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PAPER

Synthesis and structural characterization of two-coordinate low-valent 14-group metal complexes bearing bulky bis(amido)silane ligands†

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A series of germylene, stannylene and plumbylene complexes [$\eta^2(N,N)$-$Me_2Si(DippN)_2Ge$:] (**3a**), [$\eta^2(N,N)$-$Ph_2Si(DippN)_2Ge$:] (**3b**), [$\eta^2(N,N)$-$Me_2Si(DippN)_2Sn$:] (**4**), [$\eta^2(N,N)$-$Me_2Si(DippN)_2Pb$:]$_2$ (**5a**), and [$\eta^2(N,N)$-$Ph_2Si(DippN)_2Pb$:] (**5b**) (Dipp = 2,6-$i$$Pr_2C_6H_3$) bearing bulky bis(amido)silane ligands were readily prepared either by the transamination of $M[N(SiMe_3)_2]_2$ (M = Sn, Pb) and [$Me_2Si(DippNH)_2$] or by the metathesis reaction of bislithium bis(amido)silane [$\eta^1(N),\eta^1(N)$-$R_2Si(DippNLi)_2$] (R = Me, Ph) with the corresponding metal halides $GeCl_2$(dioxane), $SnCl_2$, and $PbCl_2$, respectively. Preliminary atom-transfer chemistry involving [$\eta^2(N,N)$-$Me_2Si(DippN)_2Ge$:] (**3a**) with oxygen yielded a dimeric oxo-bridged germanium complex [$\eta^2(N,N)$-$Me_2Si(DippN)_2Ge(\mu$-O)]$_2$ (**6**). All complexes were characterized by ^1H, ^{13}C, ^{119}Sn NMR, IR, and elemental analysis. X-ray single crystal diffraction analysis revealed that the metal centres in **3b**, **4**, and **5b** are sterically protected to prevent interaction between the metal centre and the nitrogen donors of adjacent molecules while complex **5a** shows a dimeric feature with a strong intermolecular Pb···N interaction.

Introduction

In past decades, it has been recognized that carbenes play important roles as transient intermediates. Since the chemistry of divalent 14-group compounds present carbene-like properties,[1,2] much attention has been recently paid to the heavier analogues of silylenes, germylenes, stannylenes, and plumbylenes. Although M(II) compounds (M = Ge(II), Sn(II), Pb(II)) are generally reactive and tend to oligomerize or polymerize, they can be stabilized kinetically by sterically demanding ligands and/or thermodynamically by inter- and intramolecular coordination, representing potential building blocks for further synthetic chemistry.[3] For example, a few of heavier analogues of carbenes such as germylenes, stannylenes, plumbylenes proved to be preparable on a sufficient scale to enable their reactivity, in particular regarding their use as ligands towards transition metals.[3] Nitrogen-based ligands, presumably due to the σ-inductive effect of the electronegative nitrogen atom, have played a pivotal role in the successful isolation of these species with the archetype being $M[N(SiMe_3)_2]_2$ (M = Ge, Sn, Pb).[4] One of our recent interests, the use and implementation of rigid chelating ligands with bulky substituent groups, led us to choose the bis(amido)silane ligand that yielded a four-membered metalloheterocycle system when coordinated to a metal centre such as alkaline earth metals.[5] We noted that two bis(amido)silane germylenes [$\eta^2(N,N)$-$i$$Pr_2Si(DippN)_2Ge$:],[6a] [$\eta^2(N,N)$-$i$$Pr_2Si(SiPh_3N)_2Ge$:],[6a] and three bis(amido)silane stannylenes [$\eta^2(N,N)$-$Ph_2Si(DippN)_2Sn$:],[6b] [(iPr)$_2Si(DippN)_2Sn$],[6a] [$\eta^2(N,N)$-$i$$Pr_2Si(SiPh_3N)_2Sn$:][6a] have been described in the literature very recently, but we anticipated that the tunable steric impact exerted by the nitrogen and silicon substituents of this ligand would be significant for the stabilization and isolability of the low-valent 14-group metal compounds.[7] In this contribution we describe the synthesis of a few germylenes [$\eta^2(N,N)$-$Me_2Si(DippN)_2Ge$:] (**3a**), [$\eta^2(N,N)$-$Ph_2Si(DippN)_2Ge$:] (**3b**), stannylene [$\eta^2(N,N)$-$Me_2Si(DippN)_2Sn$:] (**4**), and plumbylenes [$\eta^2(N,N)$-$Me_2Si(DippN)_2Pb$:]$_2$ (**5a**), [$\eta^2(N,N)$-$Ph_2Si(DippN)_2Pb$:] (**5b**) with sterically demanding bis(amido)silane ligands, as well as a dimeric germanium oxo complex [$\eta^2(N,N)$-$Me_2Si(DippN)_2Ge(\mu$-O)]$_2$ (**6**) that arises from the oxygen-transfer reaction of the germylene (**3a**) and dry oxygen.

Results and discussion

Preparation of complex [$\eta^2(N,N)$-$Ph_2Si(DippNLi)_2$] (2b)

The silanediamine [$Me_2Si(DippNH)_2$] (**1a**), [$Ph_2Si(DippNH)_2$] (**1b**), and bislithium bis(diamido)silane [$Me_2Si(DippNLi)_2$]$_2$ (**2a**) were prepared according to published protocol (Scheme 1).[7] Compound [$Ph_2Si(DippNLi)_2$] (**2b**) can be readily deprotonated

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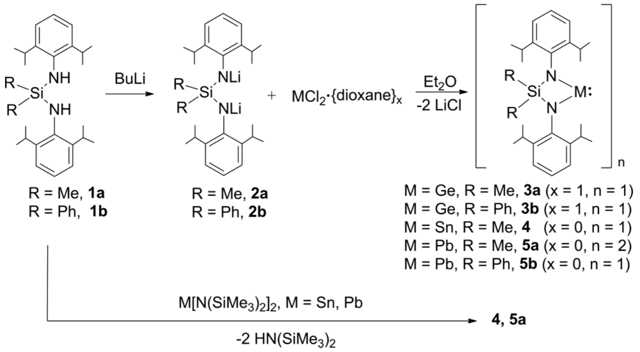


Scheme 1 Synthesis of bis(diamido)silane complexes **2b**, **3a**, **3b**, **4**, **5a** and **5b**.

by the reaction of *n*-BuLi and **1b** in a molar ratio of 2 : 1 at room temperature as a white precipitate in *n*-hexane (95%). ^{1}H NMR spectroscopy revealed two sets of resonances for the non-equivalent –C*H*(CH$_3$)$_2$ substituents, suggesting that the molecular asymmetry of dimer in the solution, similar to the observation for **2a**.[7] No signals were observed at about 2.5 ppm for the N–H resonance, excluding the existence of the free ligand (**1b**). In the ^{7}Li NMR spectrum, only one sharp resonance at $\delta = -0.98$ ppm was assigned to the equivalent coordinated lithium ions in the solution, supporting the formation of **2b**. However, the ^{7}Li NMR resonance at $\delta = -0.98$ ppm for **2b** is drastically shifted upfield relative to the signal of **2a** (^{7}Li $\delta = 1.97$ ppm), suggesting lower electrophilicity of lithium atoms in **2b**. This arises from the phenyl substitutes of **2b**.

