Synthesis of Group 14 Metal Enamido, Alkenyl, Imido and Alkenyl-Amido Complexes from a Monoanionic Pyridyl-1-azaallyl Ligand

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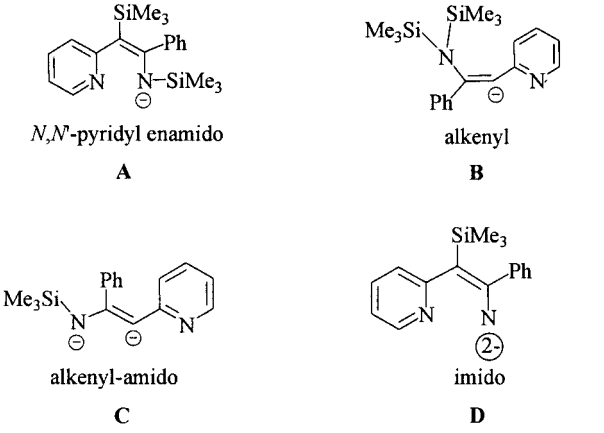
The reactivity of the lithium pyridyl-1-azaallyl complex [Li{N(SiMe$_3$)C(Ph)C(R)(C$_5$H$_4$N-2)}]$_2$ [R = SiMe$_3$ (**1**) or H (**10**)] with group 14 metal halides has been studied under various conditions. It undergoes a salt-elimination reaction with MCl$_2$ (M = Ge, Sn or Pb) to form [Ge{C(C$_5$H$_4$N-2)C(Ph)N(SiMe$_3$)$_2$}{N(SiMe$_3$)C(Ph)C(SiMe$_3$)(C$_5$H$_4$N-2)}] (**2**), [M{N(SiMe$_3$)C(Ph)C(SiMe$_3$)(C$_5$H$_4$N-2)}$_2$] [M = Sn (**3**), Pb (**4**)], and [M{N(SiMe$_3$)C(Ph)C(SiMe$_3$)(C$_5$H$_4$N-2)}Cl] [M = Ge (**5**), Sn (**6**), Pb (**7**)], where the azaaalyl moiety acts as a monodentate ligand. However, the reaction of **1** with GeCl$_4$ or HSiCl$_3$ forms [Ge{C(C$_5$H$_4$N-2)C(Ph)N(SiMe$_3$)}Cl$_2$]$_2$ (**8**) or [{(C$_5$H$_4$N-2)C(SiMe$_3$)C(Ph)N}(μ-SiHCl)]$_2$ (**9**), respectively, by elimination of both the lithium salt and Me$_3$SiCl; the reaction of **10** with GeCl$_4$ gives [{(C$_5$H$_4$N-2)C(H)C(Ph)N}(μ-GeCl$_2$)]$_2$ (**11**) in a similar manner. X-ray structural analysis of compounds **2**–**5**, **7**–**9** and **11** showed that the pyridyl-1-azaallyl ligand bonds to the metal center in enamido, alkenyl, alkenyl-amido, and imido bonding modes. A mechanism for the formation of these compounds is proposed and discussed.

Introduction

Alkali metal 1-azaallyl complexes are commonly used as monoanionic ligand-transfer reagents in the synthesis of main-group, transition-metal, and lanthanide complexes.[1] For example, [Ni{N(R)C(Ph)C(H)(R)}$_2$],[2] [Mg{N(R)C(*t*Bu)C(H)(R)}$_2$],[3] [Cu{μ-N(R)C(*t*Bu)C(H)(R)}]$_2$,[4] [Al{N(R)C(Ph)C(R)$_2$}Cl$_2$],[5] and [Yb{N(R)C(*t*Bu)C(H)(R)}$_2$][6] (R = SiMe$_3$) have been prepared. 1-Azaallyllithium complexes can be prepared by insertion of Li(CH$_{3-n}$R$_n$) (n = 1, 2 or 3; R = SiMe$_3$) into an α-H-free nitrile R′CN (R′ = *t*Bu, Ph or 2,6-Me$_2$C$_6$H$_3$). Other alkali metal 1-azaallyl complexes can be derived from the metathesis reaction of lithium complexes with MO*t*Bu (M = Na or K).[7]

We have reported the synthesis of [MCl$_2${N(SiMe$_3$)C(Ph)C(H)(C$_9$H$_6$N-2)}] (M = Hf and Zr) from the reaction of MCl$_4$ with the quinolyl-1-azaallyllithium complex [Li{N(SiMe$_3$)C(Ph)C(H)(C$_9$H$_6$N-2)}]$_2$ previously.[8] In this paper we report different reactivities of the pyridyl-1-azaallyllithium compound [Li{N(SiMe$_3$)C(Ph)C(R)(C$_5$H$_4$N-2)}]$_2$ [R = SiMe$_3$ (**1**) or H (**10**)][9] with a variety of Group 14 metal halides. It acts as both a monoanionic and dianionic ligand by using the SiMe$_3$ group as the leaving group during the metathesis reaction. The pyridyl-1-azaallyl ligand can bind to a metal in bonding modes **A**−**D** (Scheme 1).



Scheme 1

Results and Discussion

Synthesis of Group 14 Metal Pyridyl-1-azaallyl Complexes

Treatment of [Li{N(SiMe$_3$)C(Ph)C(SiMe$_3$)(C$_5$H$_4$N-2)}]$_2$ (**1**) with an equimolar amount of GeCl$_2$·dioxane in Et$_2$O afforded [Ge{C(C$_5$H$_4$N-2)C(Ph)N(SiMe$_3$)$_2$}{N(SiMe$_3$)C(Ph)C(SiMe$_3$)(C$_5$H$_4$N-2)}] (**2**) (Scheme 2). The X-ray structure shows that the germanium(II) center in **2** is bonded to an *N*,*N*′-pyridyl-enamido ligand and an η^1-alkenyl ligand, which suggests that the smaller size of the germanium

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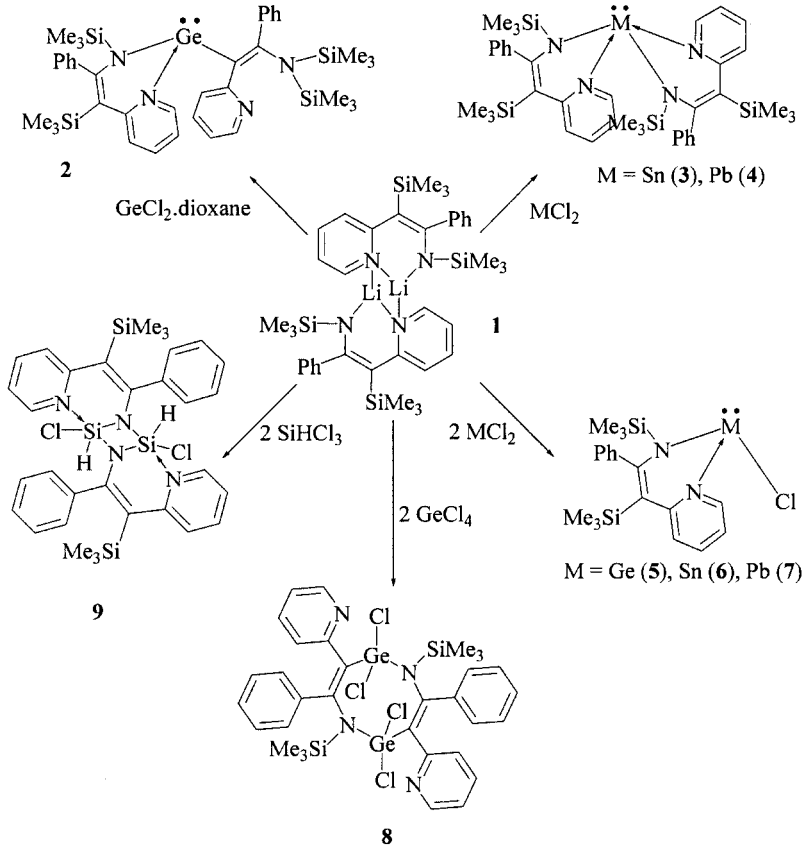


