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Guanidinate stabilized germanium(II) and tin(II) amide complexes and their catalytic activity for aryl isocyanate cyclization

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ABSTRACT

Two different synthetic routes for the preparation of guanidinate stabilized germanium(II) and tin(II) amide complexes have been established. First, the reaction of one equiv of bulky guanidine ligand either L^1H or L^2H [L^1 = {ArNC (N^iPr_2)NAr} (Ar = 2,6-Me_2–C_6H_3) and L^2 = {Ar′NC (N^iPr_2) NAr′}(Ar′ = 2,6-$^iPr_2$-C_6H_3)] with two equiv of $KN(SiMe_3)_2$ and one equiv of metal dihalide *i.e.*, MCl_2{M = Ge(dioxane) and Sn} led to the formation of guanidinate supported germanium(II) amide, *i.e.*, $L^1GeN(SiMe_3)_2$ (**1**) and tin amide, *i.e.*, $L^1SnN(SiMe_3)_2$ (**2**) and $L^2SnN(SiMe_3)_2$ (**3**) complexes, respectively. Second, deprotonation of L^1H upon treatment with $M[N(SiMe_3)_2]_2$ (M = Ge and Sn) in C_6D_6 at 80 °C for 12 h, afforded the compounds $L^1MN(SiMe_3)_2$ M = Ge(**1**) and Sn(**2**), respectively. X-ray crystal structures of **1** and **2** revealed that both are in monomeric and metal centers in distorted tetrahedral environments with one vertex occupied by a stereo chemically active lone pair of electrons. Furthermore, compounds **1**, **2** and **3** were tested for the catalytic activity in the cyclotrimerization of arylisocyanates, which are exhibiting as excellent catalysts.

Introduction

In 1970, Lappert and coworkers reported the first transition metal guanidinate complex [1]. Since then, a large number of guanidinate supported coordination complexes involving metals from across the periodic table have been described [2]. In recent years, the chemistry of guanidinate stabilized low oxidation state metal complexes with metal–metal (single or multiple bonded) or metal with non bonded electrons or both is the emerging area [3]. To isolate such unusual molecules the utilization of bulky guanidine ligand systems are very important, because these can provide steric and/or electronic protection from processes such as disproportionation, oligomerization etc. In this context, some benchmark inventions in the main group chemistry, notably, in 2007, Jones et al. reported bulky guanidinate stabilized magnesium complex with Mg–Mg bond, where the magnesium oxidation state is +1 [4]. Same research group has also been isolated guanidinate stabilized low valent Ga(I) [5] complex and Ge(I) complex containing Ge–Ge bond [6] with non bonded electrons at each metal center. On the other hand, the chemistry of the related amidinate and β-diketiminate supported low valent and/or low oxidation of main group metal complexes is well documented [7]. In group 14 low valent heteroleptic complexes, particularly, low valent amides, Richeson and co-workers reported amidinate germanium(II) and tin(II) amides [8]. Roesky et al., demonstrated the amidinate and β-diketiminate stabilized tin amides [9]. In 2004, Lappert et al. reported structurally characterized β-diketiminate stabilized low valent tin compounds including tin amide compound [10]. In contrast, guanidinate supported low valent group 14 complexes are poorly developed. Although, there are some reports on guanidinate supported germylenes, stannylenes and plumbylenes [11]. Very recently, Tacke et al. reported the structurally characterized guanidinate supported silicon amide complex [12]. Recently, Růžička and his coworkers described guanidinate stabilized tin amide complexes, but those are not structurally characterized [13]. However, in 2009, Chen, Rheingold and coworkers reported the structurally characterized germanium(II) amido complex, which is prepared by the insertion of carbodiimide into the Ge–N bond in diaminogermylene [14]. Apart from this, to the best of our knowledge no other structurally characterized guanidinate supported germanium(II) and tin(II) amide complexes are reported in the literature.

Herein, we report the synthesis and characterization of bulky guanidinate supported germanium(II) and tin(II) amide complexes.

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Furthermore, we have shown these are effective catalysts for the cyclotrimerization of arylisocyanates.

Results and discussion

Syntheses of heteroleptic germanium(II) and tin(II) amide complexes

Guanidines are compounds containing N_3C core, in which central sp^2 hybridized carbon atom is connected to one imino group and two amino groups. Various synthetic routes have been reported for the preparation of guanidines [15]. Among all, the important and widely used method of preparation, is the addition of metallated amides to bulky aryl carbodiimides (RN = C=NR), and followed by aqueous work up led to the formation of bulky aryl guanidines.

For this work we chose two bulky guanidine L^1H and L^2H [L^1 = {ArNC(N^{i}Pr$_2$)NAr} (Ar = 2,6-Me$_2$–C$_6$H$_3$) and [L^2 = {Ar′NC(N^{i}Pr$_2$)NAr′}(Ar′ = 2,6-^{i}Pr$_2$-C$_6$H$_3$)] ligand systems (Chart 1).

L^2H reported by Jones and coworkers by treating metallated amide (LiN^{i}Pr$_2$) with ^{dipp}carbodiimide *i.e.*, (ArN=C=NAr); (Ar = 2, 6-^{i}Pr$_2$-C$_6$H$_3$) and followed by aqueous work up [16]. Thus, bulky aryl carbodiimides are important precursors for the preparation guanidines and related amidines. Classical method of preparation of bulky aryl carbodiimides is the desulphurization of thiourea in the presence of HgO and magnesium sulfate in toluene at reflux temperature [17]. Recently, our group has been investigated the new synthetic route for an easy access of various bulky aryl symmetrical and unsymmetrical carbodiimides by the desulphurization of the corresponding thioureas. L^1H has been prepared by using ^{xyl}carbodiimide *i.e.*, (ArN=C=NAr); (Ar = 2,6-Me$_2$–C$_6$H$_3$) and following the same method reported by Jones and coworkers.