Preparation of complexes [η^2(*N*,*N*)-Me$_2$Si(DippN)$_2$Ge:] (3a) and [η^2(*N*,*N*)-Ph$_2$Si(DippN)$_2$Ge:] (3b)

The metathetical reaction between an equimolar ratio of **2a** and GeCl$_2$(dioxane) in *n*-hexane successfully gave [η^2(*N*,*N*)-Me$_2$Si(DippN)$_2$Ge:] (**3a**) as air- and moisture-sensitive pale-yellow needles in 53.0% isolated yield (Scheme 1). In a fashion similar to the preparation of **3a**, compound [η^2(*N*,*N*)-Ph$_2$Si(DippN)$_2$Ge:] (**3b**) was obtained by the metathesis reaction of **2b** and GeCl$_2$(dioxane) in *n*-hexane as air- and moisture-sensitive pale-yellow crystals in 80.0% isolated yield.

Both compounds **3a** and **3b** are soluble in a variety of organic solvents, exhibit sharp, reversible melting points at 128 °C (for **3a**) and 178 °C (for **3b**), and were characterized by NMR spectroscopy, elemental analysis, and for **3b** only X-ray diffraction. ^{1}H and ^{13}C NMR spectroscopy indicated a symmetrical solution structure both for **3a** and **3b** with a single set of resonances for the *i*Pr substituents and symmetrical phenyl skeletons. This suggested that complexes **3a** and **3b**, which have less steric congestion as a result of the smaller central four membered GeN$_2$Si ring, exhibit magnetically equivalent *iso*propyl groups, presumably because of relatively fast rotation (on a ^{1}H NMR time scale) about the C–N bond. This difference in only one single set of resonances for the *i*Pr groups contrasts sharply with those observed in the analogous alkaline earth metal–bis(amido)silane complexes, in which two sets of resonances for the *i*Pr groups were observed.[5] The asymmetrical conformation of alkaline earth metal–bis(amido)silane complexes in solution probably arises from solvated tetrahdrofuran molecules.[5] Two multiple resonances at $\delta = 1.41$, 3.56 ppm in ^{1}H NMR spectrum are assigned to the solvated tetrahydrofuran molecule in **3b**, supporting determination of the ratio of tetrahydrofuran molecules to bis(amido)silane ligands. No signals were observed at about 2.5 ppm for N–H resonance in the ^{1}H NMR spectra,[7] excluding the existence of the free ligand (**1a**, **1b**) in the samples.

Preparation of complex [η^2(*N*,*N*)-Me$_2$Si(DippN)$_2$Sn:] (4)

By slightly altering the reaction conditions for the preparation of **3a**, **3b**, such as the use of *n*-hexane as solvent at 0 °C, we were able to cleanly prepare in good purity bis(amido)silane stannylene [η^2(*N*,*N*)-Me$_2$Si(DippN)$_2$Sn:] (**4**) as air- and moisture-sensitive yellow crystals in 80.0% isolated yield (Scheme 1). Alternatively, complex **4** could be readily prepared by transamination of Sn[N(SiMe$_3$)$_2$]$_2$ and Me$_2$Si(DippNH)$_2$ in *n*-hexane at room temperature in high yield (90.0%) (Scheme 1). The second pathway was preferable for isolation of the product. Complex **4** has good solubility in common organic solvents, such as *n*-hexane, benzene, and toluene, exhibits a sharp, reversible melting point at 190 °C. The formation of **4** is confirmed by ^{1}H NMR spectroscopy, as evident from only one sharp resonance for the –SiC*H*$_3$ groups ($\delta = 0.28$ ppm), one set of coupled doublets for –CH(C*H*$_3$)$_2$ groups ($\delta = 1.27$ ppm, $^1J_{\text{H-H}} = 7.4$ Hz), and one set of septet for –C*H*(CH$_3$)$_2$ groups ($\delta = 3.76$ ppm), these suggest that the solid structure of **4** is maintained in solution *i.e.* no dimerization occurs in solution. No $^{117/119}$Sn satellites were discerned in the ^{1}H NMR spectrum of **4**, presumably as a result of interaction through the quadrupolar amide nitrogen centres.

In the ^{119}Sn NMR spectrum of **4**, only one sharp resonance was shown at $\delta = 514$ ppm. The chemical shift is consistent with a two-coordinate tin centre and is similar to those recently observed for complexes [Ph$_2$Si(DippN)$_2$Sn:] ($\delta = 499$ ppm)[6b] and [(*i*Pr)$_2$Si(DippN)$_2$Sn:] ($\delta = 536$ ppm).[6a]

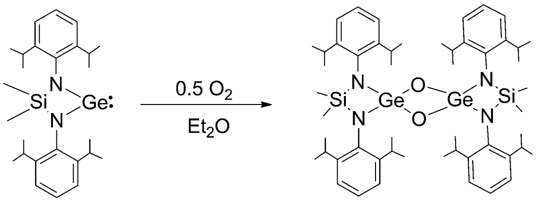
Preparation of complexes [η^2(*N*,*N*)-Me$_2$Si(DippN)$_2$Pb:]$_2$ (5a) and [η^2(*N*,*N*)-Ph$_2$Si(DippN)$_2$Pb:] (5b)

In searching for heavier analogues of silylenes, germylenes, stannylenes, and plumbylenes, most attention has focused on the lighter elements Si and Ge,[1] and no structurally characterized examples of plumbylenes have been reported containing the bis(diamido)silane ligand. The plumbylenes **5a** and **5b** were thus synthesized by the reaction of dilithium salt of the appropriate bis(amido)silane **2a**, **2b** with PbCl$_2$ in ether at room temperature (Scheme 1). These produced deep red-coloured solutions from which the solvents were partially removed *in vacuo* after 24 h. The solids were re-crystallized in the mother liquor at –30 °C and yielded dark red crystals of the pure plumbylenes **5a** and **5b**,respectively. Plumbylene **5a** was also obtained easily in a transamination reaction between Pb[N(SiMe$_3$)$_2$]$_2$ and Me$_2$Si(DippNH)$_2$ in ether at ambient temperature. It could also be re-crystallized from ether to give red crystals. Both of **5a** and **5b** are well soluble in most common organic solvents such as ether, tetrahydrofuran, exhibit sharp, reversible melting points at 148 °C (for **5a**) and 215 °C (for **5b**), and were characterized by NMR spectroscopy, elemental analysis, and X-ray diffraction.

