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

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Received 19th September 2011, Accepted 17th November 2011
DOI: 10.1039/c1dt11774b

A series of germylene, stannylene and plumbylene complexes [η^2-(N,N)-Me;Si(DippNH),Ge:] (3a), [η^2-(N,N)-Ph,Si(DippN),Ge:] (3b), [η^2-(N,N)-Me;Si(DippN),Sn:] (4), [η^2-(N,N)-Me;Si(DippN),Pb:] (5a), and [η^2-(N,N)-Ph, Si(DippN),Pb:] (5b) (Dipp = 2,6-iPr,C,H₅) bearing bulky bis(amido)silane ligands were readily prepared either by the transamination of M[N(SiMe₃)₂]₃, (M = Sn, Pb) and M[Me(Si(DippN)H)] or by the metathesis reaction of bislithium bis(amido)silane [η^2-(N,N)-R₂Si(DippNLi)] (R = Me, Ph) with the corresponding metal halides GeCl₂, SnCl₂, and PbCl₂, respectively. Preliminary atom-transfer chemistry involving [η^2-(N,N)-Me;Si(DippN),Ge:] (3a) with oxygen yielded a dimeric oxo-bridged germanium complex [η^2-(N,N)-Me;Si(DippN),Ge(μ-O)] (6). All complexes were characterized by ¹H, ¹³C, ¹⁰¹Sn 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 carbenic-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 heavy 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.4 Nitrogen-based ligands, presumably due to the σ-inductive effect of the electronagative nitrogen atom, have played a pivotal role in the successful isolation of these species with the archetype being M[N(SiMe₃)₂]₃ (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 metalloheterecycle system when coordinated to a metal centre such as alkaline earth metals.5 We noted that two bis(amido)silane germylenes [η^2-(N,N)-iPr,Si(DippN),Ge:] [η^2-(N,N)-iPr, Si(DippN),Ge:] and three bis(amido)silane stannylenes [η^2-(N,N)-Ph, Si(DippN),Sn:] and three bis(amido)silane stannylenes [η^2-(N,N)-Ph, Si(DippN),Sn:] and three bis(amido)silane stannylenes [η^2-(N,N)-Ph, Si(DippN),Sn:] and three bis(amido)silane stannylenes [η^2-(N,N)-Ph, Si(DippN),Sn:] and three bis(amido)silane stannylenes [η^2-(N,N)-Ph, Si(DippN),Sn:] and three bis(amido)silane stannylenes [η^2-(N,N)-Ph, Si(DippN),Sn:] and three bis(amido)silane stannylenes [η^2-(N,N)-Ph, Si(DippN),Sn:] and three bis(amido)silane stannylenes [η^2-(N,N)-Ph, Si(DippN),Sn:] and three bis(amido)silane stannylenes [η^2-(N,N)-Ph, Si(DippN),Sn:] 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 [η^2-(N,N)-Me, Si(DippN), Ge:] (3a), [η^2-(N,N)-Ph, Si(DippN), Ge:] (3b), stannylenes [η^2-(N,N)-Me, Si(DippN), Sn:] (4), and plumbylenes [η^2-(N,N)-Me, Si(DippN), Pb:] (5a), [η^2-(N,N)-Ph, Si(DippN), Pb:] (5b) with sterically demanding bis(amido)silane ligands, as well as a dimeric germanium oxo complex [η^2-(N,N)-Me, Si(DippN), Ge(μ-O)] (6) that arises from the oxygen-transfer reaction of the germylene (3a) and dry oxygen.

Results and discussion

Preparation of complex [η^2-(N,N)-Ph, Si(DippN)Li₂] (2b)

The silanediamine [Me, Si(DippN)Li₂] (1a), [Ph, Si(DippN)Li₂] (1b), and bislithium bis(diamido)silane [Me, Si(DippNLi₂)] (2a) were prepared according to published protocol (Scheme 1).7 Compound [Ph, Si(DippNLi₂)] (2b) can be readily deproto...
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 $-CH(CH_3)_2$ 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 substituents of 2b.