Reaction of one equivalent of free bulky guanidine either L^1H or L^2H with two equivalents of potassium hexamethyldisilazide *i.e.*, KN(SiMe$_3$)$_2$ in tetrahydrofuran at 0 °C and followed by metathesis reaction with one equivalent of metal dihalide of germanium(dioxane) or tin in THF at 0 °C led to the formation of corresponding guanidinate supported metal amides (Scheme 1).

Alternatively, we have investigated another synthetic route for the preparation of guanidinate supported germanium(II) and tin(II) amide complexes. For this synthetic route, NMR scale reactions were conducted by using Young valve NMR tube. Treatment of L^1H with M[N(SiMe$_3$)$_2$]$_2$ (M = Ge or Sn) in C_6D_6 at 80 °C for 12 h, afforded the guanidinate germanium(II) and tin(II) amide

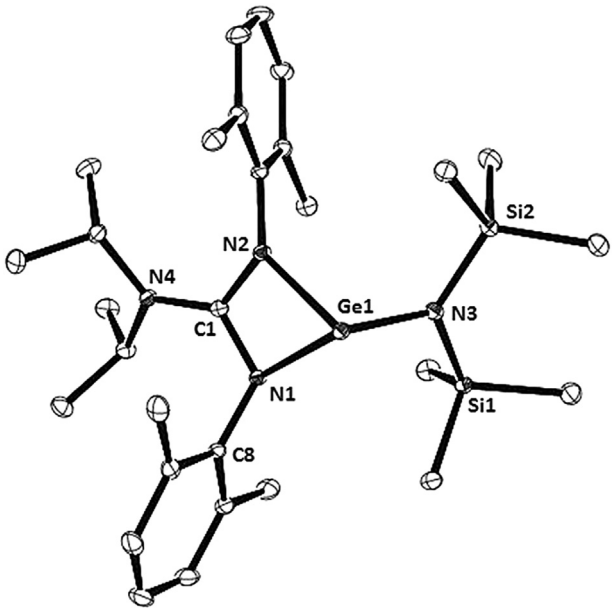


Fig. 1. Molecular Structure of **1**. ORTEP diagram of $C_{29}H_{50}N_4GeSi_2$ with the probability ellipsoids drawn at the 35% level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Ge1–N3 1.9395(12), Ge1–N1 2.0994(12), Ge1–N2 2.0424(11), Si1–N3 1.7292(13), Si2 –N3 1.7352(13), N1–C1 1.3614(18), N2–C1 1.3407(18), N4–C1 1.3716(17), N1–C8 1.4411(18); N2–Ge1–N1 64.12(5), N3–Ge1–N1 105.80(5), N3–Ge1–N2 102.15(5), Si1–N3–Si2 125.34(7), Si1–N3–Ge1 117.18(7), N1–C1–N2 108.95(13), C1–N1–Ge1 91.22(8).

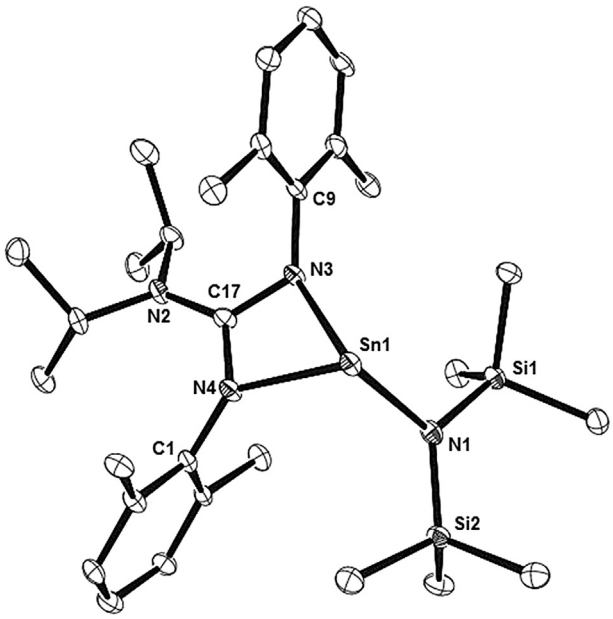


Fig. 2. Molecular Structure of **2**. ORTEP diagram of $C_{29}H_{50}N_4SnSi_2$ with the probability ellipsoids drawn at the 35% level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Sn1–N1 2.149(5), Sn1–N3 2.275(5), Sn1–N4 2.234(4), Si1–N1 1.716(5), Si2–N1 1.723(6), C17–N4 1.334(8), C17–N3 1.364(7), C17–N2 1.380(7), N4–C1 1.414(7); N3–Sn1–N4 59.13(17), N1–Sn1–N3 102.4(18), N1–Sn1–N4 101.19(18), N4–C17–N3 111.1(5), Si1–N1–Si2 124.2(3), Si1–N1–Sn1 116.9(3), C17–N4–Sn1 95.6(3).

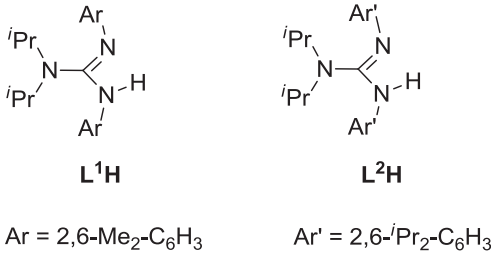
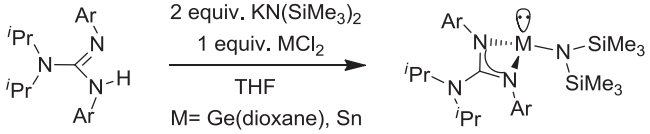


Chart 1. Ligand systems; L^1H and L^2H.

