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Synthesis and Reaction of Monomeric Germanium(II) and Lead(II) Dimethylamide and the Synthesis of Germanium(II) Hydrazide by Clevage of one N−H bond of Hydrazine

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The β-diketiminate substituted germanium(II) and lead(II) dimethylamides, $LGeNMe_2$ (**1**) and $LPbNMe_2$ (**2**), [$L = CH\{(CMe)_2(2,6\text{-}iPr_2C_6H_3N)_2\}$] have been synthesized by the reaction of $LiNMe_2$ with LGeCl and LPbCl respectively. Reaction of compound **1** with an equivalent amount of elemental sulfur leads to the germanium analogue of thioamide, $LGe(S)NMe_2$ (**3**). **2** reacts with 2-benzoyl pyridine (PhCOPy-2) to form the lead(II) alkoxide $LPbOC(NMe_2)Ph(2\text{-}Py)$ (**4**) by nucleophilic addition of "NMe_2" to the carbon oxygen double bond. The reaction of stable N-heterocyclic germylene L^1Ge [$L^1 = CH\{(C{=}CH_2)(CMe)(2,6\text{-}iPr_2C_6H_3N)_2\}$] with hydrazine yields the germanium(II) substituted hydrazide $LGeNHNH_2$ (**5**) by cleavage of one N−H bond of hydrazine. Finally, attempts to isolate lead(II) hydride LPbH from the reaction of **2** with phenylsilane ($PhSiH_3$) failed, and instead $LPbN(2,6\text{-}iPr_2C_6H_3)\{C(CH_3)CHC(CH_3){=}N(2,6\text{-}iPr_2C_6H_3)\}$ (**6**) was obtained in very low yield. We are able to prove this only by single crystal X-ray structural analysis. Compounds **1**, **2**, **3**, **4**, and **5** were characterized by microanalysis, electron impact (EI) mass spectrometry, and multinuclear NMR spectroscopy. Furthermore compounds **1**, **2**, **5**, and **6** were characterized by single crystal X-ray structural analysis, with the result that they are exhibiting monomeric structures in the solid state with trigonal-pyramidal environment at the metal center and a stereochemically active lone pair.

Introduction

In recent years the chemistry of carbene and its higher analogues has received considerable attention because of their special properties and reactivities.[1] Recently we have reported on the synthesis and reactivity of stable divalent monomeric silicon, germanium, tin, and lead compounds with small organic substituents using chelating ligands.[2−4] In literature there are some reports on the synthesis of germanium(II) and lead(II) diamides, and also few heteroleptic germanium(II) and lead(II) amides are known.[5] Herein, we present the synthesis and reaction of the first monomeric dimethylamido derivative of germanium(II) and lead(II) with the β-diketiminate ligand.

Hydrazine and its derivatives are important molecules in the field of organic and inorganic chemistry since the discovery of a new indole synthesis in 1883 by Emil Fischer.[6] In literature the cleavage of the N−N bond of hydrazine is well documented by a variety of model systems, while the N−H bond cleavage of hydrazine is rare.[7] N−H bond cleavage of hydrazine on a metal surface has been reported, and substitution reactions of the hydrogen atoms of hydrazine are well-known.[8] Herein, we report on N−H bond cleavage of hydrazine with N-heterocyclic germylene under formation of germanium(II) substituted hydrazide.

Result and Discussion

The reaction of LGeCl with $LiNMe_2$ in diethyl ether afforded $LGeNMe_2$ (**1**) in good yield (Scheme 1). It is worth

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mentioning that the reaction of LGeCl with $LiN(TMS)_2$ in diethyl ether leads exclusively to L^1Ge, [L^1 = $CH\{(C{=}CH_2)(CMe)(2,6\text{-}i\text{Pr}_2C_6H_3N)_2\}$] instead of $LGeN(TMS)_2$.[9]

Compound **1** was characterized by ^1H NMR spectroscopy, electron impact (EI) mass spectrometry, and elemental analysis. The ^1H NMR spectrum of **1** shows a singlet at 4.82 ppm for the γ-C*H* proton, and two septets (3.43, 3.37 ppm) corresponding to the C*H* protons of the *i*Pr moieties. Moreover the signal that arises at δ 2.82 ppm corresponds to the protons of the N*Me*$_2$ group. The most abundant ion in the EI mass spectrum appeared at *m*/*z* 491 for [$M^+ - NMe_2$]. **1** crystallizes in the triclinic space group $P\bar{1}$ with one monomer in the asymmetric unit (Figure 1).