Preparation of complexes [η$^5$(N,N)-Me$_2$Si(DippN)$_2$Ge] (3a) and [η$^5$(N,N)-Ph$_2$Si(DippN)$_2$Ge] (3b)

The metathetical reaction between an equimolar ratio of 2a and GeCl$_4$(dioxane) in $n$-hexane successfully gave [η$^5$(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$^5$(N,N)-Ph$_2$Si(DippN)$_2$Ge] (3b) was obtained by the metathesis reaction of 2b and GeCl$_4$(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 $^3$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 isopropyl 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 $^3$Pr groups contrasts sharply with those observed in the analogous alkaline earth metal–bis(amido)disilane complexes, in which two sets of resonances for the $^3$Pr groups were observed.$^4$ The asymmetrical conformation of alkaline earth metal–bis(amido)disilane complexes in solution probably arises from solvated tetrahydrofuran molecules.$^5$ Two multiple resonances at $\delta = 1.41$ 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)disilane ligands. No signals were observed at about 2.5 ppm for N–H resonance in the $^1$H NMR spectra,$^3$ excluding the existence of the free ligand (1a, 1b) in the samples.

Preparation of complex [η$^5$(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)disilane stannylenes [η$^5$(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) 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 –SiCH$_3$ groups ($\delta = 0.28$ ppm), one set of coupled doublets for –CH(CH$_3$)$_2$ groups ($\delta = 1.27$ ppm, $^3$J$_{HH} = 7.4$ Hz), and one set of septet for –CH(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)$^{6a}$ and [(iPr)$_2$Si(DippN)$_2$Sn] ($\delta = 536$ ppm)$^{6a}$.

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

In searching for heavier analogues of silylenes, germylences, stannylenes, and plumbolenes, most attention has focused on the lighter elements Si and Ge,$^3$ and no structurally characterized examples of plumbolenes have been reported containing the bis(amido)disilane ligand. The plumbolenes 5a and 5b were thus thus synthesized by the reaction of dilithium salt of the appropriate bis(amido)disilane 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 $\sim$30 °C and yielded dark red crystals of the pure plumbolenes 5a and 5b, respectively. Plumbylene 5a was also obtained easily in a transamination reaction between Pb[N(SiMe$_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 (CD$_2$Cl$_2$, 23 °C) of both 5a and 5b show only one doublet for the isopropyl –CH(CH$_3$)$_2$ groups and one
Preparation of complex [η²(N,N)-Me₂Si(DippN)Ge(μ-O)]₆ (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. This may lead to the isolation of heavy analogues of ketones similar to stable divalent 14-group derivative R₂M = E (M = Si, Ge, Sn, Pb; E = O, S, Se, Te). In our case, the products from chalcogen atom-transfer may enable confirmation of germerylene 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 O₂ was therefore carried out. After workup, only a dimeric germanium o xo-bridged complex [Me₂Si(DippN)Ge(μ-O)]₆ (6) was isolated in good yield (70%), rather than the expected corresponding heavy analogues of ketone (Scheme 2). Complex 6 is air-, and moisture-stable and well soluble in ether, THF, and DMSO. The ¹H NMR spectrum of compound 6 in C₆D₆ displays two sets of coupled doublets for –CH(CH₃)₂ groups (δ = 1.08 ppm, J_H,H = 6.6 Hz, δ = 1.23 ppm, J_H,H = 6.6 Hz). The two sets of resonances for the nonequivalent –C(CH₃)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 [η²,Mg]. Notably, the resonances of the –C(CH₃)₂ groups in the ¹H NMR spectrum were slightly overlapped by the signals of the lattice ether.