^{1}H NMR spectra (C$_6$D$_6$, 23 °C) of both **5a** and **5b** show only one doublet for the isopropyl –CH(C*H*$_3$)$_3$ groups and one septet signal for the $–CH(CH_3)_3$ groups as encountered for the di*iso*propylphenyl ligand owing to the molecular symmetry in the solution, demonstrating the formation of **5a** and **5b** in solution, indicating that **5a** undergoes dissociation into monomeric species in solution. This is, however, in contrast to the observation in the analogous system of a neutral dimeric magnesium complex, where two doublets for the isopropyl $–CH_3$ groups and two signals for isopropyl $–CH$ groups were observed.[5a]

Preparation of complex [η^2(*N*,*N*)-Me$_2$Si(DippN)$_2$Ge(μ-O)]$_2$ (6)

Divalent germylene **3a**, **3b**, **4**, **5a**, and **5b** were expected to exhibit diverse reaction chemistry due to their dual donor/acceptor nature and proclivity for oxidative bond forming reactions.[1a,8,9,10,11] This may lead to the isolation of heavy analogues of ketones similar to stable divalent 14-group derivative $R_2M = E$ (M = Si, Ge, Sn, Pb; E = O, S, Se, Te).[11,12] In our case, the products from chalcogen atom-transfer may enable confirmation of germerylene **3a** formation. We preliminarily explored chalcogen atom-transfer chemistry involving **3a** with the goal of isolating hitherto rare examples of Ge═O multiple bond. The further reaction of **3a** with dry O_2 was therefore carried out. After workup, only a dimeric germanium oxo-bridged complex [Me$_2$Si(DippN)$_2$Ge(μ-O)]$_2$ (**6**) was isolated in good yield (70%), rather than the expected corresponding heavy analogues of ketone (Scheme 2).[13] Complex **6** is air-, and moisture-stable and well soluble in ether, THF, and DMSO. The ^{1}H NMR spectrum of compound **6** in C_6D_6 displays two sets of coupled doublets for $–CH(CH_3)_2$ groups (δ = 1.08 ppm, $^1J_{H–H} = 6.6$ Hz; $\delta = 1.23$ ppm, $^1J_{H–H} = 6.6$ Hz). The two sets of resonances for the nonequivalent $–C(CH_3)_2$ groups in complex **6** reveal molecular asymmetry and a hindered rotation about the C–N bond in solution, similar to that observed in neutral dimeric magnesium complex [η^1,η^1-Me$_2$Si(DippN)$_2$Mg)].[5a] Notably, the resonances of the $–C(CH_3)_2$ groups in the ^{1}H NMR spectrum were slightly overlapped by the signals of the lattice ether.



3a

6

Scheme 2 The formation of complex **6**.

Single crystal and molecular structures

Single crystal X-ray diffraction experiments were carried out on **3b–6**. Thermal ellipsoid plots of the molecular structures are shown in Fig. 1–5 and selected structural parameters are presented in the legend of each figure; the crystallographic data of complexes are given in Table 1.

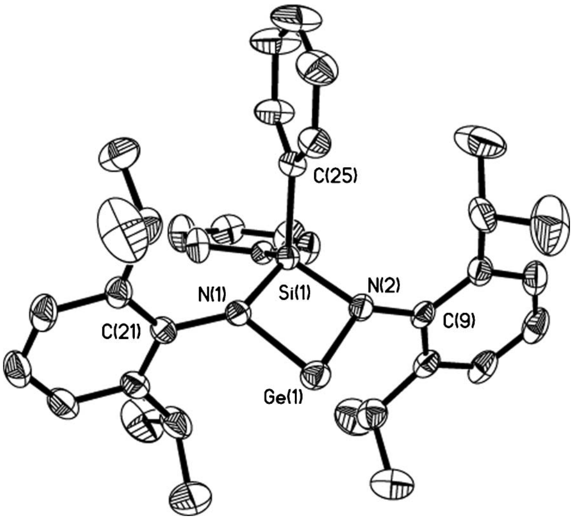


Fig. 1 Molecular structure of **3b** with thermal ellipsoids at 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Ge(1)–N(2) 1.887(3), Ge(1)–N(1) 1.888(3), Ge(1)–Si(1) 2.6616(10), N(1)–Si(1) 1.724(3), N(2)–Si(1) 1.726(3), C(25)–Si(1) 1.870(3), C(31)–Si(1) 1.859(4), C(9)–N(2), 1.421(4), C(21)–N(1) 1.433(4); N(2)–Ge(1)–N(1) 80.47(11), C(21)–N(1)–Si(1) 137.7(2), C(21)–N(1)–Ge(1) 125.0(2), Si(1)–N(1)–Ge(1) 94.83(12), C(9)–N(2)–Si(1) 132.8(2), C(9)–N(2)–Ge(1) 128.7(2), Si(1)–N(2)–Ge(1) 94.79(12), N(1)–Si(1)–N(2) 89.91(13), N(1)–Si(1)–C(31) 116.71(14), N(2)–Si(1)–C(31) 115.45(15), N(1)–Si(1)–C(25) 114.22(14), N(2)–Si(1)–C(25) 115.06(15), C(31)–Si(1)–C(25) 105.50(15).

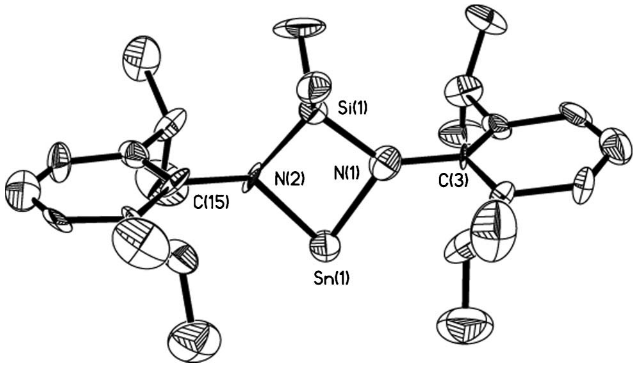


Fig. 2 Molecular structure of **4** with thermal ellipsoids at 30% probability level, only one of the two independent molecules is shown. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Sn(1)–N(1) 2.064(14), Sn(1)–N(2) 2.045(9), N(1)–C(3) 1.443(15), N(2)–C(15) 1.411(18), Si(1)–N(1) 1.719(11), Si(1)–N(2) 1.726(12); N(1)–Sn(1)–N(2) 73.6(4), N(1)–Si(1)–N(2) 91.2(5), Si(1)–N(2)–Sn(1) 97.7(4), Si(1)–N(1)–Sn(1) 97.3(6), C(1)–Si(1)–C(2) 107.5(9), C(15)–N(2)–Sn(1) 130.6(9), C(3)–N(1)–Sn(1) 129.3(8), C(2)–Si(1)–Sn(1) 124.6(8), C(1)–Si(1)–Sn(1) 127.9(5).