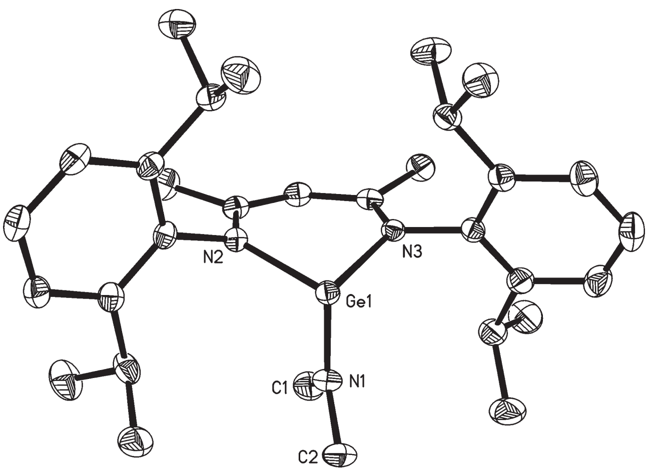

Figure 1. Molecular structure of **1**. Anisotropic displacement parameters are depicted at the 50% probability level, and all restrained refined hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [deg] are Ge1−N1 1.8712(14), Ge1−N2 2.0309(16); N1−Ge1−N2 99.84(7), N1−Ge1−N3 97.01(6).

Similarly treatment of LPbCl with $LiNMe_2$ in diethyl ether afforded the lead(II) amide, $LPbNMe_2$ (**2**), which was isolated as a pale yellow, very air sensitive, microcrystalline solid in moderate yield (Scheme 1). **2** was characterized by ^1H, ^{13}C, and ^{207}Pb NMR spectroscopy, EI mass spectrometry, and elemental analysis. The ^1H NMR spectrum of **2** shows a singlet at 4.73 ppm for the γ-C*H* proton, and two septets (δ 3.48, 3.30 ppm) corresponding to the C*H* protons of the *i*Pr moieties. Moreover the signal that arises at δ 3.80 ppm corresponds to the protons of the N*Me*$_2$ group. This resonance is shifted downfield compared to that of the analogous germanium and tin compounds (see Table 1).

Scheme 1. Preparation of Compounds **1** and **2**

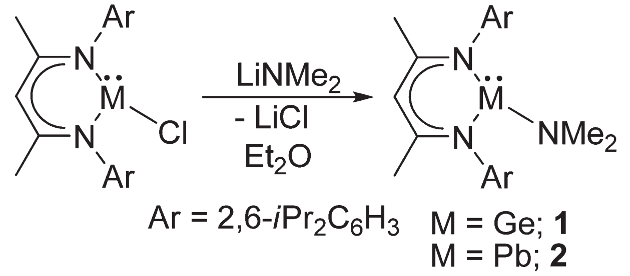

Table 1. ^1H NMR Data of Terminal NMe_2 Group in $LMNMe_2$ (M = Ge, Sn, and Pb)

compound[a]	^1H NMR (δ, ppm)
$LGeNMe_2$ (**1**)	2.82
$LSnNMe_2$[10]	3.00
$LPbNMe_2$ (**2**)	3.80

[a] L = $CH\{(CMe)_2(2,6\text{-}i\text{Pr}_2C_6H_3N)_2\}$

The ^{207}Pb NMR of **2** exhibits a singlet at 1674 ppm; this suggests that the NMe_2 group is a stronger σ-acceptor, when compared with that of chloride (^{207}Pb NMR of LPbCl δ 1413 ppm). The most abundant ion in the EI mass spectrum appeared at *m*/*z* 625 for the molecular ion [$M^+ - NMe_2$]. **2** crystallizes in the monoclinic space group *C*2/*m* with one monomer in the asymmetric unit (Figure 2).