Alternatively, we have investigated another synthetic route for the preparation of guanidinate supported germanium(II) and tin(II) amide complexes. For this synthetic route, NMR scale reactions were conducted by using Young valve NMR tube. Treatment of L^1H with M[N(SiMe$_3$)$_2$]$_2$ (M = Ge or Sn) in C_6D_6 at 80 °C for 12 h, afforded the guanidinate germanium(II) and tin(II) amide



Ar = 2,6-Me$_2$C$_6$H$_3$; M = Ge (**1**), Sn (**2**)
= 2,6-^{i}Pr$_2$C$_6$H$_3$; M =Sn (**3**)

Scheme 1. Syntheses of compounds **1**–**3**.

complexes, **1** and **2**, respectively. Deprotonation of N–H moiety of L^1H upon treatment with metal bis(amide) through an elimination of $NH(SiMe_3)_2$ which resonates at 0.9 ppm was observed in ^1H NMR spectroscopy (Scheme 2).

All these compounds (**1**–**3**) are readily soluble in organic solvents such as tetrahydrofuran, diethyl ether, toluene, benzene and hexane. Compounds **1**, **2**, and **3** were isolated as colorless, crystalline solids in 88%, 86% and 75% yields, respectively. Moreover, compounds **1**–**3** were characterized by multinuclear (^1H, ^{13}C and ^{29}Si) NMR and IR spectroscopy methods. Furthermore, compounds **1** and **2** were confirmed by single crystal X-ray structural analysis.

^1H and ^{13}C NMR spectra display the expected set of ligands proton and carbon signals. In the ^1H NMR, the complete disappearance of N–H proton of L^1H and L^2H ligand systems gives a clue for the formation of new products. And also appearance of amido resonance *i.e.*, $MN(SiMe_3)_2$, in compounds **1**–**3** (0.13–0.26 ppm) indicates the formation of guanidinate stabilized metal amido substituent. In the ^{13}C NMR, N3*C* resonance exhibit for compounds **1**, **2** and **3** at 165, 168.6 and 163.6 ppm, respectively. This is typical N3*C* resonance range (163–168.5 ppm) in ^{13}C NMR spectra, which is well in agreement with other related guanidinate metal complexes. The chemical shifts of all the ^{13}C and ^1H NMR signals observed for **1**–**3** appears slightly downfield from the corresponding signals in the free L^1H an L^2H. ^{29}Si NMR spectra for **1**–**3** exhibit in the range of −3.68 to −4.10 ppm. This is the expected ^{29}Si NMR range for the four coordinated silicon atom [18]. Efforts were made to get high resolution mass spectra for compounds **1**–**3** and turned to be unsuccessful.

X-ray crystal structures of compound 1 and 2

Maintaining an *n*-hexane solution of **1** at −30 °C overnight resulted in colorless single crystals suitable for X-ray structure analysis. Compound **1** crystallizes in the triclinic space group $P\bar{1}$ (Fig. 1).

The metal center of compound **1** resides in distorted tetrahedral environment with one vertex occupied by a stereo chemically active lone pair of electrons. The sum of angles around the germanium atom is 271.92°. An overall pyramidal ligand array around the germanium center which consist with one bidentate guanidinate and the bis(trimethylsilyl) amido nitrogen center. The Ge–N_{amido} bond distance in **1** 1.9395(12) Å is slightly longer than those of Chen, Rheingold and coworker's guanidinate Ge amide complex [14] *i.e.*, [Ge^{II}($N(SiMe_2CH_2CH_2Me_2Si)$) (^{i}PrNCN($SiMe_2CH_2CH_2Me_2Si$)N^{i}Pr] (1.880(2) Å) and. Richeson's amidinato germanium amide complex $Ge^{II}[N(SiMe_3)_2][Me_3SiNC(^tBu)NSiMe_3]$ (Ge–N_{amido} (1.9101 (19) Å) [8b].

The bond distances between germanium atom and two nitrogen atoms of the guanidinate ligand, *i.e.*, Ge1–N1 2.0994(12) Å and Ge1–N2 2.0424(11) Å are well in agreement with bond distances observed in [Ge^{II}($N(SiMe_2CH_2CH_2Me_2Si)$) (^{i}PrNCN($SiMe_2CH_2CH_2Me_2Si$)N^{i}Pr] (Ge1–N1 2.0133(17), Ge-N2 2.0328(17) Å) and $Ge^{II}[N(SiMe_3)_2][Me_3SiNC(^tBu)NSiMe_3]$ (Ge1–N1 2.037(2), Ge–N2 2.042(2) Å). However, these bond lengths are slightly longer in comparison to the other reported values [1.993(3) and 2.003(3) Å in [Ge^{II}(Giso)Cl] [Giso = {(2,6-$C_6H_3^iPr_2N)_2CNCy_2$}] [6].

The molecular structure of **2** has been determined by single crystal X-ray diffraction analysis (Fig. 2). Colorless crystals of **2** suitable for single crystal X-ray analysis were obtained from an *n*-hexane solution at −30 °C after 1 day. Compound **2** crystallizes in the monoclinic space group *P*2(1)/*n*. Selected bond lengths and bond angles are given in the caption of Fig. 2. The geometry and the coordination number of the tin atom in compound **2** are same as those observed in compound **1**. However, N3–Sn1–N4 bond angle 59.13(17)° in **2** which is acute than that of compound **1** (N2–Ge1–N1 64.12(5)°). The Sn–N_{amido} bond distance in compound **2** is 2.149(5) Å is longer than that of Ge–N_{amido} bond distance of **1** (1.9395(12) Å), this is expected due to the large covalent radii of tin element (1.39 Å) in comparison to that of germanium atom (1.20 Å) [19]. However, Sn–N_{amido} bond length is well in agreement with related amidinate stabilized tin(II) amide complexes such as $Sn^{II}[N(SiMe_3)_2][Me_3SiNC(^tBu)NSiMe_3]$ (2.121 (5) Å) and $Sn^{II}[N(SiMe_3)_2][^tBu\ NC(Ph)N\ ^tBu]$ (2.116 (6) Å).