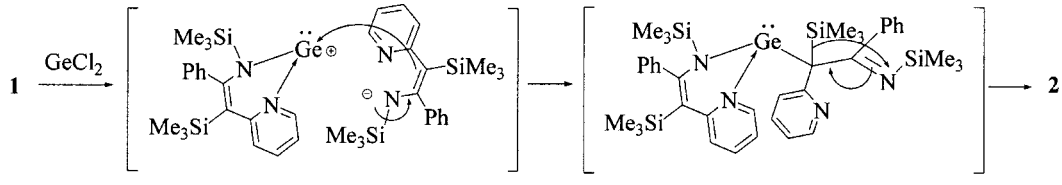
Scheme 2

center prevents both pyridyl-1-azaallyl ligands from bonding in an *N*,*N*′-chelate fashion. One of the ligands has undergone a 1,3-silyl migration in order to release the steric crowding at the germanium(II) center (Scheme 3). A similar silyl migration has been reported in the thermal isomerization of the ketimine $[Me_3SiN{=}C(CMe_3)CH(SiMe_3)_2]$ to the enamine $[(Me_3Si)_2NC(CMe_3){=}CH(SiMe_3)]$.[10] In another example, a 1,2-silyl migration on the 1-azaallyl ligand backbone results in the formation of the asymmetric distannene [{1-[N(*t*Bu)C(SiMe$_3$)C(H)]-2-[N(*t*Bu)CC(H)]C$_6$H$_4$}-Sn→Sn{1,2-[N(*t*Bu)(SiMe$_3$)CC(H)]$_2$C$_6$H$_4$}].[11]

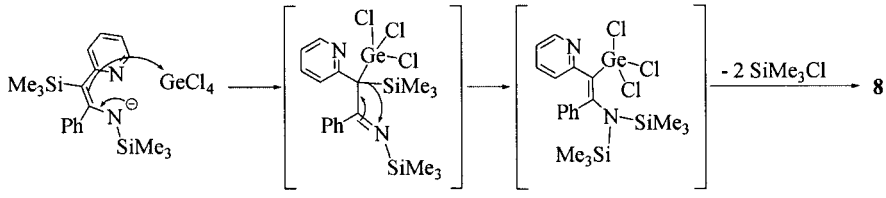
A similar reaction of **1** with MCl_2 (M = Ge, Sn or Pb) in a 1:1 or 1:2 ratio gave the metal enamides [M{N(SiMe$_3$)-C(Ph)C(SiMe$_3$)(C$_5$H$_4$N-2)}$_2$] [M = Sn (**3**) and Pb (**4**)] or [M{N(SiMe$_3$)C(Ph)C(SiMe$_3$)(C$_5$H$_4$N-2)}Cl] [M = Ge (**5**), Sn (**6**) and Pb (**7**)], respectively (Scheme 2).

The reaction of **1** with two equivalents of $GeCl_4$ in THF, however, afforded [Ge{C(C$_5$H$_4$N-2)C(Ph)N(SiMe$_3$)}Cl$_2$]$_2$ (**8**). The X-ray structure of **8** shows that the germanium center is bonded to two alkenyl-amido ligands to form an eight-membered heterocyclic ring. The pyridyl-1-azaallyl ligand acts here as a *C*-centered nucleophile, and undergoes 1,3-silyl migration and elimination of Me_3SiCl to form **8** (Scheme 4).

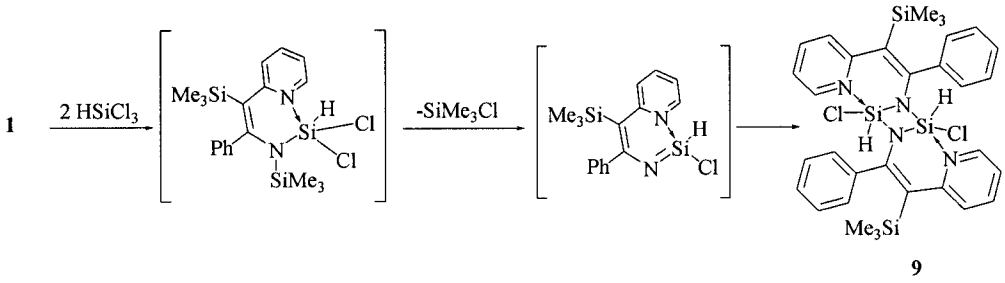
Treatment of **1** with two equivalents of $HSiCl_3$ in THF afforded [{(C$_5$H$_4$N-2)C(SiMe$_3$)C(Ph)N}(μ-SiHCl)]$_2$ (**9**).



Scheme 3



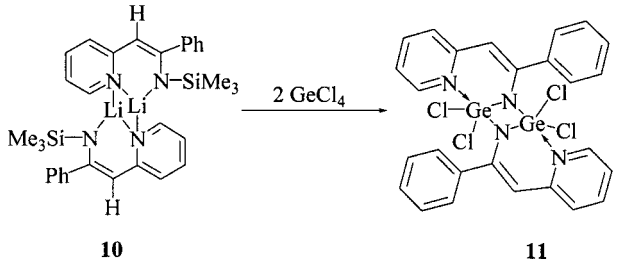
Scheme 4



Scheme 5

The X-ray structure of **9** shows that the pyridyl-1-azaallyl ligand acts as an *N*-centered nucleophile rather than a *C*-centered towards $HSiCl_3$. The intermediate $[HSi\{N(SiMe_3)C(Ph)C(SiMe_3)(C_5H_4N\text{-}2)\}Cl_2]$ eliminates Me_3SiCl and dimerizes to form compound **9** (Scheme 5). Each silicon center is bonded to two imido ligand to form a four-membered ring. A similar result has been reported in the synthesis of $ClPN(R)P(Cl)NR$ [R = C(*t*Bu)=C(H)$SiMe_3$] from the reaction of $[Li\{N(SiMe_3)C(tBu)C(H)(SiMe_3)\}]_2$ and PCl_3.[10]

In contrast, the reaction of $[Li\{N(SiMe_3)C(Ph)C(H)(C_5H_4N\text{-}2)\}]_2$ (**10**) with two equivalents of $GeCl_4$ in THF gave $[\{(C_5H_4N\text{-}2)C(H)C(Ph)N\}(\mu\text{-}GeCl_2)]_2$ (**11**), with a structure similar to that of **9** (Scheme 6). The $C_{alkenyl}-H$ bond is much stronger than the $C_{alkenyl}-SiMe_3$ bond, therefore a 1,3-H shift is less feasible than a 1,3-silyl migration. The pyridyl-1-azaallyl ligand preferably acts as an *N*-centered nucleophile; the formation of **11** is similar to that of **9**.



Scheme 6

Spectroscopic Properties

Compounds **2**−**9** and **11** are yellow crystalline solids that are soluble in Et_2O, toluene, and THF, and sparingly soluble in hydrocarbon solvents. The ^1H and ^{13}C NMR spectra of **2** display three sharp singlets in ratio of 1:1:2 assignable to the three types of $SiMe_3$ groups, this is consistent with the solid-state structure.

The ^1H and ^{13}C NMR spectra of **3**−**7** show a similar pattern and display one set of signals due to the pyridyl-1-azaallyl ligand. The chemical shifts of the ^{119}Sn NMR signals of **3** (δ = −140.0 ppm) and **6** (δ = −197.95 ppm) are similar to those of four-coordinate $[Sn\{N(SiMe_3)C(Ph)NC(Ph)=C(SiMe_3)_2\}_2]$ (δ = −141.4 ppm)[12] and three-coordinate $[\{HC(CMeNAr)_2\}SnCl]$ (δ = −224.0 ppm),[13] respectively.