We already reported on the synthesis and structure of LGe(S)X (X = Cl, F, Me, and OH) with Group 14 and 16 elements.[11] To the best of our knowledge there are no reports on amide derivatives containing heavier elements of Group 14 and 16. Herein, we describe the formation of the germanium thionamide $LGe(S)NMe_2$ (**3**) (Scheme 2). The reaction

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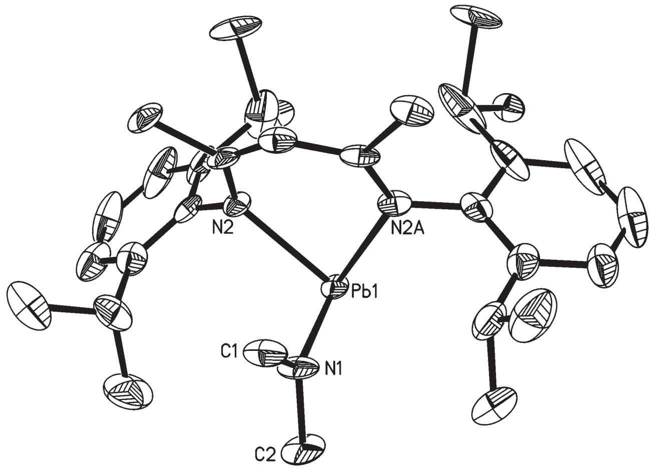


Figure 2. Molecular structure of **2**. Anisotropic displacement parameters are depicted at the 50% probability level, and all restrained refined hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [deg] are Pb1−N1 2.155(10), Pb1−N2 2.330(7); N1−Pb1−N2 94.3(3), N2−Pb1−N2A 80.7(4).

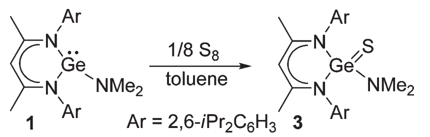
of $LGeNMe_2$ with equivalent amounts of elemental sulfur at room temperature in toluene leads after 1 day to the white compound $LGe(S)NMe_2$ (**3**) in moderate yield.

Compound **3** is soluble in benzene, tetrahydrofuran (THF), and *n*-hexane, and shows no decomposition on exposure to dry air. Compound **3** was characterized by NMR spectroscopy and EI mass spectrometry. The ^1H NMR spectrum of **3** exhibits a broad resonance at δ 2.89−2.73 ppm for the amide (NMe_2) protons, which can be compared with the singlet resonance of **1** (δ 2.82 ppm). The most abundant ion peak in the EI mass spectrum appeared at *m*/*z* 523 [$M^+ - NMe_2$].

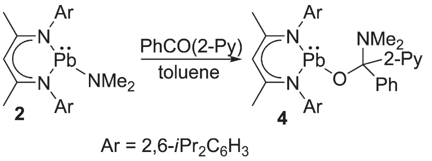
Treatment of **2** with 2-benzoyl pyridine at −20 to −10 °C leads almost quantitatively to the alkoxide **4** (Scheme 3) with the Pb−O−CNMe$_2$ core. It is worth mentioning that the corresponding reaction with **1** does not occur even at higher temperature (120 °C), but with $LSnNMe_2$[10] it proceeds at room temperature.[12] This trend is as expected because the reactivity of Group 14 amides gradually increases with increasing radii of the elements. Such an increase of reactivity was also observed when LGeH[2a,d] and LSnH[3a,b] were used. The ^1H NMR spectrum of **4** exhibits a singlet (δ 4.77 ppm) which can be assigned to the C*H* proton of the ligand backbone and another singlet resonance at δ 1.93 ppm for protons of the N*Me*$_2$ group which is different from that of the precursor **2**. The ^{207}Pb NMR resonance of **4** arises at δ 1093 ppm, which is similar to that of the phenolato substituted β-diketiminate lead compound, LPbO-2,6-*t*Bu$_2$C$_6$H$_3$ (δ 1040 ppm),[5d] but very much different, when compared with that of compound **2** ($LPbNMe_2$: δ 1674 ppm).