The bond lengths between tin and two nitrogen atoms of the guanidinate ligand *i.e.*, Sn1–N3 2.275(5) Å and Sn1–N4 2.234(4) Å are longer than those observed in compound **1** (Ge1–N1 2.0994(12) Å and Ge1–N2 2.0424(11) Å). The C–N bond distances in both compound **1** (C1–N1 (1.3614(18) Å) and C1–N2 (1.3407(18) Å)) and **2** (C17–N3 (1.364(7) Å) and C17–N4 (1.334(8) Å)) are consistent with delocalization of the π bond in the N–C–N core of the ligand.

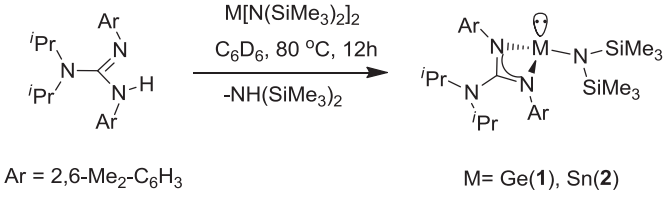
Catalytic activity

*Catalytic cyclotrimerization of arylisocyanates with complexes **1**–**3***

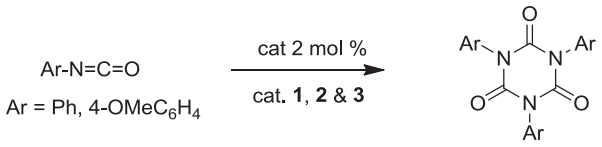
In recent years, the main group organometallic chemistry has been accepted for its catalytic potential, and promising alternative to expensive transition and lanthanide based catalysis [20]. We were inspired by the work done by two research groups, Richeson and Harder for the catalytic cyclotrimerization of arylisocyanates by using amidinate supported group 14 metal complexes and iminophosphorane chelated calcium carbene, respectively [8b,21]. We presumed such catalytic studies might be attractive targets by employing the bulky guanidinate supported low valent germanium(II) and tin(II) amide complexes. In this connection, we have observed that guanidinate supported germanium(II) and tin(II) amides are very good catalysts for the cyclotrimerization of arylisocyanates to produce triarylisocyanurates (Scheme 3).

Triarylisocyanurates, the aromatic compounds obtaining from cyclotrimerization of arylisocyanates, are used to upgrade the physical properties of a wide range of polyurethanes and coating materials [22]. And also, these are very effective activators for anionic polymerization of caprolactams to nylon-6 [23].

Various isocyanate trimerization catalysts have been described, with a majority of the conventional catalysts being anions or neutral Lewis bases [24]. Recently, Louie et al., has shown *N*-heterocyclic carbenes as efficient catalysts for the cyclotrimerization of isocyanates [25]. And also, organometallic compounds which include both transition [26] and lanthanide [27] based catalysts for trimerization of isocyanates is well documented. On the other hand



Scheme 2. Synthesis of compounds **1** and **2**.



Scheme 3. Compounds **1**–**3** catalyzed cyclotrimerization of arylisocyanates.

main group organometallic compounds based catalysis of cyclotrimerization of aryl isocyanate is poorly documented, though there are some reports [28].

The addition of complexes **1**–**3** (2 mol %) to neat arylisocyanates and followed by stirring at room temperature for 1 h led to the formation of cyclotrimerized products, *i.e.*, triarylisocyanurates in quantitative yields. Our catalysts show a high degree of selectivity of only triaryl isocyanurate formation (93–96% yield). No other isomeric products were observed. Moreover, catalysts **1**–**3** can be recovered and confirmed by the ^{1}H NMR without any decomposition products. The catalytic activity of guanidinate stabilized germanium(II) and tin(II) amide complexes **1**–**3** along with data for some related catalysts is summarized in Table 1.

From Table 1 (Entries 1–6), it is very clear that more bulky guanidinate stabilized tin(II) amide catalyst **3** is showing slightly better catalytic activity compare to **1** and **2**. Further, we extended these studies to test the catalytic activity of germanium bis(amide) and tin bis(amide) compounds (Entry 7 & 8). These compounds show less activity compare to catalysts **1**–**3** (Entries 1–6). This suggests that basicity of the proligand attached to metal site and Lewis acidity of the metal center play a role in the activity of these complexes. And also, it might be a solubility effect. Homoleptic metal catalysts may form polymeric insoluble structures in solution. However, the bulky guanidine ligand which is attached to metal atom keeps the catalyst active in solution. Furthermore, it is very important to note that bulky guanidinato stabilized tin(II) amide complex which is better catalyst than other related amidinato tin(II) amide complexes (Entries 9–13).

Conclusion

In conclusion, we have presented the synthesis and characterization of three new metal complexes of bulky guanidinate stabilized germanium(II) and tin(II) amides, which can be readily prepared by two synthetic routes; i) deprotonation of free bulky guanidine ligand with two equiv of $KN(SiMe_3)_2$ and followed by metathesis reaction with one equiv of metal dihalide of germanium or tin ii) deprotonation of ligand with metal bis(amide) of germanium or tin. Furthermore, compounds **1** and **2** were confirmed by single crystal X-ray structural analysis, and revealed that both are monomeric in nature. Moreover, compounds **1**–**3** display excellent catalytic activity for the cyclotrimerization of aryl isocyanurates.

Table 1
Data for the catalytic cyclotrimerization of arylisocyanates[a].

