengths [Å] and angles [°]: Ge1–N3 2.002(3), N3–N4 1.198(4), N4–N5 1.149(4), Ge1–N1 1.980(2), Ge1–N2 1.973(2); Ge1–N3–N4 121.5(3), N3–N4–N5 176.3(4), N1–Ge1–N2 90.69(11).

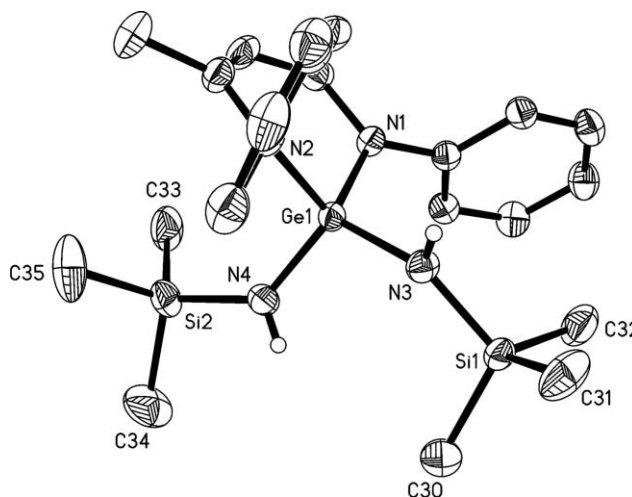


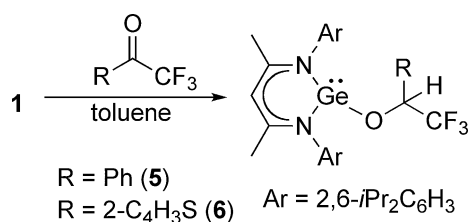
Fig. 2 Molecular structure of **4**. Thermal ellipsoids are shown at 50% probability. H atoms except N3–H and N4–H and the iso-propyl groups are omitted for clarity reasons. Selected bond lengths [Å] and angles [°]: Ge1–N1 1.8416(14), Ge1–N2 1.8413(15), Ge1–N3 1.8011(14), Ge1–N4 1.8224(15); N1–Ge1–N2 101.59(6), N1–Ge1–N3 112.77(7), N3–Ge1–N4 111.24(8), N2–Ge1–N4 111.54(7).

from the supporting ligand, and two others from the imide groups, featuring a distorted tetrahedral geometry. The four Ge–N bond lengths are almost similar. The Ge–N bond lengths of **2** and **3** and those of **4** are quite different due to the non-equal oxidation states of the germanium atoms. The formation of **4** requires the oxidation of germanium(II) to germanium(IV). Therefore the synthesis of **4** also involves a unprecedented oxidative addition–insertion with nitrene (:NSiMe₃), which is formed *in situ* from trimethylsilyl azide by elimination of dinitrogen, and insertion into the Ge(II)–H bond, which leads to the formal conversion of the GeH hydride to a NH proton.

Surprisingly there is no precedent reaction of group 14 known where nitrene is added and inserted simultaneously at the same element. We were not able to isolate any intermediate of this

reaction. No evidence was found for any tautomeric equilibrium of **4**.

In a preliminary publication we have shown some reactions of **1** with unsaturated molecules.⁵ So far we used no ketone, which might generate the germanium(II) alkoxide by nucleophilic addition reaction to the carbon oxygen double bond. Although **1** displayed no reactivity toward acetone or benzophenone at room temperature, it reacts cleanly with activated ketones namely 2,2,2-trifluoro acetophenone and 2,2,2-trifluoroacetothiophene. Treatment of **1** with 2,2,2-trifluoroacetophenone and 2,2,2-trifluoroacetothiophene leads quantitatively to the germylene alkoxides **5** and **6** respectively with a Ge(II)–O–C framework that is formed by nucleophilic hydride addition to the respective carbon of the carbonyl group (Scheme 4). Compounds **5** and **6** were monitored by ¹H NMR spectra. Sharp resonances in the ¹H NMR spectra of **5** and **6** gave the initial indication that the products have been formed in high yield.



Scheme 4 Preparation of compounds **5** and **6**

Compounds **5** and **6** have one CF₃ group each and both display an interesting NMR spectrum. The ¹H NMR spectra of **5** and **6** exhibit a quartet each (δ 4.73 and 5.04 ppm) which corresponds to the quaternary CH proton and its coupling with the three F-atoms of the CF₃ group (³J(¹H–¹⁹F) = 8 and 7 Hz respectively). The CH resonances of **5** (δ 4.73 ppm) and **6** (δ 5.04 ppm)

are upfield shifted when compared with that of LGeOC(O)H (δ 8.64 ppm).⁵ The assignment of the chemical shift for the CH proton of LGeOC(O)H should be downfield instead of upfield when compared with that of LGeH (δ 8.08 ppm).⁵ The ¹⁹F NMR resonance arises as a doublet (δ –75.76 (**5**) and –76.29 (**6**) ppm) with the same coupling constant of 8 and 7 Hz respectively. The four isopropyl groups of **5** and **6** are showing four different resonances, and even the two methyl groups in the ring backbone exhibit two different signals each in the ¹H NMR spectra.