The ^1H NMR spectra of **8**, **9** and **11** show one set of signals due to the pyridyl and phenyl rings. In the ^1H NMR spectrum of **9**, the Si−H chemical shift (δ = 5.46 ppm) is similar to that in $[SiH\{(C_{10}H_6\text{-}2)(NMe_2)\}_3]$ (δ = 6.61 ppm)[14] and $[SiH_2\{(C_6H_3\text{-}2,6)(NMe_2)_2\}]$ (δ = 4.87 ppm).[15] In the ^1H NMR spectrum of **11** the *H*-C=C signal (δ = 5.09 ppm) is shifted upfield relative to the value of δ = 6.24 ppm in $[Li\{N(SiMe_3)C(Ph)C(H)(C_5H_4N\text{-}2)\}]_2$ (**10**).

X-ray Crystal Structures

Compound **2** (Figure 1, Table 1) is a monomeric, heteroleptic germylene complex. The germanium center is bonded to an *N*,*N*′-pyridyl-enamido chelate and a monohapto η^1-alkenyl ligand. The Ge−C(26) bond length of 2.039(2) Å is similar to the Ge−C single bond lengths of 2.067 Å and 2.012 Å in $[Ge\{CH(SiMe_3)_2\}\{C(SiMe_3)_3\}]$[16] and 2.116 Å in $[Ge\{CPh(SiMe_3)C_5H_4N\text{-}2\}_2]$.[17] The Ge−N(2) bond length of 1.940(2) Å in **2** is comparable to those of 2.096(1) Å and 2.088(6) Å in $[Ge\{N(SiMe_3)_2\}_2]$[18] and 1.90(1) Å and 1.87(1) Å in $[Ge\{NCMe_2(CH_2)_3CMe_2\}_2]$.[19]

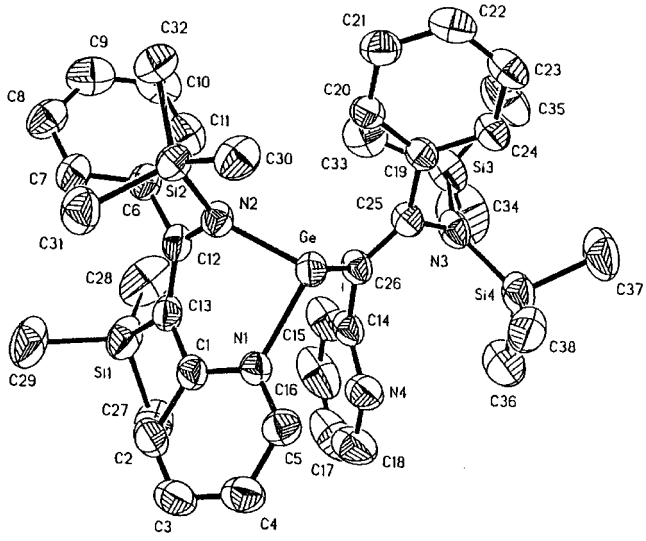


Figure 1. Molecular structure of **2**

Compounds **3** and **4** (Figure 2, Table 2) are isostructural. The $Sn-N_{amide}$ bond lengths of 2.162(2) Å and 2.174(2) Å in **3** are similar to that of 2.130 Å in the κ^1-enamidotin(II)

Table 1. Selected bond lengths (Å) and angles (°) for compound **2**

Ge−N(1)	2.065(15)	Ge−C(26)	2.039(2)
Ge−N(2)	1.942(17)	C(14)−C(26)	1.488(3)
N(2)−C(12)	1.405(2)	C(25)−C(26)	1.356(3)
C(12)−C(13)	1.357(3)	C(19)−C(25)	1.491(3)
C(13)−C(1)	1.471(3)	N(3)−C(25)	1.453(3)
Si(2)−N(2)	1.746(18)	Si(3)−N(3)	1.750(19)
Si(1)−C(13)	1.897(2)	Si(4)−N(3)	1.751(2)
N(2)−Ge−C(26)	105.16(18)	C(25)−C(26)−Ge	118.52(14)
N(2)−Ge−N(1)	86.3(7)	C(25)−C(26)−C(14)	119.6(2)
C(26)−Ge−N(1)	98.5(7)	C(14)−C(26)−Ge	118.96(13)
C(1)−N(1)−Ge	124.04(12)	N(3)−C(25)−C(19)	114.23(16)
N(1)−C(1)−C(13)	120.68(16)	C(26)−C(25)−C(19)	120.5(2)
C(12)−N(2)−Ge	118.59(13)	C(13)−C(12)−C(6)	121.87(17)
C(12)−C(13)−C(1)	119.11(17)	C(13)−C(12)−N(2)	124.23(17)

complex [Sn{N(SiMe$_3$)C(*t*Bu)C(H)C$_6$H$_3$Me$_2$-2,5}$_2$], but significantly shorter than that of 2.510(2) Å in the η^3-(1-azaallyl)tin(II) complex [Sn{N(SiMe$_3$)C(*t*Bu)C(H)(SiMe$_3$)}$_2$].[20] The Pb−N$_{amide}$ bond lengths of 2.277(7) Å and 2.275(7) Å in **4** are shorter than that of 2.381(7) Å in the η^3-(1-azaallyl)lead(II) complex [Pb{N(SiMe$_3$)C(Ph)C(SiMe$_3$)$_2$}Cl].[21] The short C(6)−C(10) and C(25)−C(29) and long N(2)−C(10) and N(4)−C(29) bond lengths correspond to double and single bonds, respectively. Thus, the bonding within the NCCCN ligand backbone is localized, and the pyridyl-1-azaallyl ligand bonds to the metal center in an enamido bonding mode.

Compounds **5** and **7** (Figure 3, Table 3) are isostructural. The metal−amide bond lengths of 1.920(2) Å and 2.279(7) Å in **5** and **7** are similar to those in **2** and **4**, respectively. The Ge−Cl bond length of 2.283(9) Å in **5** is similar to that of 2.203(10) Å in [Ge(C$_6$H$_3$-2,6-Trip$_2$)Cl][22] (Trip = C$_6$H$_2$-2,4,6-*i*Pr$_3$) and 2.295(12) Å in [{HC(CMeNAr)$_2$}GeCl].[13]

Table 2. Selected bond lengths (Å) and angles (°) for compounds **3** and **4**

[M{N(SiMe$_3$)C(Ph)C(SiMe$_3$)(C$_5$H$_4$N-2)}$_2$]	M = Sn (**3**)	M = Pb (**4**)
M−N(1)	2.441(2)	2.626(8)
M−N(2)	2.162(2)	2.277(7)
M−N(3)	2.503(2)	2.570(8)
M−N(4)	2.174(2)	2.274(7)
N(1)−C(5)	1.364(3)	1.336(12)
C(5)−C(6)	1.449(3)	1.483(13)
C(6)−C(10)	1.366(4)	1.361(13)
C(10)−N(2)	1.403(3)	1.391(12)
N(3)−C(24)	1.335(3)	1.356(12)
C(24)−C(25)	1.457(4)	1.462(12)
C(25)−C(29)	1.402(3)	1.384(13)
C(29)−N(4)	1.384(3)	1.387(11)
N(1)−M−N(2)	78.1(7)	76.5(3)
N(1)−M−N(4)	91.3(7)	94.0(3)
N(4)−M−N(3)	76.7(7)	74.3(2)
N(2)−M−N(3)	91.6(7)	97.3(3)
M−N(1)−C(5)	123.8(2)	118.6(6)
N(1)−C(5)−C(6)	121.8(2)	121.5(8)
C(5)−C(6)−C(10)	120.5(2)	119.5(8)
C(6)−C(10)−N(2)	126.6(2)	126.1(8)
C(10)−N(2)−M	124.0(2)	123.1(6)
M−N(3)−C(24)	123.8(2)	123.3(6)
N(3)−C(24)−C(25)	121.7(2)	122.4(8)
C(25)−C(29)−N(4)	126.0(2)	126.6(8)
C(29)−N(4)−M	123.9(2)	122.1(5)