Entry	Substrate	Catalyst	Time (min)	Isolated yield (%)
1	C_6H_5NCO	**1**	60	93
2	*P*-$MeOC_6H_4NCO$	**1**	60	94
3	C_6H_5NCO	**2**	30	95
4	*P*-$MeOC_6H_4NCO$	**2**	30	96
5	C_6H_5NCO	**3**	20	97
6	*P*-$MeOC_6H_4NCO$	**3**	20	96
7	*P*-$MeOC_6H_4NCO$	$Ge[N(SiMe_3)_2]_2$[b]	1440	83
8	*P*-$MeOC_6H_4NCO$	$Sn[N(SiMe_3)_2]_2$	480	91
9	C_6H_5NCO	$[Me_3SiNC(^tBu)NSiMe_3]Sn[N(SiMe_3)_2]$[c]	210	94
10	C_6H_5NCO	$[Me_3SiNC(^tBu)NSiMe_3]Ge[N(SiMe_3)_2]$[c]	16	98
11	C_6H_5NCO	$Sn[Me_3SiNC(Me)NSiMe_3]_2$[c]	10	35 (52% dimer)
12	C_6H_5NCO	$[CyNC(Me)NCy]Sn[N(SiMe_3)_2]S_4$[c]	12	95
13	C_6H_5NCO	$[CyNC(^tBu)NCy]Sn[N(SiMe_3)_2]S_4$[c]	60	68

[a] All reactions were carried out in neat aryl isocyanate (substrates) at room temperature and catalysts **1**–**3** in 2 mol %.
[b] 5 mol % catalyst was used.
[c] Data from Ref. [8].

Experimental section

General

All manipulations of air and moisture sensitive materials were performed with the rigorous barring of oxygen and moisture in flamed Schlenk-type glassware either on a duel manifold Schlenk line, or in a nitrogen-filled MBraun glovebox. NMR scale reactions were conducted in Young valve NMR tubes and sealed in a glovebox. NMR spectra were recorded on Bruker AV 400 MHz spectrometer for ^{1}H NMR ($^{13}C\{^{1}H\}$ NMR 100 MHz and ^{29}Si $\{^{1}H\}$ NMR 80 MHz). IR Spectra were recorded in Perkin–Elmer FT–IR Spectrometer. Dry *n*-hexane and tetrahydrofuran(THF) solvents were collected from MBraun Solvent Purification System and degassed by freeze-pump-thaw cycles, prior to use. C_6D_6 was purchased from Sigma–Aldrich and dried over sodium before distillation under nitrogen and storage over molecular sieves. L^2H [16] and $Ge[N(SiMe_3)_2]_2$ [29] were prepared according to reported literature procedures. $SnCl_2$, $GeCl_2$ (dioxane), $KN(SiMe_3)_2$, $Sn[N(SiMe_3)_2]_2$ were purchased from Sigma–Aldrich and used without further purification.

Synthesis and characterization of compounds 1–3

*Preparation of [{ArNC(N^{i}Pr$_2$)NAr]GeN(SiMe$_3$)$_2$}; (Ar = 2,6-Me$_2$–C$_6$H$_3$)] (**1**)*

A solution of L^1H (0.25 g, 0.711 mmol, 1.0 equiv) in THF (10 mL) was added drop by drop to a stirred suspension of $KN(SiMe_3)_2$ (0.29 g, 1.43 mmol, 2.01 equiv) in THF (5 mL) at 0 °C and stirring was continued for 12 h at room temperature. The resulting solution was added drop by drop to a stirred suspension of $GeCl_2$ (dioxane) (0.165 g, 0.711 mmol, 1.0 equiv) in THF (5 mL) at 0 °C under stirring for another 24 h at room temperature. After removal of all the volatiles, the residue was extracted with *n*-hexane (20 mL) and concentrated to about 5 mL and finally stored in a −30 °C freezer. Colorless crystals of compound suitable for X-ray diffraction analysis are obtained after one day. Yield: 0.73 g (88%). M. p. = 120–122 °C. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 0.26 (s, 18H, $NSi(CH_3)_3$), 0.67 (d, J = 8 Hz, 12H, $CH(CH_3)_2$), 2.58 (s, 12H, CH_3), 3.90 (sept, J = 8 Hz, 2H, $CH(CH_3)_2$), 6.87–6.93 (m, 4H, Ar–*H*), 7.00 (d, J = 8 Hz, 2H, Ar–*H*) ppm. ^{13}C $\{^{1}H\}$ NMR (100 MHz, C_6D_6, 25 °C): δ = 5.6 (Si–*C*), 20.7 (Ar–CH_3), 21.0(Ar–CH_3), 24.6 (*i*Pr–CH_3), 50.7 (N-*i*Pr–CH), 125.6 (Ar–*C*), 129.6 (Ar–*C*), 129.6 (Ar–*C*), 136.0 (Ar–*C*), 136.3 (Ar–*C*), 144.3 (Ar–*C*), 165.0 (NCN) ppm. ^{29}Si $\{^{1}H\}$ NMR (80 MHz, C_6D_6, 25 °C): δ = −3.68 ($NSi(CH_3)_3$) ppm. IR (KBr) ν (cm^{-1}): 2924(s), 2854(s), 1459(m), 1377(s), 932(w), 721(m).