Single crystals of **5** and **6** suitable for X-ray structural analysis were obtained from *n*-hexane solutions. **5** and **6** crystallize in the triclinic space group *P*-1 and monoclinic space group *P*2₁/*c* respectively (Table 1). The molecular structures of **5** and **6** are shown in Figs. 3 and 4. The asymmetric unit of **5** and **6** contains one formula unit of the compound, and there are two of the molecules in each unit cell. As predicted, based on the ¹H NMR spectrum and EI mass spectrum, compounds **5** and **6** contain a Ge(II)–O–CH core. The three coordinate germanium atom is surrounded by two N atoms of the β -diketiminato ligand, and an exocyclic O atom. The Ge–O bond lengths (1.862 Å, 1.855 Å) are comparable with those of compound **2** (1.828 Å).⁸ The O–C bond distances of **5** and **6** are in a narrow range of each other (1.407 Å and 1.417 Å).

The hydrogermylation of alkynes has been well known for nearly 50 years and follows a polar or a free radical pathway depending on the substituents, catalyst, solvent, and conditions.¹⁵ In contrast to this result the present hydrogermylation reaction of alkynes with **1** proceeds without any catalyst. **1** reacts with HC≡CCO₂Me and EtO₂CC≡CCO₂Et respectively at room temperature to form the vinyl germylenes **7** and **8** (Scheme 5). **7** and **8** are obtained by the 1,2-addition of **1** to the carbon–carbon triple bond.

Table 1 Crystallographic data for the structural analysis of **3**, **4**, **5**, **6**, and **8**

Parameters	3	4	5	6	8
Empirical formula	C ₂₉ H ₄₁ GeN ₅	C ₃₅ H ₆₀ GeN ₄ Si ₂	C ₃₇ H ₄₇ F ₃ GeN ₂ O	C ₃₅ H ₄₅ F ₃ GeN ₂ OS	C ₃₇ H ₅₂ GeN ₂ O ₄
Mol. Wt.	532.26	665.64	665.36	671.38	661.40
Crystal system	triclinic	monoclinic	triclinic	monoclinic	monoclinic
Space group	<i>P</i> -1	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> -1	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> [Å]	16.697(3)	10.389(2)	10.833(2)	12.142(2)	11.837(2)
<i>b</i> [Å]	17.006(3)	32.555(7)	11.879(2)	8.7405(17)	17.042(3)
<i>c</i> [Å]	17.763(4)	12.216(2)	14.500(3)	32.073(6)	17.895(4)
α [°]	101.17(3)	90	79.54(3)	90	90
β [°]	116.15(3)	112.28(3)	83.10(3)	98.61(3)	103.69(3)
γ [°]	100.60(3)	90	69.63(3)	90	90
<i>V</i> [Å ³]	4229.2(15)	3823.0(13)	1717.0(6)	3365.5(11)	3507.3(12)
<i>Z</i>	6	4	2	4	4
ρ_{calc} [Mg m ⁻³]	1.254	1.158	1.287	1.325	1.253
μ [mm ⁻¹]	1.112	0.891	0.939	1.018	0.913
<i>F</i> (000)	1692	1432	700	1408	1408
Crystal Size (mm)	0.33 × 0.30 × 0.29	0.5 × 0.4 × 0.4	0.29 × 0.20 × 0.19	0.47 × 0.43 × 0.37	0.38 × 0.15 × 0.08
θ range [°]	1.54–27.01	1.91–25.84	1.85–27.09	1.28–25.91	1.67–26.96
Reflections Collected/unique	41106/18275	30291/7365	15959/7458	25583/6486	31646/7613
	[<i>R</i> (int) = 0.0442]	[<i>R</i> (int) = 0.0476]	[<i>R</i> (int) = 0.1029]	[<i>R</i> (int) = 0.0561]	[<i>R</i> (int) = 0.0585]
Data/restraints/parameters	18275/0/979	7365/0/405	7458/0/411	6486/0/388	7613/0/413
<i>R</i> 1, <i>wR</i> 2 [<i>I</i> > 2 σ (<i>I</i>)] ^a	0.0449, 0.0905	0.0304, 0.0725	0.0724, 0.1880	0.0537, 0.1363	0.0341, 0.0738
<i>R</i> 1, <i>wR</i> 2 (all data) ^a	0.0900, 0.1019	0.0373, 0.0748	0.0968, 0.2109	0.0578, 0.1385	0.0472, 0.0777
GoF	0.999	1.033	1.102	1.199	1.016
Residual density max./min. [e Å ⁻³]	0.445/0.417	0.376/–0.617	0.873, –1.444	1.115, –0.607	0.384, –0.317

^a *R*1 = $\sum \|F_o| - |F_c|\| / \sum |F_o|$. *wR*2 = $[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{0.5}$.