The Pb−Cl bond length of 2.599(3) Å in **7** is similar to that of 2.6096(3) Å in [Pb{N(SiMe$_3$)C(Ph)C(SiMe$_3$)$_2$}Cl].[21]

Compound **8** (Figure 4, Table 4) is centrosymmetric: each germanium(IV) center is bonded to amido nitrogen and alkenyl carbon atoms with an angle of 116.7(3)°, which is

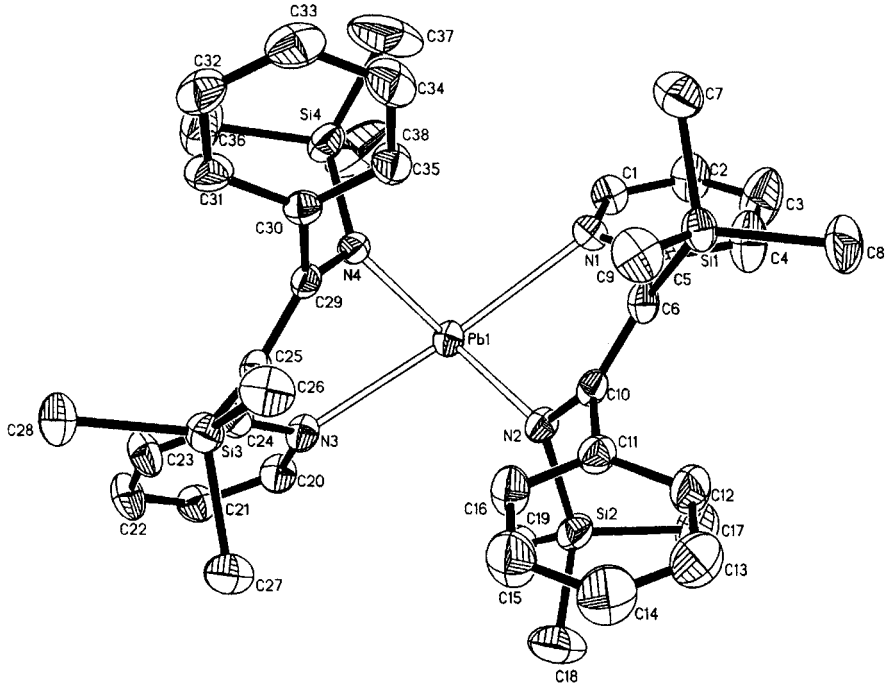


Figure 2. Molecular structure of **4**

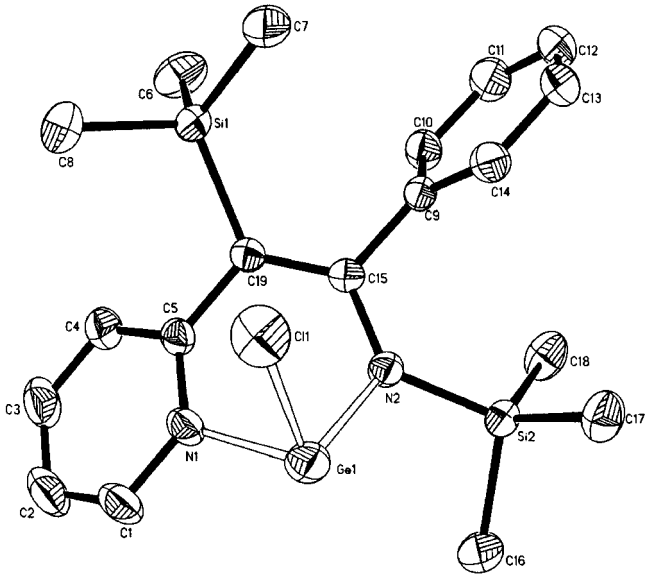


Figure 3. Molecular structure of **5**

Table 3. Selected bond lengths (Å) and angles (°) for compounds **5** and **7**

$[M\{N(SiMe_3)C(Ph)C(SiMe_3)(C_5H_4N\text{-}2)\}Cl]$	M = Ge (**5**)	M = Pb (**7**)
M−Cl	2.283(9)	2.599(3)
M−N(1)	2.021(2)	2.320(6)
M−N(2)	1.920(2)	2.279(7)
N(1)−C(5)	1.354(3)	1.365(11)
C(5)−C(19)	1.462(3)	1.467(11)
C(19)−C(15)	1.375(3)	1.411(11)
C(15)−N(2)	1.384(3)	1.352(10)
N(1)−M−N(2)	88.8(8)	78.9(2)
N(1)−M−Cl	93.6(6)	92.7(2)
N(2)−M−Cl	97.7(6)	98.9(2)
M−N(1)−C(5)	122.4(2)	111.7(5)
N(1)−C(5)−C(19)	121.6(2)	117.7(7)
C(5)−C(19)−C(15)	119.8(2)	117.4(7)
C(15)−N(2)−M	118.3(1)	99.2(5)
C(19)−C(15)−N(2)	125.2(2)	124.8(7)

Table 4. Selected bond lengths (Å) and angles (°) for compounds **8**, **9** and **11**

$[Ge\{C(C_5H_4N\text{-}2)C(Ph)N(SiMe_3)\}Cl_2]_2$ (**8**)			
Ge(1)−Cl(1)	2.143(2)	Ge(1)−N(2)	1.813(6)
Ge(1)−Cl(2)	2.157(2)	N(2)−C(7)	1.443(9)
Ge(1)−C(1)	1.924(7)	C(7)−C(1A)	1.353(10)
N(2)−Ge(1)−C(1)	116.7(3)	C(1)−Ge(1)−Cl(2)	107.1(2)
N(2)−Ge(1)−Cl(1)	107.6(2)	Cl(1)−Ge(1)−Cl(2)	102.4(1)
C(1)−Ge(1)−Cl(1)	115.6(2)	Ge(1)−N(2)−C(7)	121.3(5)
N(2)−Ge(1)−Cl(2)	106.0(2)	N(2)−C(7)−C(1A)	119.7(7)
		C(7A)−C(1)−Ge(1)	117.3(6)
$[\{(C_5H_4N\text{-}2)C(SiMe_3)C(Ph)N\}(\mu\text{-}SiHCl)]_2$ (**9**)			
Si(1)−Cl(1)	2.108(1)	N(1)−C(5)	1.361(3)
Si(1)−N(2)	1.864(2)	C(5)−C(13A)	1.465(3)
Si(1)−N(2A)	1.741(2)	C(6)−N(2)	1.371(3)
Si(1)−N(1)	2.003(2)		
N(2)−Si(1)−N(2A)	81.4(1)	Si(1)−N(1)−C(5)	126.7(2)
Si(1)−N(2A)−Si(1A)	98.6(1)	N(1)−C(5)−C(13A)	121.3(2)
N(1)−Si(1)−N(2)	170.8(8)	C(5)−C(13A)−C(6A)	119.7(2)
N(2)−Si(1)−Cl(1)	98.1(7)	C(6)−N(2)−Si(1)	130.0(1)
N(2A)−Si(1)−Cl(1)	116.6(8)	C(6)−N(2)−Si(1A)	130.6(2)
N(1)−Si(1)−Cl(1)	90.4(7)		
$[\{(C_5H_4N\text{-}2)C(H)C(Ph)N\}(\mu\text{-}GeCl_2)]_2$ (**11**)			
Ge(1)−N(2)	1.834(2)	N(2)−C(7)	1.369(3)
Ge(1)−N(2A)	1.944(2)	C(6)−C(7)	1.357(4)
Ge(1)−Cl(1)	2.172(8)	C(5)−C(6)	1.422(4)
Ge(2)−Cl(2)	2.187(9)	N(1)−C(5)	1.350(3)
Ge(1)−N(1)	2.080(2)		
N(2)−Ge(1)−N(2A)	80.7(1)	N(1)−Ge(1)−Cl(1)	86.1(7)
Ge(1A)−N(2)−Ge(1)	99.3(1)	N(1)−Ge(1)−Cl(2)	87.9(7)
N(1)−Ge(1)−N(2A)	173.7(9)	Ge(1)−N(1)−C(5)	124.1(2)
Cl(1)−Ge(1)−Cl(2)	115.7(3)	N(1)−C(5)−C(6)	121.3(3)
N(2A)−Ge(1)−Cl(1)	96.6(7)	C(5)−C(6)−C(7)	128.2(3)
N(2A)−Ge(1)−Cl(2)	96.0(7)	C(6)−C(7)−N(2)	125.3(3)
N(2)−Ge(1)−Cl(1)	122.4(8)	C(7)−N(2)−Ge(1)	127.6(2)
N(2)−Ge(1)−Cl(2)	121.9(8)	C(7)−N(2)−Ge(1A)	132.7(2)