*Preparation of [{ArNC(N^{i}Pr$_2$)NAr}SnN(SiMe$_3$)$_2$}; (Ar = 2,6-Me$_2$–C$_6$H$_3$)] (**2**)*

A solution of L^1H (0.5 g, 1.422 mmol, 1.0 equiv.) in THF (10 mL) was added drop by drop to a stirred suspension of $KN(SiMe_3)_2$ (0.57 g, 2.85 mmol, 2.01 equiv) in THF (5 mL) at 0 °C and stirring was continued overnight at room temperature. The resulting solution was added drop by drop to a stirred suspension of $SnCl_2$ (0.269 g, 1.422 mmol, 1.0 equiv) in THF (5 mL) at 0 °C and continued the stirring for another 24 h at room temperature. After removal of all the volatiles, the residue was extracted with *n*-hexane (20 mL) and concentrated to about 5 mL and finally stored in a −30 °C freezer. Colorless crystals of compound suitable for X-ray diffraction analysis are formed after one day. Yield: 0.71 g (86%). M. p. = 125–127 °C. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 0.20 (s, 18H, $NSi(CH_3)_3$), 0.66 (d, J = 8 Hz, 12H, $CH(CH_3)_2$), 2.50 (s, 6H, CH_3), 2.60 (s, 6H, CH_3), 3.84 (sept, J = 8 Hz, 2H, $CH(CH_3)_2$), 6.85–6.88 (t, 2H, Ar–*H*), 6.93 (d, J = 8 Hz, 2H, Ar–*H*), 7.01 (d, J = 8 Hz, 2H, Ar–*H*) ppm. ^{13}C $\{^{1}H\}$ NMR (100 MHz, C_6D_6, 25 °C): δ = 5.4 (Si–*C*), 20.6 (Ar–CH_3),

Table 2
Crystallographic details for **1** and **2**.

Compound	**1**	**2**
Formula	$C_{29}H_{50}GeN_4Si_2$	$C_{29}H_{50}SnN_4Si_2$
CCDC	984884	984883
Mol. mass	583.50	629.60
Temperature	100 K	100 K
Size (mm)	0.065 × 0.051 × 0.038	0.051 × 0.038 × 0.024
Crystal system, space group	Triclinic, $P\bar{1}$	Monoclinic, $P2(1)/n$
a (Å)	8.9831(2)	8.983(12)
b (Å)	12.2308(2)	12.081(17)
c (Å)	16.3278(3)	29.469(4)
α (°)	70.6050(10)	90.000
β (°)	86.1720(10)	96.122
γ (°)	69.0760 (10)	90.000
V (Å^3)	1577.81(5)	3180(2)
Z, calculated density	2, 1.228 Mg/m^3	4, 1.315
Absorption coefficient	1.070 mm^{-1}	0.902 mm^{-1}
F(000)	624	1320
Theta range for data collection	3.57–30.53 deg.	2.84–28.36 deg
Limiting indices	$-12 \le h \le 10$, $-17 \le k \le 17$, $-22 \le l \le 23$	$-6 \le h \le 11$, $-16 \le k \le 16$, $-39 \le l \le 33$
Reflections collected/unique	28,696/9470 [R(int) = 0.0372]	28,298/7794 [R(int) = 0.1355]
Completeness to theta	98.1%	98.2%
Absorption correction	SPHERE	SPHERE
Max. and min. transmission	0.7461 and 0.6296	0.7457 and 0.4420
Data/restraints/parameters	9470/0/339	7794/0/339
Goodness-of-fit on F^2	1.040	1.034
Final R indices [I > 2sigma(I)]	$R1$ = 0.0326, w$R2$ = 0.0772	$R1$ = 0.0726, w$R2$ = 0.1806

20.7 (Ar–CH_3), 24.8 (N-*i*Pr–CH_3), 51.0 (*i*Pr–*C*H), 125.1 (Ar–*C*), 129.4 (Ar–*C*), 129.6 (Ar–*C*), 134.9 (Ar–*C*), 135.8 (Ar–*C*), 145.2 (Ar–*C*), 168.5 (NCN) ppm. ^{29}Si {^{1}H} NMR (100 Hz, C_6D_6, 25 °C): −3.69 N*Si*(CH_3)$_3$) ppm. IR (KBr) ν (cm^{-1}): 2923(s), 2853(s), 1462(m), 1377(m), 721(m).

Preparation of [{Ar′NC(N^{i}Pr$_2$)NAr′}SnN(SiMe$_3$)$_2$}; (Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$) (**3**)

The compound was synthesized by using a similar procedure to that employed for the preparation of **2**, but by using L^{2}H (0.25 g, 0.539 mmol), KN($SiMe_3$)$_2$ (0.217 g, 1.08 mmol) and $SnCl_2$ (0.103 g, 0.539 mmol).Yield: 0.3 g (75%). M. p. = 141–142 °C. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 0.13 (s, 18H, Si(CH_3)$_3$), 0.76 (d, J = 8 Hz, 12H, CH(CH_3)$_2$), 1.28 (d, J = 8 Hz, 6H, CH(CH_3)$_2$), 1.345 (d, J = 4 Hz, 12H, CH(CH_3)$_2$), 1.50 (d, J = 8 Hz, 6H, CH(CH_3)$_2$), 3.62 (sept, J = 7 Hz, 2H, *CH*(CH_3)$_2$), 3.76 (sept, J = 6 Hz, 2H, *CH*(CH_3)$_2$), 4.03 (sept, J = 6.6 Hz, 2H, *CH*(CH_3)$_2$), 7.04–7.10 (m, 6H, Ar–*H*) ppm. ^{13}C {1H} NMR (100 MHz, C_6D_6, 25 °C): δ = 5.8 (Si–*C*), 23.9 (*i*Pr–CH_3), 24.4 (*i*Pr–CH_3), 24.6 (*i*Pr–CH_3), 27.3 (*i*Pr–CH_3), 28.5 (N-*i*Pr–CH_3), 28.7 (*i*Pr–CH), 28.8 (*i*Pr–*C*H), 50.5 (N-*i*Pr–*C*H), 124.7 (Ar–*C*), 125.8 (Ar–*C*), 142.5 (Ar–*C*), 144.0 (Ar–*C*), 145.6 (Ar–*C*), 163.5 (NCN) ppm. ^{29}Si {^{1}H} NMR (80 MHz, C_6D_6, 25 °C): −4.10 (N*Si*(CH_3)$_3$) ppm. IR (KBr) ν (cm^{-1}): 2921(w), 2726(m), 1456(m), 1377(m), 1306(m), 936(w), 722(s).