In the last year we have shown that the synthesis of $LGeNH_2$ was achieved by the reaction of N-heterocyclic germylene, L^1Ge, [L^1 = CH{(C=CH$_2$)(CMe)(2,6-*i*Pr$_2$C$_6$H$_3$N)$_2$}] with ammonia gas.[13] Consequently, we have demonstrated the reactivity of the N-heterocyclic silylene, L^1Si, with ammonia, hydrazine, *N*-methyl hydrazine, and diphenyl hydrazone.[14]

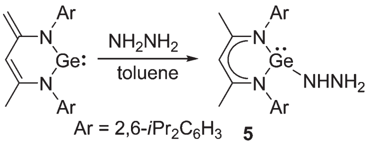
Scheme 2. Preparation of Compound **3**



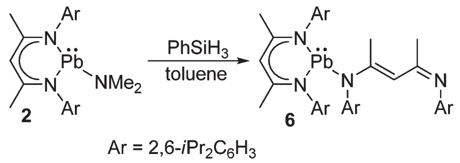
Scheme 3. Synthesis of Compound **4**



Scheme 4. Preparation of Compound **5**



Scheme 5. Preparation of Compound **6**



Here we outline the reaction of L^1Ge with hydrazine, under formation of the germanium(II) substituted hydrazide, $LGeNHNH_2$ (Scheme 4), which is different when compared with that of the silicon analogue. In the silicon case there is formation of the silicon(IV) hydrazide $L^1Si(H)$-$NHNH_2$.[14b] The synthesis of the first stable germanium(II) substituted hydrazone, LGeN(H)NCHR (R = CO_2Et and $SiMe_3$) was recently described.[15]

The addition of hydrazine to a red solution of L^1Ge in toluene leads to a rapid vanishing of the red color (Scheme 5). From the resulting yellow solution the volatiles were removed *in vacuo*, and the residue was extracted with *n*-hexane. Concentration of the solution yielded yellow crystals of $LGeNHNH_2$ (**5**) in 85% yield. The composition of **5** was supported by ^1H NMR spectroscopy, EI mass spectrometry, and elemental analysis. Furthermore, it was characterized by single crystal X-ray structural analysis. The ^1H NMR spectrum shows a doublet and triplet resonance (δ 3.16 and 0.87 ppm), which corresponds to the different protons of the $NHNH_2$ group of **5**.

Single crystals of **5** were obtained from a saturated *n*-hexane solution at −32 °C after 4 days. Compound **5** crystallizes in the triclinic space group $P\bar{1}$ with one monomer in the asymmetric unit. X-ray crystal structure analysis afforded a monomeric structure as illustrated in Figure 3. Surprisingly, **5** is monomeric in the solid state and what is even more striking, the $NHNH_2$ group is not involved in any kind of hydrogen bonding as shown by X-ray structural analysis. Compound **5**

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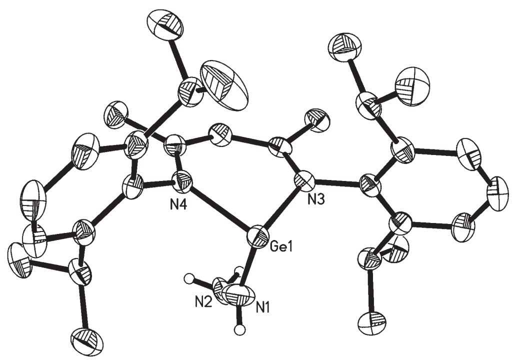

Figure 3. Molecular structure of **5**. Anisotropic displacement parameters are depicted at the 50% probability level, and all restrained refined hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [deg] are Ge1−N1 1.909(5), N1−N2 1.053(5), Ge1−N3 2.0141(19); N1−Ge1−N3 96.49(13), N2−N1−Ge1 134.6(3).