[η^2(*N*,*N*)-Ph$_2$Si(DippN)$_2$Ge:] (3b)

A systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima with symmetry and systematic absences uniquely corresponding to the monoclinic space group *P*2(1)/*c*. Subsequent solution and refinement of the structure confirmed this choice. The crystals were sealed in capillary and mounted nearly equidimensional. In spite of air- and moisture-sensitivity, the diffraction properties of the sample were excellent. The structure elucidation of **3b** revealed a monomeric complex in which the central germanium(*ii*) atom is η^2(*N*,*N*)-coordinated by one bis(amido)silane ligands (Fig. 1), showing a geometry with planar four-membered NSiNGe ring and trigonal planar coordination involving the chelating nitrogen

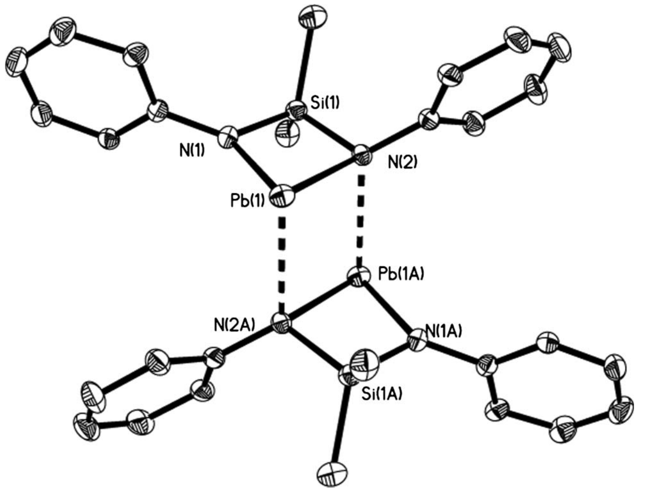


Fig. 3 Molecular structure of **5a** with thermal ellipsoids at 30% probability level. Hydrogen atoms and isopropyl groups are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Pb(1)–N(1) 2.218(3), Pb(1)–N(2) 2.417(3), N(1)–C(1) 1.438(5), N(2)–C(15) 1.468(5), Si(1)–N(1) 1.711(3), Si(1)–N(2) 1.766(3); N(1)–Pb(1)–N(2) 68.62(11), N(1)–Si(1)–N(2) 97.68(16), Si(1)–N(2)–Pb(1) 92.13(13), Si(1)–N(1)–Pb(1) 100.86(15), C(13)–Si(1)–C(14) 104.3(2), C(15)–N(2)–Pb(1) 128.5(2), C(1)–Si(1)–Pb(1) 124.6(2). Symbol A ≡ the symmetry code $(2-x, -y, 2-z)$.

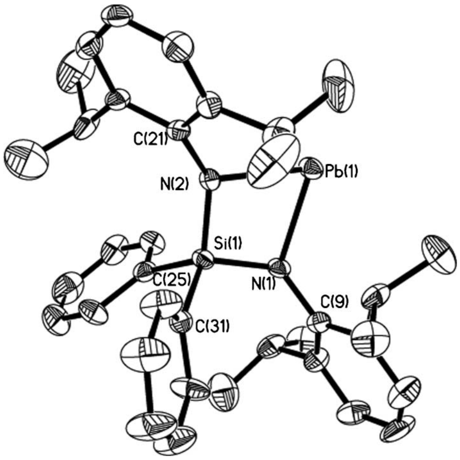


Fig. 4 Molecular structure of **5b** with thermal ellipsoids at 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Pb(1)–N(2) 2.267(7), Pb(1)–N(1) 2.206(8), Pb(1)–Si(1) 2.950(3), N(1)–Si(1) 1.712(8), N(2)–Si(1) 1.711(8), C(25)–Si(1) 1.883(10), C(31)–Si(1) 1.881(10), C(9)–N(1), 1.423(11), C(21)–N(2) 1.398(11); N(2)–Pb(1)–N(1) 70.4(3), C(21)–N(2)–Si(1) 141.6(7), C(21)–N(1)–Pb(1) 122.6(6), Si(1)–N(2)–Pb(1) 94.7(3), C(9)–N(1)–Si(1) 129.9(7), C(9)–N(1)–Pb(1) 126.0(6), Si(1)–N(2)–Pb(1) 96.9(3), N(1)–Si(1)–N(2) 97.8(4), N(2)–Si(1)–C(31) 114.7(4), N(1)–Si(1)–C(31) 113.4(4), N(2)–Si(1)–C(25) 114.5(4), N(1)–Si(1)–C(25) 110.4(4), C(31)–Si(1)–C(25) 106.1(5).

atoms. The Ge–N bond lengths were Ge(1)–N(2) 1.887(3), Ge(1)–N(1) 1.888(3) Å, respectively, slightly longer than those found in [*i*Pr$_2$Si(DippN)$_2$Ge:] (1.8627(10) Å (av.)).[6a] Compound **3b** represents a rare uncomplexed germylene heterocycle featuring an NSiNGe core to be structurally authenticated by crystallography.[6a]

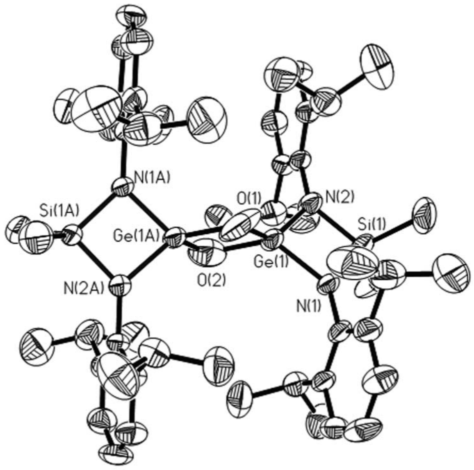


Fig. 5 Molecular structure of **6** with thermal ellipsoids at 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Ge(1)–N(2) 1.812(4), Ge(1)–N(1) 1.816(4), Ge(1)–Si(1) 2.5816(19), N(1)–Si(1) 1.735(4), Ge(1)–O(1) 1.799(8), Ge(1)–O(2) 1.875(6), Ge(1)–Ge(1A) 2.5972(14); N(2)–Ge(1)–N(1) 84.54(19), O(1)–Ge(1)–N(2) 135.8(2), O(1)–Ge (1)–N(1) 116.3(2), O(1)–Ge(1)–O(2) 90.0(3), N(1)–Ge(1)–O(2) 127.02(18), O(1)–Ge(1A)–O(2) 90.0(3), C(15)–N(1)–Ge(1) 131.8(3), Ge(1A)–O(1)–Ge(1) 92.4(6). Symbol A ≡ the symmetry code $(1/2-x, y, 1/2-z)$.