Single crystal structure determinations of 1 and 2

The crystallographic data for **1** and **2** are summarized in Table 2. Figs. 1 and 2 show pictures of molecular structure of **1** and **2**, as found in the crystal lattices. The crystals were mounted on a glass fiber. Data were collected with a Bruker SMART D8 goniometer equipped with an APEX CCD detector and with an INCOATEC micro source (MoKα radiation, λ = 0.71073 Å, multilayer optics). Temperature was controlled using an Oxford Cryostream 700 instrument. Intensities were integrated with SAINT+ [30] and corrected for absorption with SADABS [31]. The structure was solved by direct methods and refined on F^2 with SHELXL-97 [32]. Hydrogen atoms were fixed at calculated positions and their positions were refined by a riding model. All non-hydrogen atoms were refined with anisotropic displacement parameters.

General procedure for the preparation of triarylisocyanurate

*Procedure for the compound **1** catalysed cyclotrimerization of phenyl isocyanate*

To a complex **1** (0.029 g, 0.0462 mmol) neat phenyl isocyanate (0.275 g, 2.31 mmol) was added. After 60 min the reaction mixture became solidified. The resulting white solid was crushed into powder and washed with benzene 5 times (5 mL × 5) repeatedly, filtered off and dried in vacuum and yielded of (PhNCO)$_3$. The product was confirmed by ^{1}H NMR and melting point with the reported samples.

Yield: 0.256 g (93%). M. p. = 280 °C (lit. M. p. 280–281 °C). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.39–7.42 (m, 6H, C_6H_5), 7.44–7.52 (m, 9H, C_6H_5) ppm.

*Procedure for the compound **1** catalysed cyclotrimerization of p-methoxyphenyl isocyanate*

To a complex **1** (0.020 g, 0.0308 mmol) neat *p*-methoxyphenyl isocyanate (0.23 g, 1.54 mmol) was added. After 60 min a white color solid was formed. The crude solid was washed with benzene 5 times (5 mL × 5) and dried in vacuum. The desired product (*p*-OMePhNCO)$_3$ collected in 94% yield. By comparison with authentic sample of ^{1}H NMR and the melting point of the compound the product was confirmed.

Yield: 0.216 g (94%). M. p. = 257 °C (lit. M. p. 261 °C); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 3.72 (s, 9H, OCH_3), 6.875 (d, 12H, J = 12 Hz, C_6H_4), 7.16–7.19 (t, 6H, C_6H_4) ppm.

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Appendix A. Supplementary material

CCDC-984884 (**1**) and CCDC-984883 (**2**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Appendix B. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2014.09.030.