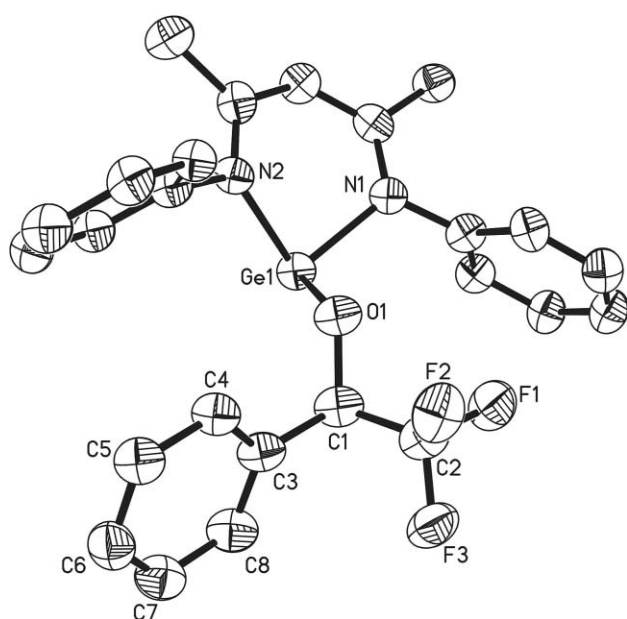


Fig. 3 Molecular structure of **5**. Anisotropic displacement parameters are depicted at the 50% probability level and all restrained refined hydrogen atoms and the isopropyl groups are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ge1–O1 1.862(3), Ge1–N1 2.002(4), O1–C1 1.407(6); N1–Ge1–N2 88.77(15), N1–Ge1–O1 97.52(15), Ge1–O1–C1 112.8(3).

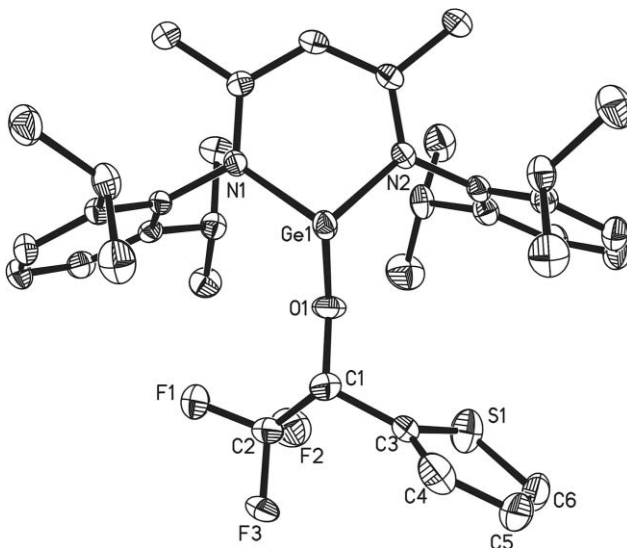
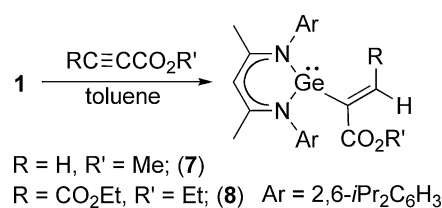


Fig. 4 Molecular structure of **6**. Anisotropic displacement parameters are depicted at the 50% probability level and all restrained refined hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ge1–O1 1.855(2), Ge1–N1 2.011(3), O1–C1 1.417(4); N1–Ge1–N2 88.45(11), N1–Ge1–O1 96.69(11), Ge1–O1–C1 112.8(2).

7 and **8** are yellow solids soluble in benzene, THF, *n*-hexane, and *n*-pentane, respectively and show no decomposition on exposure to air. **7** and **8** were characterized by multinuclear NMR spectroscopy, EI mass spectrometry, and elemental analysis. Furthermore **8** was characterized by X-ray structural analysis (Fig. 5). The ¹H NMR spectrum of **7** exhibits two broad resonances (δ 6.20 and 5.82 ppm) which correspond to the two alkenyl protons.



Scheme 5 Preparation of compounds **7** and **8**

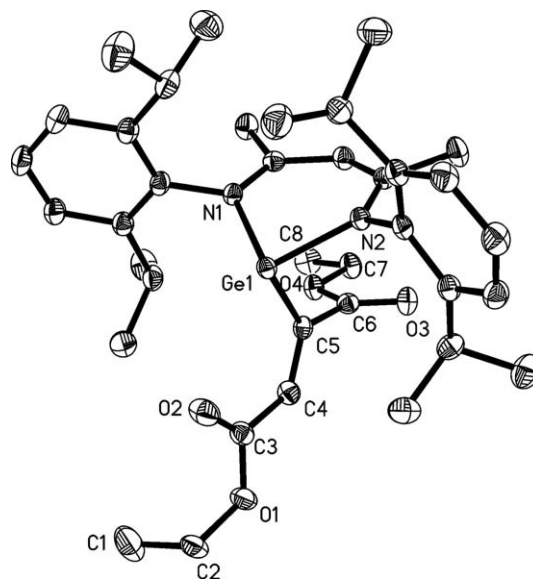
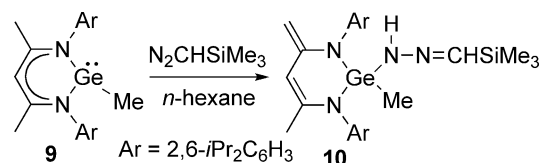


Fig. 5 Molecular structure of **8**. Anisotropic displacement parameters are depicted at the 50% probability level and all restrained refined hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ge1–C5 2.1083(18), Ge1–N1 2.0177(15), C4–C5 1.338(3); N1–Ge1–N2 91.07(6), N1–Ge1–C5 92.07(6), Ge1–C5–C4 122.03(14).