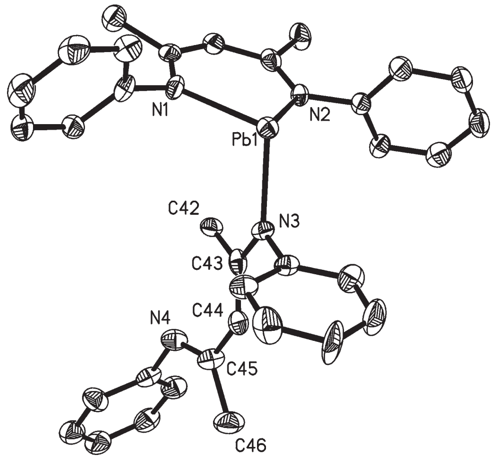

Figure 4. Molecular structure of **6**. Anisotropic displacement parameters are depicted at the 50% probability level, and all restrained refined hydrogen atoms and isopropyl groups are omitted for clarity. Selected bond lengths [Å] and angles [deg] are Pb1−N1 2.350(5), Pb1−N2 2.343(5), Pb1−N3 2.268(5), N3−C43 1.352(8), C43−C44 1.369(10), C44−C45 1.432(9), C45−N4 1.300(9); N1−Pb1−N2 83.04(19), N2−Pb1−N3 101.74(19).

is stable in the solid state as well as in solution for a longer period of time without any decomposition under an inert atmosphere. The geometry about the germanium is trigonal pyramidal. The germanium is surrounded by two nitrogen atoms from the backbone of the chelating ligand and the nitrogen of the $NHNH_2$ group.

Finally, we tried to prepare the lead(II) hydride, LPbH, by reaction of LPbCl with $AlH_3 \cdot NMe_3$, K-selectride, and $PhSiH_3$ respectively, as well as the reaction of $LPbN(TMS)_2$ or $LPbNMe_2$ (**2**) with $PhSiH_3$. In all cases we obtained the free ligand (LH) and metallic lead as the major product with small amounts of $LPbN(2,6\text{-}i\text{Pr}_2C_6H_3)\{C(CH_3)CHC(CH_3){=}N(2,6\text{-}i\text{Pr}_2C_6H_3)\}$ (**6**) (Scheme 5). The latter, **6** (Figure 4), has been analyzed by single crystal X-ray diffraction. The formation of **6** suggests that LPbH might be formed as an intermediate which immediately decomposed to LH and metallic lead. In a side reaction the free ligand reacts with LPbH to form compound **6** under elimination of hydrogen. Power and co-workers also reported on a lead bonded compound, which is formed via a hydride intermediate accompanied by hydrogen elimination.[16] From the literature it is known, that metal hydride reacts with amine to form the metal amide complexes under elimination of hydrogen.[17] Compound **6** crystallizes in the orthorhombic space group $P2_12_12_1$, with one monomer in the asymmetric unit. The structure of **6** shows that one ligand is chelating to lead, while the other is monodentate arranged. This result is due to the steric demand of the two ligands. The difference in bonding is reflected in the bond lengths within the ligands. In the monodentate case there are carbon carbon single and double bonds, which are distinctly different, while in the chelating ligand the bond lengths are at an average. The geometry at the lead center is similar to that in compound **2**, which is trigonal pyramidal with a stereochemically active lone pair.

Summary

In conclusion we have shown the synthesis of a monomeric germanium(II) and lead(II) dimethylamide derivative and their reactions. The germanium analogue of thioamide, $LGe(S)NMe_2$, was obtained by the reaction of germanium(II) dimethylamide with equivalent amounts of elemental sulfur. A lead(II)-alkoxide has been prepared by the reaction of $LPbNMe_2$ with 2-benzoyl pyridine. Finally we have shown that one N−H bond of hydrazine is cleaved with L^1Ge.

Experimental Section

All manipulations were performed under a dry and oxygen free atmosphere (N_2) using standard Schlenk line techniques or inside a MBraun MB 150-GI glovebox. All solvents were dried by a MBraun solvent purifying system prior to use. The starting materials LGeCl[18] and LPbCl[4b] were prepared using literature procedures. All other chemicals were purchased commercially and used as received. ^1H and ^{207}Pb NMR spectra were recorded on a Bruker Avance 500 MHz instrument and referenced to the deuterated solvent in case of the ^1H NMR spectra. ^{207}Pb NMR spectrum was referenced to $Pb(Me)_4$. Elemental analyses were performed by the Analytisches Labor des Instituts für Anorganische Chemie der Universität Göttingen. EI-MS were measured on a Finnigan MAT 8230 or a Varian MAT CH5 instrument. Melting points were measured in sealed glass tubes with a Büchi melting point B 540 instrument.