[η^2(*N*,*N*)-Me$_2$Si(DippN)$_2$Sn:] (4), [η^2(*N*,*N*)-Me$_2$Si(DippN)$_2$Pb:]$_2$ (5a), and [η^2(*N*,*N*)-Ph$_2$Si(DippN)$_2$Pb:] (5b)

The structures of complexes **4**, **5a**, and **5b** were determined by single-crystal X-ray diffraction analyses. The molecular structure of **4** is monomeric in the solid state and has a planar trigonal geometry about the metal centre with consideration of the lone-pair electron. The tin atom exhibits two-coordination, being bonded to two planar N-centres and forming a planar four-membered heterocyclic ring with only one bis(diamido)silane [Me$_2$Si(DippN)$_2$]$^{2-}$ ligand (Fig. 2). The tin–nitrogen bond lengths are 2.064(14) Å and 2.045(9) Å, respectively, which are comparable with those found in [Ph$_2$Si(DippN)$_2$Sn:] (2.100(3), 2.071(2) Å),[6b] and in [(*i*Pr)$_2$Si(DippN)$_2$Sn:] (2.0709(12), 2.0631(12)).[6a] The molecular structure of **5a** is, however, revealed as a dimer in solid state, exhibiting strong intermolecular Pb···N interactions (Fig. 3). This mode of dimerization has been reported previously for several plumbylenes with the lead-containing heterocycles, such as in [PhB(Bu^{t}N)$_2$Pb]$_2$,[14] [(C$_3$H$_6$)Si(Bu^{t}N)$_2$Pb]$_2$,[15] and in [DippN(CH$_2$)$_3$N(Dipp)Pb].[16a] The lead–nitrogen bond lengths are 2.218(3) Å and 2.417(3) Å, respectively, which are within the range of those found in {[{N(2,6-^{i}Pr$_2$C$_6$H$_3$)C(Me)}$_2$CH]Pb}{B(C$_6$F$_5$)$_4$} (2.242(4), 2.228(4) Å),[16b] and in [DippN(CH$_2$)$_3$N(Dipp)Pb] (2.125(4), 2.136(5)).[16a] The length of the intermolecular Pb(1)···N(2A) separation (2.587(3) Å) is only slightly longer than the values of Pb–N bond lengths found in **5a**, indicative of the strengths of the interaction. In addition, the dimerization *via* strong intermolecular Pb···N interaction obviously has a strong impact on the geometric parameters of N-heterocyclic plumbylene, namely the Pb centre is asymmetrically bound to the nitrogen atoms within the

Table 1 Crystal and Data Collection Parameters of Complexes **3b**, **4**, **5a**, **5b**, and **6**

Compounds	**3b**	**4**	**5a**	**5b**	**6**
Formula	$C_{40}H_{52}SiN_2OGe$	$C_{26}H_{40}N_2SiSn$	$C_{52}H_{80}N_4Si_2Pb_2$	$C_{36}H_{44}N_2SiPb$	$C_{56}H_{90}Ge_2N_4O_3Si_2$
F_w	677.52	527.38	1231.78	740.01	1068.68
Cryst. size (mm)	0.35 × 0.27 × 0.08	0.18 × 0.16 ×0.13	0.15 × 0.18 × 0.20	0.42 × 0.48 × 0.31	0.15 × 0.14 × 0.25
Cryst. syst.	Monoclinic	Orthorhombic	Monoclinic	Tetragonal	Monoclinic
Space group	$P2_1/n$	$Pna2_1$	$P2_1/n$	$P4_32_12$	$P2/n$
a (Å)	10.8195(15)	17.83(4)	12.444(4)	12.4575(10)	13.449(4)
b (Å)	18.818(3)	8.55(2)	18.724(6)	12.4575(10)	10.478(4)
c (Å)	19.240(3)	36.69(8)	12.638(4)	43.426(7)	21.692(7)
α (°)	90	90	90	90	90
β (°)	103.039(2)	90	116.420(4)	90	90.705(5)
γ (°)	90	90	90	90	90
V (Å^3)	3816.1(9)	5595(22)	2637.3(16)	6739.2(13)	3056.5(18)
Z	4	8	2	8	2
D_c (g cm^{-3})	1.179	1.252	1.551	1.459	1.157
ε (mm^{-1})	0.865	0.970	6.457	5.068	1.064
F (000)	1440	2192	1224	2960	1132
T (K)	298(2)	293	293	298(2)	293(2)
Range (°)	1.99–25.50	2.22–25.01	1.91–26.01	1.88–27.00	1.77–25.01
Reflns measured	19903	18142	11715	38768	11715
Unique reflns	7076	7707	5195	7339	5382
θ_{max} (°)	25.50	25.01	26.01	27.00	25.01
R_{int}	0.0437	0.0626	0.0350	0.1244	0.0605
Min and max transmn	0.7516 and 0.9340	0.8448 and 0.8843	0.3583 and 0.4442	0.1947 and 0.3026	0.7769 and 0.8654
$R1$, $wR2$ [$I > 2\sigma(I)$]^a	0.0543, 0.1317	0.0760, 0.1899	0.0259, 0.0563	0.0618, 0.1129	0.0739, 0.1946
$R1$, $wR2$ (all data)^b	0.0888, 0.1495	0.1122, 0.2075	0.0403, 0.0593	0.0946, 0.1233	0.1385, 0.2312
GOF	1.026	1.037	0.944	1.063	0.871
Flack parameter	—	0.00(17)	—	0.032(12)	—
Δr (max) (e×Å^{-3})	0.532	1.032	1.168	1.432	1.207
Δr (min) (e×Å^{-3})	−0.330	−0.863	−0.775	−1.313	−0.084

^{a} $R1 = \Sigma|Fo| - |Fc|/\Sigma|Fo|$. ^{b} $wR2 = [\Sigma w(Fo^2 - Fc^2)^2/\Sigma w(Fo^2)^2]^{0.5}$.

four-membered ring (Pb(1)–N(1) 2.218(3) Å, Pb(1)–N(2) 2.417(3) Å). However, the molecular structure of **5b** is rigorously monomeric with no close-range intermolecular interactions in the solid state and actually isostructual to **5a** without considering the intermolecular Pb···N interactions. This difference in solid-state packing is likely a consequence of added intra-ligand repulsion in **5b**. The presence of encumbered Ph_2Si– group within the same heterocycle results in the aryl rings in **5b** being pushed even further toward the Pb centre, leading to greater steric coverage. The lead–nitrogen bond lengths are 2.267(7) Å and 2.206(8) Å, respectively, which are significantly shorter than those found in **5a**, obviously due to the lack of the intermolecular Pb···N interactions.