Compound **8** crystallizes in the monoclinic space group $P2_1/c$, with one monomer in the asymmetric unit, and with two molecules in the unit cell. Single crystals were obtained from a saturated *n*-hexane solution at $-32\text{ }^\circ\text{C}$ in a freezer after two days (Table 1). The coordination polyhedron around the germanium atom features a distorted tetrahedral geometry with a stereochemically active lone pair.

Moreover we conducted the reaction of LGeMe (**9**)⁴ with trimethylsilyl diazomethane, which resulted in the formation of [L'Ge(Me)(NHNCHSiMe₃)] (**10**), instead of nitrogen elimination and creation of LGe(Me)=CHSiMe₃ (Scheme 6). The reaction proceeds with migration of a hydrogen atom from a methyl group of the ligand backbone to the end-on nitrogen atom of the diazo group. In the ¹H NMR spectrum of **10** the resonances clearly show the existence of NH (δ 6.76 ppm) CH (δ 5.78 ppm), and the CH₂ moiety (δ 3.83 and 3.21 ppm). The NH proton of **10** is upfield



Scheme 6 Preparation of compound **10**

shifted when compared with that of the GeH (δ 8.08 ppm) proton of LGeH (**1**), which is similar to those in the case of compounds LGeN(H)NCHCO₂Et (δ 7.25 ppm).⁶

The formation of **10** may be compared with that of **4**. In both compounds an oxidation of the Ge(II) to Ge(IV) occurred and a migration of a hydrogen atom from a methyl group of the ligand backbone to the end-on nitrogen of the diazo group is observed.

Experimental

General considerations

All manipulations were performed in a dry and oxygen-free atmosphere (N₂ or Ar) by using Schlenk-line and glove-box techniques. Solvents were purified with the M-Braun solvent drying system. Compounds LGeH⁵ and LGeMe⁴ were prepared by literature methods. Other chemicals were purchased and used as received. ¹H, ¹³C, ¹⁹F, and ²⁹Si NMR spectra were recorded on a Bruker 500 MHz instrument and referenced to the deuterated solvent in the case of the ¹H and ¹³C NMR spectra. ¹⁹F and ²⁹Si NMR spectra were referenced to CFCl₃ and to SiMe₄ respectively. Elemental analyses were performed by the Analytisches Labor des Instituts für Anorganische Chemie der Universität Göttingen. Mass spectra were obtained on a Finnigan Mat 8230 instrument. Melting points were measured in a sealed glass tube with a Büchi melting point B 540 instrument and are not corrected.

Synthesis of [{HC(CMeNAr)₂}GeOH] (Ar = 2,6-*i*Pr₂C₆H₃) (**2**).

Dry N₂O was bubbled into a solution of **1** (0.49 g, 1.00 mmol) in toluene (20 mL) at room temperature. After 30 min the gas flow of N₂O was disconnected, and all the volatiles were removed in vacuum. The residue was treated with *n*-hexane (40 mL) and after filtration and drying in vacuum, **2** was obtained as a yellow microcrystalline powder. Yield: 0.480 g (95%). ¹H NMR (500 MHz, C₆D₆): δ 7.09–7.17 (m, 6H, Ar-*H*), 4.91 (s, 1H, γ -CH), 3.71 (sept, 2H, CH(CH₃)₂), 3.31 (sept, 2H, CH(CH₃)₂), 1.65 (s, 1H, OH), 1.60 (s, 6H, CH₃), 1.30 (d, 6H, CH(CH₃)₂), 1.28 (d, 6H, CH(CH₃)₂), 1.20 (d, 6H, CH(CH₃)₂), 1.11 (d, 6H, CH(CH₃)₂) ppm. ¹³C{¹H} NMR (125.77 MHz, C₆D₆): δ 161.48 (CN), 142.75, 141.22, 125.82, 123.55 (Ar-C), 94.24 (γ -C), 29.16 (CH(CH₃)₂), 28.60 (CH(CH₃)₂), 26.69 (CH(CH₃)₂), 24.73 (CH(CH₃)₂), 24.58 (CH(CH₃)₂), 24.08 (CH(CH₃)₂), 23.25 (CH₃) ppm. For comparison see ref. 8.

Synthesis of [{HC(CMeNAr)₂}GeN₃] (3**) and [HC(CCH₂)(CMe)(NAr)₂Ge(NHSiMe₃)₂] (Ar = 2,6-*i*Pr₂C₆H₃) (**4**).** An excess of trimethylsilyl azide was slowly added drop by drop to a 20 mL toluene solution of **1** (0.98 g, 2 mmol). Then the reaction mixture was stored overnight. After that the solvent and excess trimethylsilyl azide were removed in vacuum. The residue was extracted with *n*-hexane (35 mL) and the extract concentrated to about 20 mL. After one day at room temperature colorless crystals of **3** are formed. Then the residual extract is stored in a freezer at –30 °C. After two days colorless crystals of **4** had formed.