Synthesis of $LGeNMe_2$ (1). A solution of LGeCl (0.52 g, 1.0 mmol) in diethyl ether (20 mL) was added drop by drop to a stirred suspension of $LiNMe_2$ (0.051 g, 1.0 mmol) in diethyl ether (10 mL) at −78 °C. The reaction mixture was warmed to room temperature and stirred for another 12 h. The precipitate was filtered off, and the solvent was partially reduced (ca. 20 mL). Storage of the remaining solution in a freezer at −32 °C overnight afforded yellow crystals of **1** suitable for X-ray diffraction analysis. Yield 0.45 g (84%). Mp 225 °C. ^1H NMR (500 MHz, C_6D_6): δ 7.12−7.18 (m, 6H, Ar-*H*), 4.82 (s, 1H, γ-C*H*), 3.43 (sept, J = 6.86 Hz, 2H, C*H*$(CH_3)_2$), 3.37 (sept, J = 6.86 Hz, 2H, C*H*$(CH_3)_2$), 2.82 (s, 6H, $N(CH_3)_2$), 1.59 (s, 6H, CH_3), 1.33 (d, J = 6.86 Hz, 6H, $CH(CH_3)_2$), 1.29 (d, J = 6.86 Hz, 6H, $CH(CH_3)_2$), 1.26 (d, J = 6.86 Hz, 6H, $CH(CH_3)_2$), 1.13 (d, J = 6.86 Hz, 6H, $CH(CH_3)_2$) ppm. EI-MS (70 eV): m/z (%): 491 (100) $[M^+ - NMe_2]$. Anal. Calcd for $C_{31}H_{47}GeN_3$ (534.36): C 69.68, H 8.87, N 7.86; Found: C 69.82, H 9.54, N 7.80.

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Table 2. Crystallographic Data for the Structural Analyses of Compounds **1**, **2**, **5**, and **6**

	1	**2**	**5**	**6**
empirical formula	$C_{31}H_{47}GeN_3$	$C_{31}H_{47}N_3Pb$	$C_{29}H_{44}GeN_4$	$C_{64}H_{96}N_4Pb$
formula weight	534.31	668.91	521.27	1128.64
CCDC no.	730406	730405	745454	759550
T [K]	133(2)	133(2)	133(2)	133(2)
crystal system	triclinic	monoclinic	triclinic	orthorhombic
space group	$P\bar{1}$	$C2/m$	$P\bar{1}$	$P2_12_12_1$
a [Å]	10.453(2)	8.9507(18)	8.6062(17)	15.632(3)
b [Å]	12.286(3)	22.604(5)	11.553(2)	17.187(3)
c [Å]	13.016(3)	14.904(3)	15.055(3)	22.730(5)
α [deg]	66.98(3)	90	97.44(3)	90
β [deg]	80.50(3)	99.12(3)	98.64(3)	90
γ [deg]	72.40(3)	90	106.20(3)	90
V [Å^3]	1464.4(6)	2977.2(10)	1397.8(5)	6107(2)
Z	2	4	2	4
D_{calcd} [g cm^{-3}]	1.212	1.492	1.239	1.229
μ [mm^{-1}]	1.069	5.689	1.119	2.802
F(000)	572	1344	556	2364
θ range [deg]	1.70 - 27.02	1.38 - 25.92	1.87 - 27.04	1.49 - 25.94
reflections collected	13048	12107	12150	26179
independent reflections	6309 (R_{int} = 0.0270)	2956 (R_{int} = 0.1014)	6002 (R_{int} = 0.0332)	11787 (R_{int} = 0.0575)
data/restraints/parameters	6309/0/331	2956/0/184	6002/4/338	11787/0/622
$R1$, $wR2$ [$I > 2\sigma(I)$]^a	0.0279, 0.0640	0.0667, 0.1752	0.0419, 0.1006	0.0475, 0.0768
$R1$, $wR2$ (all data) ^{a}	0.0335, 0.0657	0.0679, 0.1766	0.0524, 0.1051	0.0643, 0.0809
GoF	1.055	1.143	1.027	1.030
$\Delta\rho$(max), $\Delta\rho$(min) [e Å^{-3}]	0.331, −0.233	9.439, −4.106	0.920, −0.637	1.665, −1.331

^{a} $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{0.5}$.