[η^2(*N*,*N*)-$Me_2Si(DippN)_2Ge(\mu$-O)]$_2$ (6)

The crystallographic data quality of **3a** is not warranted for publication in this case because of the poor crystal nature, but it could be further confirmed by the elucidated structure of germanium oxo complex **6**. The molecular structure of **6** is dimeric in solid state and contains planar NSiNGe and Ge_2O_2 arrays that are mutually rotated by 49.3 and 63.0°, with average endocyclic Ge–O and Ge–N bond lengths of 1.837(7) Å and 1.814(4) Å (Fig. 5). The dimeric structure of **6** lies about a twofold axis with the twofold axis passing through O(1) and O(2). A related amide-substituted 1,3-cyclodigermoxane, [Ge{N(SiMe$_3$)$_2$}$_2$(μ-O)]$_2$, was previously prepared through the direct reaction of Ge{N(SiMe$_3$)$_2$}$_2$ and oxygen.[17] The germanium–oxygen bond lengths in **6** are 1.799(8) Å and 1.875(6) Å, respectively, which are comparable with those found in [(iPr)$_2$Si(DippN)$_2$Ge((μ-O)]$_2$ (1.8045(18), 1.8063(19) Å).[6a]

To compare the steric and electronic effects of bis-(diamido)silane ligands, crystal and physical data for a few of bis(diamido)silane germylenes, stannylenes and plumbylenes are collected in Table 2. The corresponding values shown that metal–nitrogen bond lengths varied slightly with ligands but the melting points, crystal systems, bond angles in addition to space groups are mainly related to the substituents of ligands. For example, the metal–nitrogen bond lengths found in four stannylenes are almost comparable while the melting points, crystal systems as well as chemical shifts in ^{119}Sn NMR spectra are significantly distinct. In addition, the presence of more encumbered groups on silicon of ligands will result in the substituents on nitrogen of the ligands being pushed further toward the metal centre, leading to wider angles, *e.g.* **5a** and **5b**.

Conclusions

This work has demonstrated that a series of low coordinate group 14 compounds featuring sterically encumbered bis(diamido)silane ligand have been readily prepared. The ligands employed are hindered enough to facilitate the isolation of rigorously monomeric, two-coordinate germylenes **3a**, **3b**, stannylene **4**, and plumbylenes **5a** (dimeric), **5b** but the formation of a dimeric arrangement of **6** suggests the difficulty associated with isolating a monomeric germanone ($R_2Ge{=}O$) under ambient conditions, probably due to the highly polar nature of the Ge═O π-bond that makes this unit prone to dimerization/oligomerization to yield thermodynamically more stable σ-lingages.[18] Complexes **3–5** are highly

Table 2 Crystal and physical data collection of bis(diamido)silane germylenes, stannylenes and plumbylenes

Compounds	Crystal system	M–N Bond lengths (Å)		N–M–N (deg)	Mp (°C)	^{119}Sn (δ ppm)	Ref.
[η^2(N,N)-$Ph_2Si(DippN)_2Ge$:]	Monoclinic	1.888(3)	1.887(3)	80.47(11)	178	—	[a]
[η^2(N,N)-$i$$Pr_2Si(SiPh_3N)_2Ge$:]	Monoclinic	1.8834(14)	1.8829(14)	83.31(6)	197	—	[6a]
[η^2(N,N)-$i$$Pr_2Si(DippN)_2Ge$:]	Monoclinic	1.8627(10)	1.8627(10)	81.26(6)	172	—	[6a]
[η^2(N,N)-$Ph_2Si(DippN)_2Sn$:]	Orthorhombic	2.1000(3)	2.071(2)	74.62(10)	190–195	499	[6b]
[η^2(N,N)-$Me_2Si(DippN)_2Sn$:]	Orthorhombic	2.064(14)	2.045(9)	73.6(4)	190	514	[a]
[η^2(N,N)-$i$$Pr_2Si(DippN)_2Sn$:]	Monoclinic	2.0709(12)	2.0631(12)	74.60(5)	130	536	[6a]
[η^2(N,N)-$i$$Pr_2Si(SiPh_3N)_2Sn$:]	Monoclinic	2.0888(15)	2.0882(15)	76.28(6)	114	527	[6a]
[η^2(N,N)-$Ph_2Si(DippN)_2Pb$:]	Tetragonal	2.267(7)	2.206(8)	70.4(3)	215	—	[a]
[η^2(N,N)-$Me_2Si(DippN)_2Pb$:]$_2$	Monoclinic	2.218(3)	2.417(3)	68.62(11)	148	—	[a]

[a] This work.

potential as precursors in catalysis and materials chemistry. Work is proceeding along these lines.

Experimental

All manipulations were carried out in an argon atmosphere under anaerobic conditions using standard Schlenk, vacuum line and glove box techniques. The solvents were thoroughly dried, deoxygenated and distilled in an argon atmosphere prior to use. DMSO-d_6 was degassed and dried over molecular sieves for 24 h before use. C_6D_6 was dried with metallic sodium before use. The ^{1}H NMR, ^{13}C NMR, and ^{119}Sn NMR spectra were recorded with a Bruker DRX-600 spectrometer. IR measurements were carried out on a NICOLET 360 FT-IR spectrometer from Nujol mulls prepared in a dry box. Melt points were measured in sealed argon-filled capillaries without temperature correction with an apparatus XT4-100A (Electronic and Optical Instruments, Beijing). $GeCl_2$·Dioxane, $SnCl_2$, and $PbCl_2$ were purchased from Aldrich. $Me_2Si(DippNH)_2$,[7] $Me_2Si(DippNLi)_2$,[7] $Ph_2Si(DippNH)_2$,[7] and $M[N(SiMe_3)_2]_2$ (M = Ge, Sn, Pb)[19] were prepared according to the literature.

Synthesis of complex [η^2(N,N)-$Ph_2Si(DippNLi)_2$] (2b)

To a solution of $Ph_2Si(DippNH)_2$ (1.1 g, 2.0 mmol) in n-hexane (50 mL), 1.6 mL n-BuLi (2.5 M, 4.0 mmol) was added *via* a syringe at 0 °C. After the suspension was stirred for 3 h at room temperature and then filtered. The collected precipitate was washed with n-hexane (3 × 10 mL) to afford **2b** as pure white solid (0.54 g, 87.8%). Mp > 300 °C, decomp.^{1}H NMR (DMSO–d_6, 23 °C): δ = 0.86 (d, 24 H, ^1J = 6.6 Hz, $(CH_3)_2C$), 3.57 (sept, 2 H, Me_2CH), 3.83 (sept, 2 H, Me_2CH), 5.91–7.66 (m, 16 H, Ph); ^{13}C{^{1}H} NMR (DMSO–d_6, 23 °C): δ = 24.0, 24.6 (2 s, $(CH_3)_2C$), 27.2, 28.4 (2 s, $(CH_3)_2C$), 107.6, 118.0, 121.2, 122.8, 126.6, 135.2, 137.6, 138.3, 144.5, 146.4, 154.6 (12 s, C for [Ph]); ^{7}Li{^{1}H} NMR (DMSO–d_6, 23 °C): δ = –0.98; Anal. Calcd. for $C_{36}H_{44}N_2SiLi$: C 79.09%, H 8.11%, N 5.12%; Found: C 78.67%, H 8.26%, N 5.03%.