3. Yield: 0.34 g (32%); mp 190 °C; ¹H NMR (500 MHz, C₆D₆): δ 7.04–7.13 (m, 6H, Ar-*H*), 4.98 (s, 1H, γ -CH), 3.73 (sept, 2H, CH(CH₃)₂), 3.10 (sept, 2H, CH(CH₃)₂), 1.53 (s, 6H, CH₃), 1.32 (d, 6H, CH(CH₃)₂), 1.18 (d, 12H, CH(CH₃)₂), 1.15

(d, 6H, CH(CH₃)₂), 1.05 (d, 6H, CH(CH₃)₂) ppm; IR (Nujol, KBr, cm^{–1}): $\tilde{\nu}$ = 2068 (N₃); EI-MS (70 eV): *m/z* (%): 491 (100) [M – N₃]⁺. Found C, 64.06; H, 8.11%. Calcd for C₂₉H₄₁GeN₅ (532.26), C, 65.43; H, 7.76%.

4. Yield: 0.37 g (28%); mp 200 °C; ¹H NMR (500 MHz, C₆D₆): δ 7.21 (s, 2H, NH), 7.04–7.13 (m, 6H, Ar-*H*), 5.29 (s, 1H, γ -CH), 3.87 (s, 1H, CH), 3.86 (sept, 2H, CH(CH₃)₂), 3.74 (sept, 2H, CH(CH₃)₂), 3.28 (s, 1H, CH), 1.58 (s, 6H, CH₃), 1.32 (d, 6H, CH(CH₃)₂), 1.18 (d, 12H, CH(CH₃)₂), 1.15 (d, 6H, CH(CH₃)₂), 1.05 (d, 6H, CH(CH₃)₂), 0.01 (s, 18H, Si(CH₃)₃) ppm; ²⁹Si{¹H} NMR (125.77 Hz, C₆D₆): δ 5.53 (Si(CH₃)₃) ppm; EI-MS (70 eV): *m/z* (%): 651 (100) [M – Me]⁺. Found C, 64.83; H, 8.36%. Calcd for C₃₅H₆₀GeN₄Si₂ (665.64), C, 63.15; H, 9.08%.

Synthesis of [{HC(CMeNAr)₂}GeOCHPhCF₃] (Ar = 2,6-*i*Pr₂C₆H₃) (5**).** A solution of 2,2,2-trifluoroacetophenone (0.175 g, 1.00 mmol in 5 mL toluene) was added by cannula to a solution of **1** (0.49 g, 1.00 mmol in toluene 20 mL) at room temperature. After 12 h all volatiles were removed in vacuum, and the remaining residue was extracted with *n*-hexane (25 mL). The solution was concentrated and kept in a freezer to obtain **5** as yellow crystals, which are suitable for X-ray diffraction analysis. Yield: 0.545 g (82%); mp 182 °C; ¹H NMR (500 MHz, C₆D₆): δ 6.74–7.28 (m, 11H, Ar-*H*), 4.73 (q, 1H, CH), 4.65 (s, 1H, γ -CH), 3.73 (sept, 2H, CH(CH₃)₂), 3.29 (sept, 1H, CH(CH₃)₂), 3.07 (sept, 1H, CH(CH₃)₂), 1.60 (d, 3H, CH(CH₃)₂), 1.50 (d, 3H, CH(CH₃)₂), 1.48 (s, 3H, CH₃), 1.41 (s, 3H, CH₃), 1.35 (d, 3H, CH(CH₃)₂), 1.21 (d, 3H, CH(CH₃)₂), 1.15 (d, 3H, CH(CH₃)₂), 1.11 (d, 3H, CH(CH₃)₂), 1.02 (d, 3H, CH(CH₃)₂), 0.72 (d, 3H, CH(CH₃)₂) ppm; ¹³C{¹H} NMR (125.77 MHz, C₆D₆): δ 164.71, 164.39 (CN), 145.03–124.59 (Ar-C), 96.38 (γ -C), 75.84 (q, CH), 29.00 (CH(CH₃)₂), 28.90 (CH(CH₃)₂), 28.77 (CH(CH₃)₂), 28.63 (CH(CH₃)₂), 26.61 (CH(CH₃)₂), 25.71 (CH(CH₃)₂), 24.86 (CH(CH₃)₂), 24.81 (CH(CH₃)₂), 24.79 (CH(CH₃)₂), 24.56 (CH(CH₃)₂), 24.19 (CH₃), 23.99 (CH(CH₃)₂), 22.62 (CH₃), 22.51 (CH(CH₃)₂) ppm; ¹⁹F{¹H} NMR (188.29 MHz): δ –75.76 (d, 3F, CF₃, ³*J* (¹⁹F-¹H) = 8 Hz) ppm; EI-MS (70 eV): *m/z* (%): 666 (100) [M]⁺. Found: C, 66.65; H, 7.24; N, 4.12%. Calcd for C₃₇H₄₇F₃GeN₂O (665.36), C, 66.78; H, 7.12; N, 4.21%.