References

[1] G. Chandra, A.D. Jenkins, M.F. Lappert, R.C. Srivastava, J. Chem. Soc. (1970) 2550–2558.
[2] (a) M.P. Coles, Dalton Trans. (2006) 985–1001;
(b) F.T. Edelmann, Adv. Organomet. Chem. 57 (2008) 183–352;
(c) F.T. Edelmann, Chem. Soc. Rev. 41 (2012) 7657–7672;
(d) P.J. Bailey, S. Pace, Coord. Chem. Rev. 214 (2001) 91–141.
[3] (a) C. Jones, Coord. Chem. Rev. 254 (2010) 1273–1289;
(b) M. Asay, C. Jones, M. Driess, Chem. Rev. 111 (2011) 354–396;
(c) A. Stasch, C. Jones, Dalton Trans. 40 (2011) 5659–5672;
(d) M. Westerhausen, Angew. Chem. Int. Ed. 47 (2008) 2185–2187;
(e) S. Krieck, L. Yu, M. Reiher, M. Westerhausen, Eur. J. Inorg. Chem. (2010) 197–216.
[4] S.P. Green, C. Jones, A. Stasch, Science 318 (2007) 1754–1757.
[5] C. Jones, P.C. Junk, J.A. Platts, A. Stasch, J. Am. Chem. Soc. 128 (2006) 2206–2207.
[6] S.P. Green, C. Jones, P.C. Junk, K.-A. Lippert, A. Stasch, Chem. Commun. (2006) 3978–3980.
[7] (a) Y.-C. Tsai, Coord. Chem. Rev. 256 (2012) 722–758;
(b) S. Nagendran, H.W. Roesky, Organometallics 27 (2008) 457–492;
(c) S.S. Sen, S. Khan, P.P. Samuel, H.W. Roesky, Chem. Sci. 3 (2012) 659–682;
(d) S.S. Sen, S. Khan, S. Nagendran, H.W. Roesky, Acc. Chem. Res. 45 (2012) 578–587;
(e) S.K. Mandal, H.W. Roesky, Acc. Chem. Res. 45 (2012) 298–307;
(f) H.W. Roesky, S.S. Kumar, Chem. Commun. (2005) 4027–4038;
(g) H.W. Roesky, J. Organomet. Chem. 730 (2013) 57–62;
(h) A.H. Cowley, J. Organomet. Chem. 689 (2004) 3866–3872;
(i) H.W. Roesky, Inorg. Chem. 43 (2004) 7284–7293;
(j) R.J. Baker, C. Jones, Coord. Chem. Rev. 249 (2005) 1857–1869;
(k) B. Blom, M. Stoelzel, M. Driess, Chem. Eur. J. 19 (2013) 40–62;
(l) S. Yao, Y. Xiong, M. Driess, Organometallics 30 (2011) 1748–1767;
(m) S.J. Bonyhady, C. Jones, S. Nembenna, A. Stasch, A.J. Edwards, G.J. McIntyre, Chem. Eur. J. 16 (2010) 938–955.
[8] (a) S.R. Foley, G.P.A. Yap, D.S. Richeson, Organometallics 18 (1999) 4700–4705;
(b) S.R. Foley, Y. Zhou, G.P.A. Yap, D.S. Richeson, Inorg. Chem. 39 (2000) 924–929.
[9] (a) S.S. Sen, M.P. Kritzler-Kosch, S. Nagendran, H.W. Roesky, T. Beck, A. Pal, R. Herbst-Irmer, Eur. J. Inorg. Chem. (2010) 5304–5311;
(b) A. Jana, H.W. Roesky, C. Schulzke, A. Döring, T. Beck, A. Pal, R. Herbst-Irmer, Inorg. Chem. 48 (2009) 193–197.
[10] P.B. Hitchcock, J. Hu, M.F. Lappert, J.R. Severn, Dalton Trans. (2004) 4193–4201.
[11] (a) C. Jones, R.P. Rose, A. Stasch, Dalton Trans. (2008) 2871–2878;
(b) S.R. Foley, G.P.A. Yap, D.S. Richeson, Polyhedron 21 (2002) 619–627;
(c) A. Stasch, C.M. Forsyth, C. Jones, P.C. Junk, New J. Chem. 32 (2008) 829–834.
[12] F.M. Mück, K. Junold, J.A. Baus, C. Burschka, R. Tacke, Eur. J. Inorg. Chem. 2013 (2013) 5821–5825.
[13] T. Chlupatý, Z. Padělková, F. DeProft, R. Willem, A. Růžička, Organometallics 31 (2012) 2203–2211.
[14] T. Chen, W. Hunks, P.S. Chen, G.T. Stauf, T.M. Cameron, C. Xu, A.G. DiPasquale, A.L. Rheingold, Eur. J. Inorg. Chem. (2009) 2047–2049.
[15] (a) C. Alonso-Moreno, A. Antinolo, F. Carrillo-Hermosilla, A. Otero, Chem. Soc. Rev. 43 (2014) 3406–3425;
(b) A.K. Ghosh, W.G.J. Hol, E. Fan, J. Org. Chem. 66 (2001) 2161–2164;
(c) M. Tamaki, G. Han, V.J. Hruby, J. Org. Chem. 66 (2001) 1038–1042;
(d) Y.-Q. Wu, S.K. Hamilton, D.E. Wilkinson, G.S. Hamilton, J. Org. Chem. 67 (2002) 7553–7556.
[16] G. Jin, C. Jones, P.C. Junk, K.-A. Lippert, R.P. Rose, A. Stasch, New J. Chem. 33 (2009) 64–75.
[17] M. Findlater, N.J. Hill, A.H. Cowley, Dalton Trans. (2008) 4419–4423.
[18] A. Baishya, M.Kr Barman, T. Peddarao, S. Nembenna, J. Organomet. Chem. 769 (2014) 112–118.
[19] B. Cordero, V. Gomez, A.E. Platero-Prats, M. Reves, J. Echeverria, E. Cremades, F. Barragan, S. Alvarez, Dalton Trans. (2008) 2832–2838.
[20] (a) S. Harder, Chem. Rev. 110 (2010) 3852–3876;
(b) P.P. Power, Nature 463 (2010) 171–177.
[21] L. Orzechowski, S. Harder, Organometallics 26 (2007) 2144–2148.
[22] (a) J. Tang, T. Mohan, J.G. Verkade, J. Org. Chem. 59 (1994) 4931–4938;
(b) Y. Nambu, T. Endo, J. Org. Chem. 58 (1993) 1932–1934;
(c) B. Srinivas, C.-C. Chang, C.-H. Chen, M.Y. Chiang, I.-T. Chen, Y. Wang, G.-H. Lee, J. Chem. Soc. Dalton Trans. (1997) 957–963.
[23] J.-S. Tang, J.G. Verkade, Angew. Chem. Int. Ed. Engl. 32 (1993) 896–898.
[24] (a) A.G. Giuglio-Tonolo, C. Spitz, T. Terme, P. Vanelle, Tetrahedron Lett. 55 (2014) 2700–2702;
(b) S.M. Raders, J.G. Verkade, J. Org. Chem. 75 (2010) 5308–5311.
[25] H.A. Duong, M.J. Cross, J. Louie, Org. Lett. 6 (2004) 4679–4681.
[26] (a) M. Ozaki, Y. Obora, Y. Tada, Y. Ishii, J. Organomet. Chem. 741–742 (2013) 109–113;
(b) F. Paul, S. Moulin, O. Piechaczyk, P.L. Floch, J.A. Osborn, J. Am. Chem. Soc. 129 (2007) 7294–7304.
[27] H.-M. Wang, H.-X. Li, X.-Y. Yu, Z.-G. Ren, J.-P. Lang, Tetrahedron 67 (2011) 1530–1535.
[28] (a) J. Shi, Z. Guo, X. Wei, D. Liu, M.F. Lappert, Synlett (2011) 1937–1939;
(b) Z. Guo, S. Wang, H. Tong, J. Chao, X. Wei, Inorg. Chem. Commun. 33 (2013) 68–72;
(c) F.M. Moghaddam, M.G. Dekamin, G.R. Koozehgari, Lett. Org. Chem. 2 (2005) 734–738.
[29] D.H. Harris, M.F. Lappert, J. Chem. Soc. Chem. Commun. (1974) 895–896.
[30] SAINT+, Bruker AXS Inc., Madison, Wisconsin, USA, 1999 (Program for Reduction of Data collected on Bruker CCD Area Detector Diffractometer V. 6.02.).
[31] SADABS, Bruker AXS, Madison, Wisconsin, USA, 2004.
[32] G.M. Sheldrick, Acta Crystallogr. Sect. A 64 (2008) 112–122.