Synthesis of complex [η^2(N,N)-$Me_2Si(DippN)_2Ge$:] (3a)

To a mixture of **2a** (0.422 g, 1.00 mmol) and $GeCl_2$·dioxane (0.232 g, 1.0 mmol), n-hexane (30 mL) was added at 0 °C *via* a syringe. After the solution was stirred for 2 days at room temperature the light yellow solution was filtered through Celite. The solvent of the filtrate was concentrated to about 5 mL under reduced pressure to afford **3a** as colorless needles (0.26 g, 53.0%). Mp = 128 °C. ^{1}H NMR (C_6D_6, 23 °C): δ = 0.29 (s, 6 H, Si-CH_3), 1.27 (d, 28 H, ^1J = 7.2 Hz, $(CH_3)_2C$), 3.85 (sept, 8 H, Me_2CH), 7.03–7.22 (m, 6 H, Ph); ^{13}C{^{1}H} NMR (C_6D_6, 23 °C): δ = 5.3 (s, $(CH_3)_2Si$), 26.5 (s, $(CH_3)_2C$), 27.3 (s, $(CH_3)_2C$), 123.3, 142.9, 143.8, 148.5 (4 s, C for [Ph]); IR(Nujol Mull, cm^{-1}): $\tilde{\nu}$ = 2919(s), 2852(s), 2725(w), 2031(w), 1460(w), 1376(s), 1311(w), 1250(s), 1202(s), 1155(m), 916(s), 776(s), 722(s). Anal. Calcd. for $C_{26}H_{40}N_2SiGe$: C 64.83, H 8.33, N 5.90; Found: C 64.70, H 8.19, N 5.77.

Synthesis of complex [η^2(N,N)-$Ph_2Si(DippN)_2Ge$:] (3b)

To a mixture of **2b** (0.546 g, 1.00 mmol) and $GeCl_2$·dioxane (0.232 g, 1.0 mmol) in a Schlenk flask (100 mL), n-hexane (50 mL) was added *via* a syringe at 0 °C. After the suspension was stirred for about 5 h, tetrahydrofuran (15 mL) was added. The clear solution was stirred for further 48 h at room temperature and then filtered through Celite. The filtrate was concentrated to about 35 mL to afford **3b** as colorless solid at room temperature for several days (0.542 g, 58.0%). Mp = 178 °C. ^{1}H NMR (C_6D_6, 23 °C): δ = 1.05, 1.06 (d, 24 H, $(CH_3)_2C$), 1.41 (m, 4 H, THF), 3.56 (m, 4 H, THF), 3.75 (sept, 4 H, Me_2CH), 6.96–7.44 (m 16 H, Ph); ^{13}C{^{1}H}NMR (C_6D_6, 23 °C): δ = 144.3, 141.0, 135.7, 134.8, 129.9, 124.1, 123.6 (7 s, C for [Ph]), 67.5, 25.4 (2 s, C for THF), 25.0 (s, C for $(CH_3)_2C$), 28.6 (s, C for $(CH_3)_2C$); IR (Nujol Mull, cm^{-1}): $\tilde{\nu}$ = 3085(s), 3028(s), 2948(s), 2873(w), 1942(w), 1460(w), 1376(s), 1311(w), 1210(s), 1107(m), 895(s), 786(s), 678(s). Anal. Calcd. for $C_{40}H_{52}SiN_2OGe$: C 70.90, H 7.74, N 4.13; Found: C 70.52, H 7.33, N 4.01. Single crystals suitable for X-ray diffraction analysis were obtained from re-crystallization at room temperature in a mixed solvent of n-hexane and tetrahydrofuran (2 : 1).

Synthesis of complex [η^2(N,N)-$Me_2Si(DippN)_2Sn$:] (4)

To a mixture of **2a** (0.422 g, 1.00 mmol) and $SnCl_2$ (0.19 g, 1.0 mmol), n-hexane (30 mL) was added at 0 °C *via* a syringe. After the solution was stirred for 2 days at room temperature the orange solution was filtered through Celite. The solvent of the filtrate was concentrated to about 5 mL under reduced pressure and then kept at –30 °C to afford **4** as yellow crystals (0.42 g, 80.0%). Alternatively, to a mixture of **1a** (0.410 g, 1.00 mmol) and $Sn[N(SiMe_3)_2]_2$ (0.439 g, 1.0 mmol), n-hexane (20 mL) was added *via* a syringe. After the solution was stirred for 18 h at room temperature the volatile components were removed under reduced pressure. The resulting residue was extracted with n-hexane (3 × 10 mL). The solvent of the solution was concentrated to about 5 mL and then kept at –30 °C to afford **4** as yellow crystals

(0.47 g, 90.0%). Mp = 190 °C. ^{1}H NMR ($CDCl_3$, 23 °C): δ = 0.23 (s, 6 H, Si-CH_3), 1.29 (d, 28 H, $(\mathrm{C}H_3)_2\mathrm{C}$), 3.77 (sept, 8 H, $\mathrm{Me_2C}H$), 6.96–7.25 (m, 6 H, Ph); ^{13}C{^{1}H} NMR ($CDCl_3$, 23 °C): δ = 5.2 (s, $(C\mathrm{H}_3)_2\mathrm{Si}$), 25.4 (br, $(C\mathrm{H}_3)_2\mathrm{C}$), 27.5 (s, $(\mathrm{CH}_3)_2C$), 122.5, 122.8, 142.7, 143.8 (4 s, *C* for [Ph]); ^{119}Sn{^{1}H} NMR ($CDCl_3$, 23 °C): δ = 514 (s); IR (Nujol Mull, cm^{-1}): $\tilde{\nu}$ = 2919(s), 2853(s), 2725(w), 2031(w), 1461(w), 1376(s), 1312(w), 1250(s), 1203(s), 1155(m), 916(s), 776(s), 722(s). Anal. Calcd. for $C_{26}H_{40}N_2SiSn$: C 59.22, H 7.63, N 5.30; Found: C 59.04, H 7.55, N 5.20. Single crystals suitable for X-ray diffraction analysis were obtained from re-crystallization at room temperature in *n*-hexane.