Synthesis of [{HC(CMeNAr)₂}GeOCH(2-C₄H₃S)CF₃] (Ar = 2,6-*i*Pr₂C₆H₃) (6**).** A solution of 2,2,2-trifluorothiophene (0.175 g, 1.00 mmol in 5 mL toluene) was added by cannula to a solution of **1** (0.49 g, 1.00 mmol in toluene 20 mL) at room temperature. After 12 h all volatiles were removed in vacuum, and the remaining residue was extracted with *n*-hexane (25 mL). The extract was concentrated to about 15 mL and stored in a –30 °C freezer. Yellow crystals of **6** suitable for X-ray diffraction analysis had formed after two days. Yield: 0.570 g (85%); mp 171 °C; ¹H NMR (500 MHz, C₆D₆): δ 6.93–7.12 (m, 6H, Ar-*H*), 6.67 (d, 1H, C₄H₃S), 6.45 (dd, 1H, C₄H₃S), 6.26 (d, 1H, C₄H₃S), 5.04 (q, 1H, CH), 4.66 (s, 1H, γ -CH), 3.69 (sept, 1H, CH(CH₃)₂), 3.63 (sept, 1H, CH(CH₃)₂), 3.28 (sept, 1H, CH(CH₃)₂), 3.15 (sept, 1H, CH(CH₃)₂), 1.58 (d, 3H, CH(CH₃)₂), 1.48 (s, 3H, CH₃), 1.42 (s, 3H, CH₃), 1.41 (d, 3H, CH(CH₃)₂), 1.32 (d, 3H, CH(CH₃)₂), 1.20–1.14 (m, 6H, CH(CH₃)₂), 1.12 (d, 3H, CH(CH₃)₂), 1.07 (d, 3H, CH(CH₃)₂), 0.98 (d, 3H, CH(CH₃)₂) ppm; ¹³C{¹H} NMR (125.77 MHz, C₆D₆): δ 164.65, 164.34 (CN), 145.21–123.54 (Ar-C), 96.49 (γ -C), 75.43 (q,

CH), 28.93 (CH(CH₃)₂), 28.88 (CH(CH₃)₂), 28.76 (CH(CH₃)₂), 28.59 (CH(CH₃)₂), 26.46 (CH(CH₃)₂), 25.96 (CH(CH₃)₂), 24.89 (CH(CH₃)₂), 24.65 (CH(CH₃)₂), 24.45 (CH(CH₃)₂), 24.28 (CH(CH₃)₂), 24.05 (CH(CH₃)₂), 23.40 (CH(CH₃)₂), 22.68 (CH₃), 22.56 (CH₃) ppm; ¹⁹F{¹H} NMR (188.29 MHz): δ -76.29 (d, 3F, CF₃, ³J (¹⁹F-¹H) = 7 Hz) ppm; EI-MS (70 eV): *m/z* (%): 672 (100) [M]⁺. Found: C, 62.58; H, 6.68; N, 4.17; S, 5.33%. Calcd for C₃₅H₄₅F₃GeN₂OS (671.38), C, 62.61; H, 6.76; N, 4.17; S, 4.78%.

Synthesis of [HC(CMeNAr)₂]GeC(CO₂Me)CH₃] (Ar = 2,6-*i*Pr₂C₆H₃) (7). A solution of HC≡CCO₂Me (0.085 g, 1.00 mmol in 5 mL toluene) was added drop by drop by cannula to a solution of **1** (0.490 g, 1.00 mmol in toluene 15 mL) at room temperature. After overnight constant stirring at ambient temperature all volatiles were removed in vacuum, and the remaining residue was extracted with *n*-hexane (15 mL) and after removal of all the volatiles compound **7** was obtained as a yellow powder. Yield: 0.49 g (85 %); mp 161 °C. ¹H NMR (500 MHz, C₆D₆): δ 7.09–7.16 (m, 6H, Ar-*H*), 6.20 (br, 1H, CH₂), 5.82 (br, 1H, CH₂), 4.88 (s, 1H, γ-CH), 3.70 (sept, 2H, CH(CH₃)₂), 3.47 (s, 3H, CO₂CH₃), 3.46 (sept, 2H, CH(CH₃)₂), 1.58 (s, 6H, CH₃), 1.31 (d, 6H, CH(CH₃)₂), 1.27 (d, 6H, CH(CH₃)₂), 1.18 (d, 6H, CH(CH₃)₂), 1.15 (d, 6H, CH(CH₃)₂) ppm; EI-MS: *m/z* (%) 576 (100) [M]⁺. Found: C, 68.89; H, 8.16; N, 4.20%. Calcd for C₃₃H₄₆GeN₂O₂ (575.37), C, 68.89; H, 8.06; N, 4.87%.