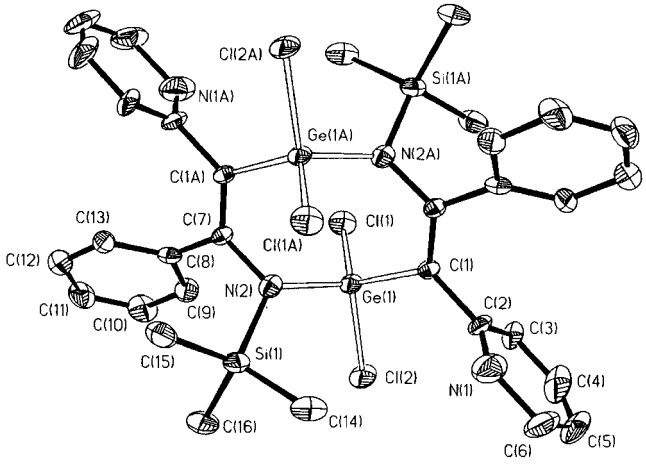


Figure 4. Molecular structure of **8**

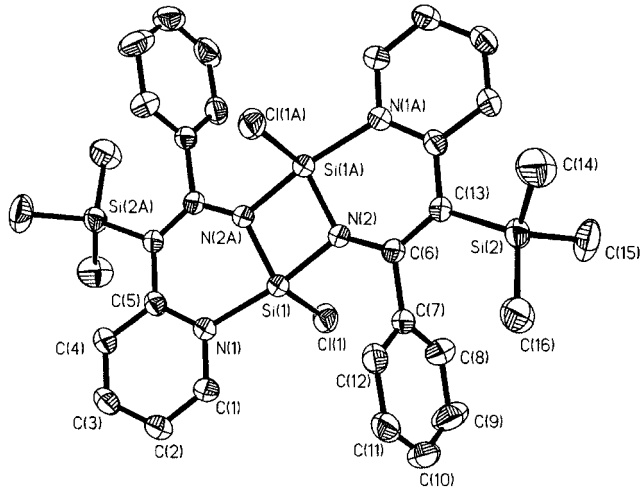


Figure 5. Molecular structure of **9**

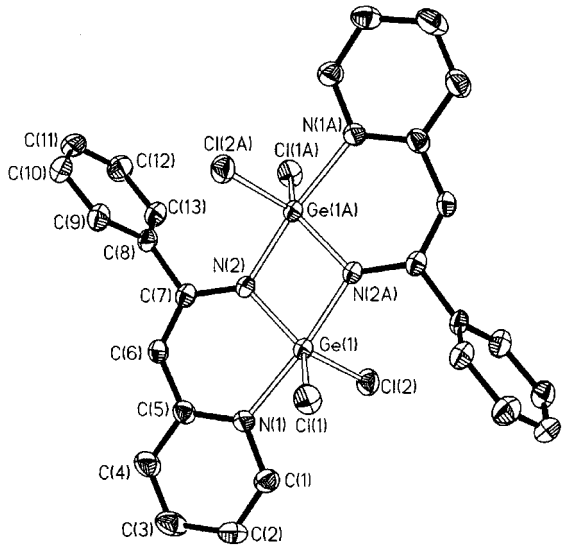


Figure 6. Molecular structure of **11**

larger than the N−Ge−C angle of 105.2(2)° in **2**. The Ge(1)−C(1) [1.924(7) Å] and Ge(1)−N(2) [1.813(6) Å] bond lengths in **8** are shorter than the Ge−C and Ge−N distances of 2.039(2) Å and 1.942(17) Å, respectively, in **2**.

The molecular structures of **9** (Figure 5, Table 4) and **11** (Figure 6, Table 4) are similar. They are centrosymmetric with the metal centers bonded to two imino nitrogen atoms to form a planar N_2M_2 ring [M = Si (**9**), Ge (**11**)]. The geometry around the metal center is trigonal bipyramidal with the N-donor at the axial position. The average bond length of 1.802 Å within the Si_2N_2 ring in **9** is longer than that of 1.750 Å in [{μ-MesN}Si(H)(*t*Bu)]$_2$ [23] and 1.770 Å in [Me_2Si(μ-*N*-C_9H_6N)(μ-*N*-C_9H_6N)SiMe_2].[24] The Ge−N_{imino} bond lengths of 1.843(2) Å and 1.944(2) Å in **11** are longer than those reported in similar Ge_2N_2 ring systems, such as [{N(CH_3)CH_2CH_2N(CH_3)}Ge{μ-NSi(O*t*C_4H_9)}]$_2$ (1.836 Å and 1.843 Å).[25]

Conclusion

A series of Group 14 metal pyridyl-1-azaallyl complexes has been synthesized: [Ge{C(C_5H_4N-2)C(Ph)N($SiMe_3$)$_2$}-{N($SiMe_3$)C(Ph)C($SiMe_3$)(C_5H_4N-2)}] (**2**), [M{N($SiMe_3$)C-(Ph)C($SiMe_3$)-(C_5H_4N-2)}$_2$] [M = Sn (**3**), Pb (**4**)], [M{N($SiMe_3$)C(Ph)C($SiMe_3$)(C_5H_4N-2)}Cl] [M = Ge (**5**), Sn (**6**), Pb (**7**)], [Ge{C(C_5H_4N-2)C(Ph)N($SiMe_3$)}Cl_2]$_2$ (**8**), [{(C_5H_4N-2)C($SiMe_3$)C(Ph)N}(μ-SiHCl)]$_2$ (**9**) and [{(C_5H_4N-2)C(H)C(Ph)N}(μ-$GeCl_2$)]$_2$ (**11**). The results show that the pyridyl-1-azaallyl ligand bonds to the metal center in enamido and alkenyl bonding modes in compound **2**, an enamido mode in compounds **3**−**7**, an alkenyl-amido mode in compound **8**, and an imido mode in compounds **9** and **11**.