Synthesis of complex [η^2(N,N)-$Me_2Si(DippN)_2Pb$:]$_2$ (5a). To a mixture of **2a** (0.422 g, 1.00 mmol) and $PbCl_2$ (0.28 g, 1.0 mmol), *n*-hexane (30 mL) was added at 0 °C *via* a syringe. After the solution was stirred for 2 days at room temperature the deep-red solution was filtered through Celite. The solvent of the filtrate was concentrated to about 5 mL under reduced pressure and then kept at −30 °C to afford **5a** as red crystals (0.52 g, 85.0%). Alternatively, to a mixture of **1a** (0.410 g, 1.00 mmol) and Pb[N(SiMe$_3$)$_2$]$_2$ (0.53 g, 1.0 mmol), ether (20 mL) was added *via* a syringe. After the solution was stirred for 18 h at room temperature the volatile components were removed under reduced pressure. The resulting residue was extracted with ether (3 × 10 mL). The solvent of the solution was concentrated to about 5 mL and then kept at −30 °C to afford **5a** as red crystals (0.51 g, 82.0%). Mp = 148 °C. ^{1}H NMR (C_6D_6, 23 °C): δ = 0.24 (s, 6 H, Si-CH_3), 6.65–7.22 (br., 6 H, Ph), 3.80 (sept, 4 H, $\mathrm{Me_2C}H$), 1.21 (d, 24 H, $(\mathrm{C}H_3)_2\mathrm{C}$); ^{13}C{^{1}H} NMR ($C_6D_6$, 23 °C): δ = 121.9 (s. *C* for [Ph]), 123.4 (s, *C* for [Ph]), 142.4 (s, *C* for [Ph]), 145.4 (s, *C* for [Ph]), 26.28 (s, $(\mathrm{CH}_3)_2C$), 9.97 (s, $(C\mathrm{H}_3)_2\mathrm{C}$), 1.03 (s, $(C\mathrm{H}_3)_2\mathrm{Si}$); IR (Nujol Mull, cm^{-1}): $\tilde{\nu}$ = 2918(s), 2852(s), 2721(w), 2032(w), 1460(w), 1374(s), 1310(w), 1247(s), 1200(s), 916(s), 842(s), 776(s), 722(s). Anal. Calcd. for $C_{26}H_{40}N_2SiPb$: C 50.72, H 6.50, N 4.53; Found: C 50.60, H 6.43, N 4.44. Single crystals suitable for X-ray diffraction analysis were obtained from re-crystallization at room temperature in ether.

Synthesis of complex [η^2(*N*,*N*)-$Ph_2Si(DippN)_2Pb$:] (5b)

To a mixture of **2b** (0.546 g, 1.0 mmol) and $PbCl_2$ (0.278 g, 1.0 mmol) in 100 mL Schlenk flask, ether (30 mL) was added *via* a syringe. The suspension was stirred at ambient temperature for 48 h, and then filtered through Celite. The filtrate was concentrated to about 5 mL under reduced pressure to afford **5b** as air- and moisture-sensitive red crystals at −30 °C (0.54 g, 80.0 %). Mp = 178 °C. ^{1}H NMR (C_6D_6, 23 °C): δ = 1.03,1.04 (d, 24 H, $(\mathrm{C}H_3)_2\mathrm{C}$), 3.88 (sept, 4 H, $\mathrm{Me_2C}H$), 6.81–7.46 (m, 16 H, Ph); ^{13}C{^{1}H} NMR (C_6D_6, 23 °C): δ = 26.3, (s, $(C\mathrm{H}_3)_2\mathrm{C}$), 26.9 (s, $(\mathrm{CH}_3)_2C$), 122.1, 123.6, 127.0, 128.5, 134.3, 142.4, 145.4, 145.9 (8 s, *C* for [Ph]); IR (Nujol Mull, cm^{-1}): $\tilde{\nu}$ = 3080(s), 3028(s), 2948(s), 2850(w), 2023(w), 1944(w), 1467(w), 1371(s), 1210(s), 1105(m), 897(s), 780(s), 674(s). Anal. Calcd. for $C_{36}H_{44}N_2PbSi$: C 58.43, H 5.99, N 3.79; Found: C 58.31, H 5.81, N 3.69. Single crystals suitable for X-ray diffraction analysis were obtained from re-crystallization at −30 °C in a mixed solvent of *n*-hexane and tetrahydrofuran (2 : 1).

Synthesis of complex [η^2(*N*,*N*)-$Me_2Si(DippN)_2Ge(\mu\text{-}O)$]$_2$ (6)

A solution of **3a** (0.481 g, 1.00 mmol) in ether (30 mL) was stirred 2 h in the presence of dry oxygen (11.2 mL, 0.5 mmol). The solvent of the solution was concentrated to about 5 mL under reduced pressure and then kept at −30 °C to afford **6** as light yellow crystals (0.75 g, 70.0%). Mp >250 °C decomp. ^{1}H NMR (C_6D_6, 23 °C): δ = 0.21 (s, 6 H, Si-CH_3), 6.84–7.30 (m, 6 H, Ph), 3.75 (sept, 4 H, $\mathrm{Me_2C}H$), 1.08 (d, 12 H, $(\mathrm{C}H_3)_2\mathrm{C}$), 1.23 (d, 12 H, $(\mathrm{C}H_3)_2\mathrm{C}$); ^{13}C{^{1}H} NMR ($C_6D_6$, 23 °C): δ = 123.5 (s. *C* for [Ph]), 125.4 (s, *C* for [Ph]), 135.4 (s, *C* for [Ph]), 146.9 (s, *C* for [Ph]), 27.9 (s, $(\mathrm{CH}_3)_2C$), 24.3, 24.9 (2 s, $(C\mathrm{H}_3)_2\mathrm{C}$), 1.65 (s, $(C\mathrm{H}_3)_2\mathrm{Si}$); IR (Nujol Mull, cm^{-1}): $\tilde{\nu}$ = 2921(s), 2852(s), 2725(w), 2031(w), 1461(w), 1376(s), 1312(w), 1250(s), 1153(m), 1083(w), 1019(w), 966(w), 800(w), 722(s). Anal. Calcd. for $C_{56}H_{90}Ge_2N_4O_3Si_2$: C 62.93, H 8.49, N 5.24; Found: C 62.61, H 8.27, N 5.15. Single crystals suitable for X-ray diffraction analysis were obtained from re-crystallization at room temperature in ether.

X-ray structure determination

Suitable single crystals were sealed under argon in thin-walled glass capillaries. X-ray diffraction data were collected on a SMART APEX CCD diffractometer (graphite-monochromated Mo-*K*α radiation, φ-ω-scan technique, λ = 0.71073 Å). The intensity data were integrated by means of the SAINT program.[20] SADABS[21] was used to perform area-detector scaling and absorption corrections. The structures were solved by direct methods and were refined against F^2 using all reflections with the aid of the SHELXTL package.[22] All non-hydrogen atoms in **3b**–**6** were refined anisotropically. Crystallographic parameters for compounds **3b**, **4**, **5a**, **5b** and **6**, along with details of the data collection and refinement, are collected in Table 1.

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