Synthesis of [HC(CMeNAr)₂]GeC(CO₂Et)CHCO₂Et] (Ar = 2,6-*i*Pr₂C₆H₃) (8). A solution of diethylacetylene dicarboxylate (0.170 g, 1.00 mmol in 5 mL toluene) was added drop by drop by cannula to a solution of **1** (0.490 g, 1.00 mmol in toluene 15 mL) at room temperature. After 24 h under constant stirring at ambient temperature the red solution turned yellow. All volatiles were removed in vacuum, and the remaining residue was extracted with *n*-hexane (25 mL) and concentrated to about 15 mL and stored in a -30 °C freezer. Yellow crystals of **8** suitable for X-ray diffraction analysis are formed after two days. Yield: 0.53 g (80 %); mp 117 °C. ¹H NMR (500 MHz, C₆D₆): δ 7.07–7.15 (m, 6H, Ar-*H*), 6.68 (s, 1H, CH), 4.91 (s, 1H, γ-CH), 3.99 (q, 2H, CH₂), 3.91 (sept, 2H, CH(CH₃)₂), 3.82 (q, 2H, CH₂), 3.34 (sept, 2H, CH(CH₃)₂), 1.63 (s, 6H, CH₃), 1.34 (d, 6H, CH(CH₃)₂), 1.29 (d, 6H, CH(CH₃)₂), 1.21 (d, 6H, CH(CH₃)₂), 1.14 (d, 6H, CH(CH₃)₂), 1.05 (t, 3H, CH₂CH₃), 0.74 (t, 3H, CH₂CH₃) ppm. EI-MS: *m/z* (%) 633 (100) [M-Et]⁺. Found: C, 68.25; H, 9.83; N, 4.53%. Calcd for C₃₇H₅₂GeN₂O₄ (661.40), C, 69.29; H, 8.21; N, 4.75%.

Synthesis of [HC(CCH₃)(CMe)(NAr)₂Ge(Me)(NHNCHSiMe₃)] (Ar = 2,6-*i*Pr₂C₆H₃) (10). A solution of trimethylsilyl diazomethane (0.5 mL, 2 M, in *n*-hexane) was slowly added drop by drop to a Schlenk flask containing **9**[†] (0.50 g, 1 mmol) in 15 mL *n*-hexane. The solution slowly changed the color from red to yellow. After constant stirring overnight at ambient temperature all volatiles were removed in vacuum, and the remaining residue was extracted with *n*-hexane (15 mL) and after removal of all the volatiles from the extract compound **10** was obtained as a yellow solid. Yield: 0.45 g (72%). mp 103 °C. ¹H NMR (500 MHz, C₆D₆): δ 7.02–7.14 (m, 6H, Ar-*H*), 6.76 (s, 1H, NH), 5.78 (s, 1H, γ-CH), 5.26 (s, 1H, CH), 3.83 (s, 1H, CH₂), 3.71 (sept, 1H, CH(CH₃)₂), 3.58 (sept, 2H, CH(CH₃)₂), 3.51 (sept, 1H, CH(CH₃)₂), 3.21 (s, 1H, CH₂), 1.54 (s, 3H, CH₃), 1.41 (d, 3H, CH(CH₃)₂), 1.39 (d, 3H, CH(CH₃)₂), 1.22–1.27 (m, 12H,

CH(CH₃)₂), 1.16 (d, 3H, CH(CH₃)₂), 1.05 (d, 3H, CH(CH₃)₂), 0.17 (s, 9H, Si(CH₃)₃) ppm; ²⁹Si{¹H} NMR (125.77 Hz, C₆D₆): δ -8.76 (Si(CH₃)₃) ppm; EI-MS (70 eV): *m/z* (%): 605 (25) [M - Me]⁺, 491 (100) [M-Me, NHNCHTMS]⁺. Found: C, 65.81; H, 9.14%. Calcd. for C₃₄H₅₄GeN₄Si (619.54), C, 65.91; H, 8.79%.

Crystallographic details for compounds 3, 4, 5, 6, and 8. Suitable crystals of **3**, **4**, **5**, **6**, and **8** were mounted on a glass fiber and data was collected on an IPDS II Stoe image-plate diffractometer (graphite monochromated Mo Kα radiation, λ = 0.71073 Å) at 133(2) K. The data was integrated with X-Area. The structures were solved by Direct Methods (SHELXS-97)¹⁶ and refined by full-matrix least square methods against *F*² (SHELXL-97).¹⁶ All non-hydrogen atoms were refined with anisotropic displacement parameters. Crystallographic data are presented in Table 1.

Conclusion

Germanium(II) hydroxide has been prepared by the reaction of LGeH with nitrous oxide as a mono oxygen source. The corresponding reaction of LGeH with trimethylsilyl azide resulted in the formation of two compounds, the terminal germanium(II) azide and germanium(IV) diamide. Germanium(II) alkoxides have been prepared by the reaction of LGeH with activated ketones with the outcome of compounds containing the Ge(II)–O–CH core. Furthermore LGeH reacts with terminal and internal alkynes generating the vinyl substituted germylene, rather than the elimination of dihydrogen in the case of terminal alkynes. Compounds **2**, **3**, **5–8** represent a unique new class of germylene compounds with an electron lone pair on germanium(II) that is prone for complexation reaction with transition metal fragments. Moreover it is interesting to mention that most of the compounds are stable in air and moisture and highly soluble in common organic solvents. Finally it was shown that the trimethylsilyl diazomethane coordinates end-on to the germanium atom under migration of a hydrogen atom from a methyl group of the ligand backbone to the coordinate N atom.

Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft.