Experimental Section

General Remarks: All manipulations were performed under an inert atmosphere of dinitrogen gas by standard Schlenk techniques. Solvents were dried over and distilled from CaH_2 (hexane) and/or Na (Et_2O, toluene and THF). Anhydrous $SnCl_2$, $PbCl_2$, $GeCl_4$, and $HSiCl_3$ were purchased from Aldrich Chemicals and used without further purification. $GeCl_2$·dioxane[26] and [Li{N($SiMe_3$)C-(Ph)C(R)(C_5H_4N-2)}]$_2$ (R = Ph, H)[9] were prepared by literature procedures. The ^{1}H, ^{13}C and ^{119}Sn NMR spectra were recorded on Bruker WM-300 or Varian 400 instruments. All spectra were recorded in [D_6]benzene or [D_8]THF, and the chemical shifts are quoted relative to $SiMe_4$ and $SnMe_4$ for ^{1}H/^{13}C and ^{119}Sn, respectively.

[Ge{C(C_5H_4N-2)C(Ph)N($SiMe_3$)$_2$}{N($SiMe_3$)C(Ph)C($SiMe_3$)-(C_5H_4N-2)}] (2): A solution of **1** (3.75 g, 5.41 mmol) in Et_2O (30 mL) was added slowly to a suspension of $GeCl_2$·dioxane (1.25 g, 5.41 mmol) in Et_2O (25 mL) at 0 °C. The orange mixture was warmed to ambient temperature and stirred for 16 h. The solvent was then removed under reduced pressure and the residue was extracted with toluene (50 mL). The precipitate was filtered and the orange filtrate was concentrated. *n*-Hexane (5 mL) was added and the solution was kept at 4 °C for 1 day to yield orange crystals of **2**. Yield: 2.55 g (62%); m.p.: 206−208 °C (dec.). $C_{38}H_{54}GeN_4Si_4$: calcd. C 60.75, H 7.19, N 7.46; found C 60.69, H 7.19, N 7.70. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ = −0.04 (s, 9 H, $SiMe_3$), 0.06 (s, 18 H, $SiMe_3$), 0.21 (s, 9 H, $SiMe_3$), 6.52 (t, J = 6.3 Hz, 1 H, py), 6.67 (br, 1 H, py), 7.05 (m, 5 H, Ph), 7.12 (br, 3 H, py), 7.50 (m, 5 H, Ph), 7.77 (d, J = 6.9 Hz, 2 H, py), 8.59 (d, J = 4.8 Hz, 1 H, py) ppm. ^{13}C{^{1}H} NMR (300 MHz, C_6D_6, 25 °C): δ = 2.94, 3.02, 3.11 ($SiMe_3$), 114.21 (*C*$SiMe_3$), 117.93, 118.98, 119.13, 123.73, 124.20, 124.96, 125.59, 127.39, 127.79, 128.33, 128.79, 129.00, 130.69, 131.13, 135.05, 136.66, 144.09, 145.31, 147.22, 147.99, 150.80, 153.57 (Ph and Py), 155.88 (py*C*Ge), 166.79, 171.46 (N*C*Ph) ppm.

[Sn{N($SiMe_3$)C(Ph)C($SiMe_3$)(C_5H_4N-2)}$_2$] (3): A solution of **1** (0.71 g, 1.02 mmol) in Et_2O (30 mL) was added slowly to a suspension of $SnCl_2$ (0.19 g, 1.02 mmol) in Et_2O (25 mL) at 0 °C. The yellow mixture was then warmed to ambient temperature and stirred for 16 h. The solvent was removed under reduced pressure and the residue was extracted with toluene (50 mL). The precipitate was filtered and the yellow filtrate was concentrated. *n*-Hexane (5 mL) was added and kept at 4 °C for 1 day to yield yellow crystals of **3**. Yield: 0.42 g (52%); m.p.: 149−151 °C (dec.). $C_{38}H_{54}N_4Si_4Sn$: calcd. C 57.20, H 6.82, N 7.02; found C 56.82, H 6.83, N 6.94. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ = −0.16 (s, 9 H, $SiMe_3$), −0.03 (s, 9 H, $SiMe_3$), −0.01 (s, 9 H, $SiMe_3$), 0.22 (s, 9 H, $SiMe_3$), 6.49 (br, 1 H, py), 6.57 (m, 2 H, py), 7.08 (m, 5 H, Ph), 7.49 (m, 3 H, py), 7.75 (d, J = 6.90 Hz, 5 H, Ph), 8.83 (br, 1 H, py), 9.09 (br, 1 H, py) ppm. ^{13}C{^{1}H} NMR (300 MHz, C_6D_6, 25 °C): δ = 1.38, 2.41, 3.65, 4.59 ($SiMe_3$), 118.08, 118.77 (*C*$SiMe_3$), 118.87, 123.91, 124.10, 124.80, 125.64, 127.23, 127.68, 128.56, 129.28, 130.47, 131.12, 135.20, 135.58, 137.07, 141.95, 144.29, 146.06, 147.51, 147.68, 147.98, 151.68, 158.76, 159.24 (Ph and Py), 168.17, 173.09 (N*C*Ph) ppm. ^{119}Sn{^{1}H} NMR (149 MHz, C_6D_6, 25 °C): δ = −140.00 ppm.

[Pb{N($SiMe_3$)C(Ph)C($SiMe_3$)(C_5H_4N-2)}$_2$] (4): A solution of **1** (0.96 g, 1.38 mmol) in Et_2O (20 mL) was added slowly to a solution of $PbCl_2$ (0.38 g, 1.38 mmol) in Et_2O (20 mL) at −90 °C in the absence of light. The yellow suspension was warmed to ambient temperature and stirred for 18 h. The precipitate was then filtered. *n*-Hexane was added to the filtrate, concentrated under reduced

pressure and stored at −30 °C. Compound **4** was obtained as yellow crystals. Yield: 0.45 g (37%); m.p.: 201−203 °C. $C_{38}H_{54}N_4PbSi_4$: calcd. C 51.49, H 6.14, N 6.32; found C 51.12, H 6.06, N 6.27. ^{1}H NMR (300 MHz, [D$_8$]THF, 25 °C): δ = −0.28 (s, 9 H, $SiMe_3$), −0.21 (s, 9 H, $SiMe_3$), 6.95−7.01 (m, 1 H, 5-py), 7.18−7.24 (d, J = 8.0 Hz, 1 H, 3-py), 7.35−7.41 (m, 3 H, Ph), 7.42−7.48 (m, 2 H, Ph), 7.55−7.64 (m, 1 H, 4-py), 8.45 (d, J = 4.1 Hz, 1 H, 6-py) ppm. ^{13}C{^{1}H} NMR (300 MHz, [D$_8$]THF, 25 °C): δ = 1.17, 2.34 ($SiMe_3$), 119.48 (*C*$SiMe_3$), 121.80, 123.43, 125.29, 128.52, 129.64, 131.79, 135.90, 142.62, 148.02, 150.03, 159.77 (Ph and Py), 164.63 (N*C*Ph).

[Ge{N(SiMe$_3$)C(Ph)C(SiMe$_3$)(C$_5$H$_4$N-2)}Cl] (5): A solution of **1** (0.94 g, 1.36 mmol) in Et_2O (30 mL) was added slowly to a solution of $GeCl_2$·dioxane (0.66 g, 2.85 mmol) in Et_2O (30 mL) at 0 °C. The yellow suspension was warmed to ambient temperature and stirred for 18 h. The precipitate was then filtered. Hexane was added to the filtrate and concentrated, yielding pale-yellow crystals of **5**. Yield: 0.76 g (62%); m.p.: 124−125 °C. $C_{19}H_{27}ClGeN_2Si_2$: calcd. C 50.98, H 6.08, N 6.25; found C 50.77, H 5.91, N 6.13. ^{1}H NMR (300 MHz, [D$_8$]THF, 25 °C): δ = −0.22 (s, 9 H, $SiMe_3$), −0.18 (s, 9 H, $SiMe_3$), 7.33−7.40 (m, 4 H, Ph), 7.41−7.49 (d, 1 H, 5-py), 7.49−7.63 (m, 1 H, Ph), 7.63−7.66 (d, J = 7.4 Hz, 1 H, 3-py), 7.95 (t, J = 7.1 Hz, 1 H, 4-py), 8.70 (d, J = 5.5 Hz, 1 H, 6-py) ppm. ^{13}C{^{1}H} NMR (300 MHz, [D$_8$]THF, 25 °C): δ = 1.62, 3.08 ($SiMe_3$), 95.62 (*C*$SiMe_3$), 120.69, 126.33, 127.97, 129.28, 130.06, 131.11, 133.53, 140.47, 144.38, 145.61, 155.57 (Ph and Py), 164.94 (N*C*Ph) ppm.