Synthesis of LPbNMe$_2$ (2). A solution of LPbCl (0.660 g, 1.0 mmol) in diethyl ether (20 mL) was added drop by drop to a stirred suspension of LiNMe$_2$ (0.051 g, 1.0 mmol) in diethyl ether (10 mL) at −78 °C. The reaction mixture was warmed to room temperature and stirred for another 12 h. The precipitate was filtered off, and the solvent was partially reduced (ca. 20 mL). Storage of the remaining solution in a freezer at −32 °C overnight afforded yellow crystals of **2** suitable for X-ray diffraction analyses. Yield 0.47 g (70%). Mp 195 °C. ^{1}H NMR (500 MHz, C_6D_6): δ 7.10−7.19 (m, 6H, Ar-*H*), 4.73 (s, 1H, γ-C*H*), 3.80 (s, 6H, N(C*H*$_3$)$_2$), 3.48 (sept, J = 6.82 Hz, 2H, C*H*(CH$_3$)$_2$), 3.30 (sept, J = 6.82 Hz, 2H, C*H*(CH$_3$)$_2$), 1.71 (s, 6H, C*H*$_3$), 1.32 (d, J = 6.82 Hz, 6H, CH(C*H*$_3$)$_2$), 1.29 (d, J = 6.82 Hz, 6H, CH(C*H*$_3$)$_2$), 1.25 (d, J = 6.82 Hz, 6H, CH(C*H*$_3$)$_2$), 1.16 (d, J = 6.82 Hz, 6H, CH(C*H*$_3$)$_2$) ppm. ^{207}Pb NMR (104.63 Hz, C_6D_6): δ 1674 ppm. EI-MS (70 eV): m/z (%): 625 (100) [M$^+$ − NMe$_2$]. Anal. Calcd for $C_{31}H_{47}N_3Pb$ (669.35): C 55.66, H 7.08, N 6.28; Found: C 55.70, H 7.77, N 6.15.

Synthesis of LGe(S)NMe$_2$ (3). A solution of **1** (0.530 g, 1.00 mmol) in toluene (30 mL) was slowly added to a suspension of elemental sulfur (0.032 g, 1.00 mmol) in toluene (15 mL) by cannula at room temperature. After 0.5 h under constant stirring at ambient temperature the red solution turned slightly yellow. All volatiles were removed *in vacuo*, and the remaining residue was extracted with toluene (15 mL). The solvent was removed *in vacuo* to yield **3** as a slight yellow powder. Yield 0.340 g (60%). Mp 230 °C. ^{1}H NMR (300 MHz, C_6D_6): δ 7.02−7.16 (m, 6H, Ar-*H*), 4.70 (s, 1H, γ-C*H*), 3.47 (sept, J = 6.72 Hz, 2H, C*H*(CH$_3$)$_2$), 3.15 (sept, J = 6.72 Hz, 2H, C*H*(CH$_3$)$_2$), 2.89−2.73 (br, 6H, N(C*H*$_3$)$_2$), 1.60 (d, J = 6.72 Hz, 6H, CH(C*H*$_3$)$_2$), 1.44 (s, 6H, C*H*$_3$), 1.29 (d, J = 6.72 Hz, 6H, CH(C*H*$_3$)$_2$), 1.18 (d, J = 6.72 Hz, 6H, CH(C*H*$_3$)$_2$), 1.07 (d, J = 6.72 Hz, 6H, CH(C*H*$_3$)$_2$) ppm. EI-MS (70 eV): m/z (%): 523 (100) [M$^+$ − NMe$_2$].