![Scheme 2](image)

**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.

[η²(N,N)-Ph₅Si(DippN)₂Ge] (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 P2₁/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 η²(N,N)-coordinated by one bis(amido)isilane ligands (Fig. 1), showing a geometry with planar four-membered NSiNGe ring and trigonal planar coordination involving the chelating nitrogen.
atoms. The Ge–N bond lengths were Ge(1)–N(2) 1.887(3), Ge(1)– N(1) 1.883(3) Å, respectively, slightly longer than those found in [IPr,Si(DippN),Ge]: 1.8627(10) Å (av.). Compound 3b represents a rare uncomplexed germylene heterocycle featuring an NSiNGe core to be structurally authenticated by crystallography.

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\begin{align*}
\text{Fig. 3} & \quad \text{Molecular structure of 5a 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) 2.218(3), Pb(1)–N(1) 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, z).}
\end{align*}
\]

\[
\begin{align*}
\text{Fig. 4} & \quad \text{Molecular structure of 5b with thermal ellipsoids at 30\% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Pb(1)–N(2) 2.267(7), Pb(1)–N(1) 2.206(8), Pb(1)–Si(1) 2.950(3), N(1)–Si(1) 1.712(8), N(2)–Si(1) 1.711(8), C(25)–Si(1) 1.883(10), C(31)–Si(1) 1.881(10), C(9)–N(1) 1.423(11), C(21)–N(2) 1.398(11); N(2)–Pb(1)–N(1) 70.4(3), C(21)–N(2)–Si(1) 141.4(7), C(21)–N(1)–Pb(1) 122.6(6), Si(1)–N(1)–Pb(1) 94.7(3), C(9)–N(1)–Si(1) 129.9(7), C(9)–N(1)–Pb(1) 126.0(6), Si(1)–N(2)–Pb(1) 96.9(3), N(1)–Si(1)–N(2) 97.8(4), N(2)–Si(1)–C(31) 114.7(4), N(1)–Si(1)–C(31) 113.4(4), N(2)–Si(1)–C(25) 114.5(4), N(1)–Si(1)–C(25) 110.4(4), C(31)–Si(1)–C(25) 106.1(5).
\end{align*}
\]

\[
\begin{align*}
\text{Fig. 5} & \quad \text{Molecular structure of 6 with thermal ellipsoids at 30\% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Ge(1)–N(2) 1.812(4), Ge(1)–N(1) 1.816(4), Ge(1)–Si(1) 2.5816(19), N(1)–Si(1) 1.735(4), O(1)–N(1) 1.799(8), Ge(1)–O(2) 1.875(6), Ge(1)–Ge(1A) 2.5972(14), N(2)–Ge(1)–N(1) 84.54(19), O(1)–Ge(1)–N(2) 135.8(2), O(1)–Ge(1)–N(1) 116.3(2), O(1)–Ge(1)–O(2) 90.0(3), N(1)–Ge(1)–O(2) 172.02(18), N(1)–Ge(1A)–O(2) 90.0(3), C(15)–N(1)–Ge(1) 131.8(3), Ge(1A)–O(1)–Ge(1) 92.4(6). Symbol A = the symmetry code (1/2–x, y, 1/2–z).
\end{align*}
\]

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\begin{align*}
\text{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 one bis(diamido)silane [MeSi(DippN)], 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 [Ph2Si(DippN),Sn] (2.100(3), 2.071(2) Å), and in [(IPr)2Si(DippN),Sn] (2.0709(12), 2.0631(12)). 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 plumbynes with the lead-containing heterocycles, such as in [PhB(Bu′N)2Pb]14, [(C2H5)2Si(Bu′N)2Pb]15, and in [DippN(CH3)2N(Dipp)Pb].16 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 [{(C2H5)2Si(Ph)2N}2Pb] (2.136(4), 2.125(4), 2.127(4) Å).16 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
\end{align*}
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Table 1 Crystal and Data Collection Parameters of Complexes 3b, 4, 5a, 5b, and 6