[Sn{N(SiMe$_3$)C(Ph)C(SiMe$_3$)(C$_5$H$_4$N-2)}Cl] (6): A solution of **1** (0.86 g, 1.23 mmol) in Et_2O (30 mL) was added slowly to a solution of $SnCl_2$ (0.47 g, 2.47 mmol) in Et_2O (30 mL) at 0 °C. The yellow suspension was warmed to ambient temperature and stirred for 18 h. The precipitate was then filtered. The filtrate was removed under reduced pressure and the residue was extracted with THF/*n*-hexane (1:10) and concentrated to yield **6** as a yellow solid. Yield: 0.51 g (42%); m.p.: 210−213 °C. $C_{19}H_{27}ClN_2Si_2Sn$: calcd. C 46.22, H 5.51, N 5.67; found C 46.29, H 5.58, N 5.88. ^{1}H NMR (300 MHz, [D$_8$]THF, 25 °C): δ = −0.28 (s, 9 H, $SiMe_3$), −0.27 (s, 9 H, $SiMe_3$), 7.13−7.26 (m, 1 H, 5-py), 7.30−7.35 (m, 3 H, Ph), 7.35−7.40 (m, 2 H, Ph), 7.44−7.47 (m, 1 H, 4-py), 7.56−7.59 (d, J = 8.7 Hz, 1 H, 3-py), 8.48 (d, J = 6.0 Hz, 1 H, 6-py) ppm. ^{13}C{^{1}H} NMR (300 MHz, [D$_8$]THF, 25 °C): δ = 0.96, 1.96 ($SiMe_3$), 100.12 (*C*$SiMe_3$), 118.72, 127.56, 128.69, 130.89, 135.14, 140.72, 147.36, 160.03 (Ph and Py), 162.93 (N*C*Ph) ppm. ^{119}Sn{^{1}H} NMR (149 MHz, [D$_8$]THF, 25 °C): δ = −197.95 ppm.

[Pb{N(SiMe$_3$)C(Ph)C(SiMe$_3$)(C$_5$H$_4$N-2)}Cl] (7): A solution of **1** (1.25 g, 1.80 mmol) in THF (20 mL) was added slowly to a solution of $PbCl_2$ (1.10 g, 3.96 mmol) in THF (20 mL) at −90 °C. The yellow suspension was warmed to ambient temperature and stirred for 18 h. The volatiles were then removed under reduced pressure and the residue was extracted with toluene. The yellow mixture was filtered and concentrated to give yellow crystals of the title compound. Yield: 0.73 g (69%); m.p.: 190−192 °C. $C_{19}H_{27}ClN_2PbSi_2$: calcd. C 39.19, H 4.67, N 4.81; found C 38.94, H 4.53, N 4.73. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ = −0.07 (s, 9 H, $SiMe_3$), −0.08 (s, 9 H, $SiMe_3$), 6.40 (m, 1 H, 5-py), 6.90 (m, 1 H, 3-py), 7.07 (m, 1 H, 4-py), 7.23−7.27 (m, 2 H, Ph), 7.47−7.50 (m, 3 H, Ph), 8.24 (d, J = 4.1 Hz, 1 H, 6-py) ppm. ^{13}C{^{1}H} NMR (300 MHz, C_6D_6, 25 °C): δ = 2.07, 2.94 ($SiMe_3$), 89.40 (*C*$SiMe_3$), 120.50, 123.30, 128.63, 129.00, 130.67, 130.79, 138.33, 145.26, 159.49 (Ph and Py), 166.23 (N*C*Ph) ppm.

[Ge{C(C$_5$H$_4$N-2)C(Ph)N(SiMe$_3$)}Cl$_2$]$_2$ (8): A solution of **1** (1.48 g, 2.13 mmol) in THF (30 mL) was added slowly to a solution of $GeCl_4$ (0.54 mL, 4.69 mmol) in THF (20 mL) at −90 °C. The yellow solution was warmed to ambient temperature and stirred for two days. The volatiles were removed under reduced pressure and the residue was extracted with toluene. The yellow mixture was filtered and concentrated to give yellow crystals of the title compound. Yield: 0.84 g (48%); m.p.: 226−227 °C. $C_{32}H_{36}Cl_4Ge_2N_4Si_2$: calcd. C 46.88, H 4.43, N 4.83; found C 46.51, H 4.31, N 4.63. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ = 0.03 (s, 4 H, $SiMe_3$), 0.31 (s, 5 H, $SiMe_3$), 6.86 (t, J = 7.1 Hz, 1 H, 5-py), 6.98 (d, J = 7.1 Hz, 1 H, 3-py), 7.08−7.15 (m, 3 H, Ph), 7.17−7.22 (m, 2 H, Ph), 7.41 (t, J = 7.7 Hz, 1 H, 4-py), 7.73 (d, J = 5.5 Hz, 1 H, 6-py) ppm. ^{13}C{^{1}H} NMR (300 MHz, C_6D_6, 25 °C): δ = 2.60 ($SiMe_3$), 119.13 (*C*$SiMe_3$), 122.97, 126.04, 127.80, 128.91, 129.67, 132.07, 133.09, 139.98, 145.62 (Ph and Py), 167.73 (N*C*Ph) ppm.

[{(C$_5$H$_4$N-2)C(SiMe$_3$)C(Ph)N}(μ-SiHCl)]$_2$ (9): A solution of **1** (1.28 g, 1.84 mmol) in THF (30 mL) was added slowly to a solution of $HSiCl_3$ (0.41 mL, 4.05 mmol) in THF (20 mL) at −90 °C. The yellow solution was warmed to ambient temperature and stirred for two days. The volatiles were removed under reduced pressure and the residue was extracted with toluene. The yellow mixture was filtered and concentrated to give yellow crystals of the title compound. Yield: 0.97 g (79%); m.p.: 232−233 °C. $C_{32}H_{38}Cl_2Si_4N_4$: calcd. C 58.07, H 5.79, N 8.46; found C 58.55, H 5.62, N 7.64. ^{1}H NMR (300 MHz, [D$_8$]THF, 25 °C): δ = −0.16 (s, 6 H, $SiMe_3$), 0.41 (s, 3 H, $SiMe_3$), 5.46 (s, 1 H, SiH), 6.92−6.96 (t, J = 6.0 Hz, 1 H, 5-py), 6.99−7.02 (d, J = 7.4 Hz, 1 H, 3-py), 7.11−7.19 (m, 2 H, Ph), 7.36−7.37 (m, 3 H, Ph), 7.41−7.44 (m, 1 H, 4-py), 7.80−7.82 (d, J = 5.8 Hz, 1 H, 6-py) ppm. ^{13}C{^{1}H} NMR (300 MHz, [D$_8$]THF, 25 °C): δ = 2.90, 3.13 ($SiMe_3$), 101.36 (*C*$SiMe_3$), 118.44, 123.80, 126.05, 127.92, 128.35, 128.91, 129.59, 139.36, 141.80, 155.89 (Ph and Py) 162.51 (N*C*Ph) ppm.