Synthesis of LPbOC(NMe$_2$)Ph(2-Py) (4). A solution of 2-benzoyl pyridine (0.180 g, 1.00 mmol in 5 mL toluene) was added by cannula to a solution of **2** (0.670 g, 1.00 mmol in toluene 20 mL) at −30 °C. The reaction mixture was warmed to room temperature and stirred for another 2 h. After that all volatiles were removed *in vacuo*, and the remaining residue was extracted with *n*-hexane (25 mL), concentrated to about 15 mL and stored in a freezer at −30 °C. Yellow crystals of **4** are formed after 4 days. Yield: 0.66 g (78%). Mp 164 °C. ^{1}H NMR (500 MHz, C_6D_6): δ 7.80 (d, 2H, *o*-Ph), 7.45 (d, 1H, *o*-Py), 7.23 (t, 2H, *m*-Ph), 7.01−7.18 (m, 7H, Ar-*H*, *p*-Ph), 6.80 (t, 1H, *p*-Py), 6.47 (d, 1H, *m*-Py), 6.34 (m, 1H, *m*-Py), 4.77 (s, 1H, γ-C*H*), 3.80−3.40 (br, 4H, C*H*(CH$_3$)$_2$), 1.93 (s, 6H, N(C*H*$_3$)$_2$), 1.76 (s, 6H, C*H*$_3$), 1.33−1.09 (m, 24H, CH(C*H*$_3$)$_2$) ppm. ^{207}Pb NMR (104.63 Hz, C_6D_6): δ 1093 ppm. Anal. Calcd for $C_{43}H_{56}N_4OPb$ (852.42): C 60.61, H 6.62, N 6.57; Found C 60.74, H 7.11, N, 6.41.

Synthesis of LGeNHNH$_2$ (5). NH$_2$NH$_2$ (1 mL, 1 M in THF) was added to a red solution of L^{1}Ge (0.490 g, 1 mmol) in toluene (20 mL) at 0 °C. The reaction mixture was allowed to warm to room temperature. After that the reaction mixture was stirred for additional 30 min. All volatiles were removed *in vacuo*, and the residue was extracted with *n*-hexane (30 mL). The solution was reduced to half of the volume. Storage of the solution at −32 °C in a freezer for 2 days yielded **5** as yellow crystals suitable for single crystal X-ray diffraction analysis. Yield: 0.44 g (85%). Mp 134 °C. ^{1}H NMR (300 MHz, C_6D_6): δ 7.10−7.17 (m, 6H, Ar-*H*), 4.71 (s, 1H, γ-C*H*), 3.50−3.43 (m, 4H, C*H*(CH$_3$)$_2$), 3.16 (d, 1H, N*H*$_2$), 1.59 (s, 6H, C*H*$_3$), 1.41 (d, J = 6.67 Hz, 6H, CH(C*H*$_3$)$_2$), 1.33 (d, J = 6.67 Hz, 6H, CH(C*H*$_3$)$_2$), 1.25 (d, J = 6.67 Hz, 6H, CH(C*H*$_3$)$_2$), 1.13 (d, J = 6.67 Hz, 6H, CH(C*H*$_3$)$_2$), 0.87 (t, 1H, N*H*) ppm. EI-MS (70 eV): m/z (%): 475 (100) [M$^+$ − (NHNH$_2$, Me)]. Anal. Calcd for $C_{29}H_{44}GeN_4$ (522.28): C 66.81, H 8.51, N 10.75; Found: C 66.73, H 8.97, N 9.70.

Synthesis of LPbN(2,6-*i*Pr$_2$C$_6$H$_3$){C(CH$_3$)CHC(CH$_3$)=N-(2,6-*i*Pr$_2$C$_6$H$_3$)} (6). PhSiH$_3$ (0.108 g, 1.00 mmol) was added by cannula to a solution of **2** (0.670 g, 1.00 mmol in toluene 30 mL) at −78 °C. The reaction mixture was warmed to room temperature and stirred for another 1 h. After that all volatiles were removed in vacuo, and the remaining residue was extracted with *n*-hexane (40 mL) and concentrated to about 15 mL and stored in a freezer at −30 °C. A few yellow crystals of **6** formed after 1 day.

Crystallographic Details for Compounds 1, 2, 5, and 6. Suitable crystals of **1**, **2**, **5**, and **6** 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)[19] and refined by full-matrix least-squares methods against F^2 (SHELXL-97).[19] All non-hydrogen atoms were refined with anisotropic displacement parameters. Crystallographic data are presented in Table 2.

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Supporting Information Available: X-ray data for **1**, **2**, **5**, and **6** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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