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<td>0.3583 and 0.4442</td>
<td>0.1334 and 0.2026</td>
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<td>0.0259 and 0.0563</td>
<td>0.0618 and 0.1129</td>
<td>0.0739 and 0.1946</td>
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<td>0.0946 and 0.1233</td>
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<td>Δr (max) (e Å⁻³)</td>
<td>0.532</td>
<td>1.032</td>
<td>1.168</td>
<td>1.432</td>
<td>1.207</td>
</tr>
<tr>
<td>Δr (min) (e Å⁻³)</td>
<td>−0.330</td>
<td>−0.863</td>
<td>−0.775</td>
<td>−1.313</td>
<td>−0.804</td>
</tr>
</tbody>
</table>

* R₁ = Σ |Fo| − |Fc| / Σ |Fo|, wR₂ = Σw(Fo² − Fc²)² / Σw(Fo²)².²

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 Pb₃Si₃ 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.

[νr(N,N)-(N,N)-Me₂Si(DippN)₂Ge(μ-O)]₆ (6)
The crystallographic data 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 NSiGe and Ge₂O 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-cyclogermoxane, [Ge{N(SiMe₃)₃}₃(μ-O)]₇, was previously prepared through the direct reaction of Ge[N(SiMe₃)₃]₃ and oxygen. 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 [(μ-Pr),Si(DippN)₂Ge(μ-O)]₆ (1.8045(18), 1.8063(19) Å).²

To compare the steric and electronic effects of bis-(diamido) silane ligands, crystal and physical data for a few of bis(diamido) silane germynes, stannylenes and plumbylenes are collected in Table 2. The corresponding values show 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 ¹¹⁹Sn 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 germynes 3a, 3b, stannylene 4, and plumbylene 5a (dimeric), 5b but the formation of a dimeric arrangement of 6 suggests the difficulty associated with isolating a monomeric germanone (R₂Ge=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.² Complexes 3–5 are highly...
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–d6 was degassed and dried over molecular sieves for 24 h before use. C6D6 was dried with metallic sodium before use. The 1H NMR, 13C NMR, and 119Sn 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). GeCl2-Dioxide, SnCl2, and PbCl2 were purchased from Aldrich. Me2Si(DippNH)2,7 Me2Si(DippNLi)2,7 Ph3Si(DippNH)2,7 and M[(SiMe3)2]2 (M = Ge, Sn, Pb) were prepared according to the literature.

Synthesis of complex [η6(N,N)-Ph2Si(DippNLi)2] (2b)
To a solution of Ph2Si(DippNLi)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. 1H NMR (DMSO–d6, 23 °C): δ = 0.86 (d, 24 H, 1J = 6.6 Hz, (CH3)2C), 3.57 (sept, 2 H, H, Me(CH2)3), 3.83 (sept, 2 H, Me(CH2)3), 5.91–7.66 (m, 16 H, Ph); 13C(1H) NMR (DMSO–d6, 23 °C): δ = 24.0, 24.6 (2 s, (CH3)2C), 27.2, 28.1, 28.2 (2 s, (CH3)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]); 119Sn(1H) NMR (DMSO–d6, 23 °C): δ = 0.98. Anal. Calcd. for C8H46SnSiLi: C 79.09%, H 8.11%, N 5.12%; Found: C 78.67%, H 8.26%, N 5.03%.

Synthesis of complex [η6(N,N)-Me3Si(DippNLi)2]Ge (3a)
To a mixture of 2a (0.422 g, 1.0 mmol) and GeCl2-dioxide (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. 1H NMR (C6D6, 23 °C): δ = 0.29 (s, 6 H, Si-CH3), 1.27 (d, 28 H, 1J = 7.2 Hz, (CH3)2C), 3.85 (sept, 8 H, Me,CH) 7.03–7.22 (m, 6 H, Ph); 13C{1H} NMR (C6D6, 23 °C): δ = 5.3 (s, (CH3)2Si, 26.5 s, (CH3)2C), 27.3 (s, (CH3)2C), 123.3, 142.9, 143.8, 148.5 (4 s, C for [Ph]); IR (Nujol mull, cm–1): ν = 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 C8H46SnSiGe: C 64.83, H 8.33, N 5.90; Found: C 64.70, H 8.19, N 5.77.