[{(C$_5$H$_4$N-2)C(H)C(Ph)N}(μ-GeCl$_2$)]$_2$ (11): A solution of **10** (0.84 g, 1.53 mmol) in THF (30 mL) was added slowly to a solution of $GeCl_4$ (0.38 mL, 3.36 mmol) in THF (20 mL) at −90 °C. The yellow suspension was warmed to ambient temperature and stirred for two days. The volatiles were removed under reduced pressure and the residue was extracted with toluene. The yellow mixture was filtered and concentrated to give yellow crystals of the title compound. Yield: 0.39 g (37%); m.p.: 210−211 °C. $C_{26}H_{36}Cl_4Ge_2N_4$: calcd. C 46.23, H 2.90, N 8.29; found C 46.03, H 3.08, N 8.23. ^{1}H NMR [300 MHz, C_6D_6/[D$_8$]THF (2:1), 25 °C]: δ = 5.09 (s, 1 H, *H*CC), 6.57 (t, J = 6.6 Hz, 1 H, 5-py), 6.68 (d, J = 8.5 Hz, 1 H, 3-py), 6.91 (t, J = 8.0 Hz, 1 H, 4-py), 7.10−7.14 (m, 5 H, Ph), 8.65 (d, J = 6.3 Hz, 1 H, 6-py) ppm. ^{13}C{^{1}H} NMR (300 MHz, C_6D_6/[D$_8$]THF 2:1, 25 °C): δ = 96.51 (H*C*C), 116.70, 119.56, 121.62, 124.71, 125.92, 126.85, 129.69, 130.36, 139.85, 142.27, 145.48 (Ph and Py), 155.79 (N*C*Ph) ppm.

X-ray Crystallographic Study: Single crystals were sealed in Lindemann glass capillaries under nitrogen. The X-ray data of **2**−**5**, **7**−**9**, and **11** were collected on a Rigaku R-AXIS II imaging plate using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) from a rotating-anode generator operating at 50 kV and 90 mA. Crystal data for **2**−**5**, **7**−**9**, and **11** are summarized in Table 5 and 6. The structures were solved by direct phase determination using the computer program SHELXTL-PC[27] on a PC 486 and refined by full-matrix least-squares with anisotropic thermal parameters for the non-hydrogen atoms. Hydrogen atoms were introduced in their idealized positions and included in structure factor calculations with assigned isotropic temperature factor calculations.

CCDC-250383 to -250390 (**2**−**5**, **7**−**9** and **11**, respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/

Table 5. Crystallographic data for compounds **2**−**5**

	2	**3**	**4**	**5**
Formula	$C_{38}H_{54}GeN_4Si_4$	$C_{38}H_{54}N_4Si_4Sn$	$C_{38}H_{54}N_4PbSi_4$	$C_{19}H_{27}ClGeN_2Si_2$
Mol. mass	751.80	797.90	886.40	447.65
Color	orange	yellow	yellow	yellow
Cryst. syst.	monoclinic	triclinic	triclinic	monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$C2/c$
a (Å)	15.233(3)	11.986(2)	10.3383(14)	33.0609(15)
b (Å)	17.245(3)	12.005(2)	12.1593(16)	6.4912(3)
c (Å)	17.625(4)	17.091(3)	19.033(3)	21.3079(10)
α (°)	90	73.89(3)	99.863(2)	90
β (°)	111.76(3)	85.94(3)	96.010(3)	91.5900(10)
γ (°)	90	63.27(3)	113.164(2)	90
V (Å^3)	4300.1(15)	2106.2(7)	2127.7(5)	4571.0
Z	4	2	2	8
$D_{calcd.}$ (g cm^{-3})	1.161	1.258	1.384	1.301
μ (mm^{-1})	0.853	0.750	4.107	1.567
F(000)	1592	832	896	1856
Cryst. size (mm)	0.30 × 0.25 × 0.24	0.24 × 0.22 × 0.18	1.21 × 0.82 × 0.46	0.80 × 0.34 × 0.29
2θ range (°)	1.44−25.58	2.02−26.00	1.87−25.00	1.91−28.02
Index range	$0 \le h \le 18$, $-20 \le k \le 20$, $-21 \le l \le 19$	$-14 \le h \le 13$, $-13 \le k \le 0$, $-21 \le l \le 20$	$-12 \le h \le 11$, $-14 \le k \le 14$, $-22 \le l \le 18$	$-37 \le h \le 43$, $-8 \le k \le 8$, $-27 \le l \le 28$
No. of rflns. collected	11403	7173	11333	14869
No. of indep. rflns.	6811	6770	7400	5516
$R1$, $wR2$ [$I > 2(\sigma)I$]	0.0567, 0.1420	0.0616, 0.1688	0.0613, 0.1613	0.0403, 0.0998
$R1$, $wR2$ (all data)	0.0763, 0.1530	0.1162, 0.1966	0.0669, 0.1646	0.0679, 0.1082
Goodness of fit, F^2	1.091	1.175	1.048	0.933
No. of data/restraints/params.	6811/0/433	6770/0/425	7400/0/424	5516/0/226
Largest diff peaks (e·Å^{-3})	0.316 to −0.372	0.957 to −0.926	3.551 to −1.759	0.709 to −0.453

Table 6. Crystallographic data for compounds **7**−**9** and **11**

	7	**8**	**9**	**11**
Formula	$C_{19}H_{27}ClN_2PbSi_2$	$C_{32}H_{36}Cl_4Ge_2N_4Si_2$	$C_{33}H_{38}Cl_4N_4Si_4$	$C_{26}H_{36}Cl_4Ge_2N_4$
Mol. mass	582.25	819.81	744.83	675.44
Color	yellow	yellow	yellow	yellow
Cryst. syst.	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$
a (Å)	10.0657(9)	10.541(3)	9.2060(18)	10.891(2)
b (Å)	37.042(3)	14.276(4)	13.528(3)	10.0333(19)
c (Å)	18.7631(15)	12.879(4)	17.123(3)	12.227(2)
α (°)	90	90	90	90
β (°)	98.403(2)	110.786(6)	94.69(3)	92.150(4)
γ (°)	90	90	90	90
V (Å^3)	6920.8(10)	1181.9(9)	2125.3(7)	1335.2(4)
Z	12	2	2	2
$D_{calcd.}$ (g cm^{-3})	1.676	1.503	1.164	1.680
μ (mm^{-1})	7.538	2.049	0.417	2.676
F(000)	3384	832	776	672
Cryst. size (mm)	0.54 × 0.26 × 0.21	0.16 × 0.13 × 0.11	0.60 × 0.40 × 0.40	0.32 × 0.31 × 0.20
2θ range (°)	1.55-22.50	2.21-25.00	1.92-24.00	2.46-28.09
Index range	$-10 \le h \le 10$, $-38 \le k \le 39$, $-18 \le l \le 20$	$-11 \le h \le 12$, $-16 \le k \le 14$, $-15 \le l \le 14$	$0 \le h \le 10$, $-15 \le k \le 15$, $-19 \le l \le 19$	$-14 \le h \le 13$, $-13 \le k \le 13$, $-10 \le l \le 16$
No. of rflns. collected	30866	9917	5303	9182
No. of indep. rflns.	8988	3177	3056	3222
$R1$, $wR2$ [$I > 2(\sigma)I$]	0.0604, 0.1252	0.0682, 0.1514	0.0902, 0.2415	0.0319, 0.0617
$R1$, $wR2$ (all data)	0.1691, 0.1564	0.1241, 0.1736	0.0960, 0.2494	0.0588, 0.0683
Goodness of fit, F^2	0.849	0.826	1.022	0.908
No. of data/restraints/params.	8988/28/667	3177/0/200	3056/0/218	3222/0/164
Largest diff peaks (e·Å^{-3})	2.646 to −1.438	1.376 to −1.549	0.578 to −0.751	0.364 to −0.319

retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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