References

- For recent reviews of divalent germanium: (a) S. Nagendran and H. W. Roesky, *Organometallics*, 2008, **27**, 457–492; (b) M. F. Lappert and R. S. Rowe, *Coord. Chem. Rev.*, 1990, **100**, 267–292.
- (a) T. Hiyama, and T. Kusumoto, *Comprehensive Organic Synthesis*, Pergamon: Oxford, U.K., 1991, **8**, 763–792; (b) C. D. Beard and J. C. Craig, *J. Am. Chem. Soc.*, 1974, **96**, 7950–7954; (c) T. Saegusa, Y. Ito, S. Kobayashi and K. Hirota, *J. Am. Chem. Soc.*, 1967, **89**, 2240–2241; (d) J. A. Connor, P. D. Rose and R. M. Turner, *J. Organomet. Chem.*, 1973, **55**, 111–119; (e) G. A. Razuvaev, *J. Organomet. Chem.*, 1980, **200**, 243–259; (f) G. Manuel, G. Bertrand and P. Mazerolles, *J. Organomet. Chem.*, 1978, **146**, 7–16; (g) G. F. Bradley and S. R. Stobart, *J. Chem. Soc., Dalton Trans.*, 1974, 264–269; (h) R. D. Adams, F. A. Cotton, W. R. Cullen, D. L. Hunter and L. Mihichuk, *Inorg. Chem.*, 1975, **14**, 1395–1399; (i) U. Blaukat and W. P. Neumann, *J. Organomet. Chem.*, 1973, **63**, 27–39.
- L. W. Pineda, V. Jancik, K. Starke, R. B. Oswald and H. W. Roesky, *Angew. Chem.*, 2006, **118**, 2664–2667; L. W. Pineda, V. Jancik, K. Starke, R. B. Oswald and H. W. Roesky, *Angew. Chem., Int. Ed.*, 2006, **45**, 2602–2605.

- 4 Y. Ding, Q. Ma, H. W. Roesky, R. Herbst-Irmer, I. Usón, M. Noltemeyer and H.-G. Schmidt, *Organometallics*, 2002, **21**, 5216–5220.
- 5 A. Jana, D. Ghoshal, H. W. Roesky, I. Objartel, G. Schwab and D. Stalke, *J. Am. Chem. Soc.*, 2009, **131**, 1288–1293.
- 6 A. Jana, S. S. Sen, H. W. Roesky, C. Schulzke, S. Dutta and S. K. Pati, *Angew. Chem.*, 2009, **121**, 4310–4312; A. Jana, S. S. Sen, H. W. Roesky, C. Schulzke, S. Dutta and S. K. Pati, *Angew. Chem., Int. Ed.*, 2009, **48**, 4246–4248.
- 7 (a) C. Ni, B. D. Ellis, G. J. Long and P. P. Power, *Chem. Commun.*, 2009, 2332–2334; (b) Y. Xiong, S. Yao and M. Driess, *J. Am. Chem. Soc.*, 2009, **131**, 7562–7563.
- 8 L. W. Pineda, V. Jancik, H. W. Roesky, D. Neculai and A. M. Neculai, *Angew. Chem.*, 2004, **116**, 1443–1445; L. W. Pineda, V. Jancik, H. W. Roesky, D. Neculai and A. M. Neculai, *Angew. Chem., Int. Ed.*, 2004, **43**, 1419–1421.
- 9 A. Jana, B. Nekoueishahraki, H. W. Roesky and C. Schulzke, *Organometallics*, 2009, **28**, 3763–3766.
- 10 H. Zhu, J. Chai, H. Fan, H. W. Roesky, C. He, V. Jancik, H.-G. Schmidt, M. Noltemeyer, W. A. Merrill and P. P. Power, *Angew. Chem.*, 2005, **117**, 5220–5223; H. Zhu, J. Chai, H. Fan, H. W. Roesky, C. He, V. Jancik, H.-G. Schmidt, M. Noltemeyer, W. A. Merrill and P. P. Power, *Angew. Chem., Int. Ed.*, 2005, **44**, 5090–5093.
- 11 (a) A. C. Filippou, P. Portius and G. Kociok-Köhn, *Chem. Commun.*, 1998, 2327–2328; (b) M. Veith and A. Rammo, *Z. Anorg. Allg. Chem.*, 2001, **627**, 662–668.
- 12 M. Denk, R. K. Hayashi and R. West, *J. Am. Chem. Soc.*, 1994, **116**, 10813–10814.
- 13 (a) N. J. Hardman, C. Cui, H. W. Roesky, W. H. Fink and P. P. Power, *Angew. Chem.*, 2001, **113**, 2230–2232; N. J. Hardman, C. Cui, H. W. Roesky, W. H. Fink and P. P. Power, *Angew. Chem., Int. Ed.*, 2001, **40**, 2172–2174; (b) R. J. Wright, A. D. Phillips, T. L. Allen, W. H. Fink and P. P. Power, *J. Am. Chem. Soc.*, 2003, **125**, 1694–1695.
- 14 Y. Ding, H. Hao, H. W. Roesky, M. Noltemeyer and H.-G. Schmidt, *Organometallics*, 2001, **20**, 4806–4811.
- 15 R. J. P. Corriu and J. J. E. Moreau, *J. Organomet. Chem.*, 1972, **40**, 55–72.
- 16 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, **64**, 112–122.