Synthesis of complex [η6(N,N)-Ph2Si(DippN)2]Ge (3b)
To a mixture of 2b (0.546 g, 1.0 mmol) and GeCl2-dioxide (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. 1H NMR (C6D6, 23 °C): δ = 1.05, 1.06 (d, 24 H, (CH3)2C), 1.41 (m, 4 H, THF), 3.56 (m, 4 H, THF), 3.75 (sept, 4 H, Me,CH) 6.96–7.44 (m, 16 H, Ph); 13C{1H} NMR (C6D6, 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 (CH3)2C), 28.6 (s, C for (CH3)2C, IR (Nujol mull, cm–1): ν = 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 C26H36SnGe: 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 [η6(N,N)-Me3Si(DippN)2]Sn (4)
To a mixture of 2a (0.422 g, 1.0 mmol) and SnCl2 (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, 1.0 mmol) and Sn[N(SiMe3)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. 1H NMR (CDCl₃, 23 °C): δ =
0.23 (s, 6 H, Si-CH₃), 1.29 (d, 28 H, (CH₂-C), 3.77 (sept, 8 H,
Me₂C), 6.96–7.25 (m, 6 H, Ph); 13C(¹H) NMR (CDCl₃, 23 °C):
δ = 52.5 (s, (CH₂-C)), 25.4 (br, (CH₂-C)), 27.5 (s, (CH₂-C)), 122.5,
122.8, 142.7, 143.8 (4 s, C for [Ph]); 195Si[¹H] NMR (CDCl₃,
23 °C): δ = 514 (s); IR (Nujol Mull, cm⁻¹): ν = 2919(s), 2853(s),
2725(w), 2031(w), 1461(w), 1376(s), 1215(s), 1203(s), 1155(m),
916(s), 776(s), 722(s). Anal. Calcd. for C₆H₆N₃Si₄N₃: 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 [p²(N,N)-Me₆Si(DippN)Pb] (5a).
A mixture of 2a (0.422 g, 1.00 mmol) and PbCl₂ (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(SiMe₃)]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 x 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. 1H
NMR (CD₂Cl₂, 23 °C): δ = 0.24 (s, 6 H, Si-CH₃), 6.65–7.22 (br, 6 H,
Ph), 3.80 (sept, 4 H, Me₂CH₂), 1.21 (d, 24 H, (CH₂-C),); 13C(¹H)
NMR (CD₂Cl₂, 23 °C): δ = 121.9 (s. C for [Ph]), 123.4 (s and C for
[Ph]), 142.4 (s, C for [Ph]), 145.4 (s, C for [Ph]), 26.28 (s, (CH₂-C),)
9.97 (s, (CH₂-C), 1.03 (s, (CH₂-C),) Si); IR (Nujol Mull, cm⁻¹): ν =
2918(s), 2852(s), 2725(w), 2032(w), 1461(w), 1376(s), 1215(s), 1203(s),
1155(m), 916(s), 776(s), 722(s). Anal. Calcd. for C₆H₆N₃Ge(μ-O)₃:
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-Kα radiation, φ-ω scan technique, λ = 0.71073 Å).
The intensity data were integrated by means of the SANT program.²⁰
SADABS²¹ was used to perform area-detector scaling and absorption
corrections. The structures were solved by direct methods
and were refined against F² using all reflections with the aid of
the SHEXLTL 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.

Acknowledgements
We acknowledge support from the National Natural Science
Foundation of China (NSFC; Grant 20872017) and Shannxi
Normal University.

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