Subvalent Group 14 metal compounds
XIV*. The X-ray crystal structures of two monomeric Group 14 metal bisamides, $Ge[N(SiMe_3)_2]_2$ and $Sn[\overline{NC(Me)_2(CH_2)_3C}Me_2]_2$

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Abstract

The crystalline Group 14 metal bisamides $Ge[N(SiMe_3)_2]_2$ (**1**) and $Sn[\overline{NC(Me)_2(CH_2)_3C}Me_2]_2$ (**2**) have been characterised by X-ray diffraction. The complexes are monomeric, and possess the bent V-shaped geometry consistent with a singlet ground state. **1** has ⟨Ge–N⟩ 1.876(5) Å, N–Ge–N′ 107.1(2)° (*c.* 6° greater than in the gas phase); cell constants $a=16.632(4)$, $b=20.323(5)$, $c=13.148(3)$ Å; space group *Pccn*; $Z=8$; $R=0.059$, $R_w=0.062$. **2** has ⟨Sn–N⟩ 2.102(6) Å, N–Sn–N′ 109.7(2)° (the largest recorded for a monomeric tin(II) amide); cell constants $a=10.796(2)$, $b=14.388(2)$, $c=12.930(2)$ Å, $\beta=97.40(1)$°; space group $P2_1/c$; $Z=4$; $R=0.038$, $R_w=0.051$.

Introduction

Compounds containing germanium, tin or lead in oxidation state +2 have long been known. In general they adopt structures in the solid state in which the metal atom achieves a coordination number higher than two. For instance, whilst Group 14 element dihalides MX_2 ($M=Si$, Ge, Sn or Pb; $X=F$, Cl, Br or I) are monomeric in the vapour phase [1], in the solid they are polymeric, having bridging halides. Other complexes containing ligands of small steric demand are also polymeric in the solid, e.g. $[Sn(Cl)(\eta\text{-}C_5H_5)]_n$ [2, 3] and $[Sn(OMe)X]_n$ ($X=Cl$, Br or I) [4].

Bulky organic ligands have been used to impose low coordination numbers in Group 14 element complexes. A range of such ligands has been applied, including aryl (^-Ar), alkyl (^-R), amido ($^-NR_2$), aryloxo (^-OAr) and arylthiolato (^-SAr) groups. The chemistry of alkyl and aryl compounds of silicon, germanium and tin in oxidation state +2 has recently been reviewed [5]. Even when ligands of reasonably large steric demand are present, monomeric Ge(II), Sn(II) or Pb(II) structures are only rarely achieved, as illustrated by the cyclotristannane $[Sn(C_6H_3Et_2\text{-}2,6)_2]_3$ [6] and the linear trimers $[\{M(SAr)\}\{\mu\text{-}(SAr)_2M(SAr)_2\text{-}\mu\}\{M(SAr)\}]$ ($Ar=C_6H_3Pr^i_2\text{-}2,6$; $M=Sn$ or Pb) [7].

Dimeric structures with bridging through oxygen, sulfur, nitrogen or halogen atoms are found in $[Sn(OBu^t)_2]_2$ [8], $[SnS(CH_2)_2N(Bu^t)(CH_2)_2S]_2$ [9], $[Sn(NMe_2)_2]_2$ [10] and the heteroleptic complexes $[Sn(\mu\text{-}X)NR_2]_2$ ($X=Cl$ and $NR_2=N(SiMe_3)_2$; or $X=F$, Cl or Br and $NR_2=\overline{NC(Me)_2(CH_2)_3C}Me_2$) [11] and $[Sn(Cl)(\mu\text{-}OBu^t)]_2$ [12]. The amide $[Sn[N(Bu^t)SiMe_2NBu^t]_n$ has a structure in the crystal which contains both monomeric and dimeric units [13]. Association may still occur when two bulky groups coordinate, as in $[Sn(\mu\text{-}OBu^t)X]_2$ ($X=OBu^t$ [8] or $N(SiMe_3)_2$ [14]) and $[Pb\{N(SiMe_3)_2\}\{\mu\text{-}SC(SiMe_3)_3\}]_2$ [15]. The compound $[Sn\{CH(SiMe_3)_2\}_2]_2$, although monomeric in the gas phase [16], is dimeric in the solid state, possessing a *trans*-structure involving a tin–tin bond [17, 18]; the isoleptic germanium compound $[Ge\{CH(SiMe_3)_2\}_2]_2$ is similar [18, 19]. The dimeric structure of $[Sn(\mu\text{-}OBu^t)(OBu^t)]_2$ is maintained even in the gas phase at *c.* 100 °C/10^{-1} torr [8]. Crystalline $Sn(NCS)[N(SiMe_3)_2]$ exists as monomeric units stabilised by weak Sn···S intermolecular interactions [20].

A small number of divalent Group 14 element complexes MX_2 having monohapto X^- ligands have monomeric structures in the solid state. In Ge, Sn and Pb chemistry, these include $M(OCBu^t_3)_2$ ($M=Ge$ or Sn) [8], $M(OC_6H_2Bu^t_2\text{-}2,6\text{-}Me\text{-}4)_2$ [21], $M'(SC_6H_2Bu^t_3\text{-}$

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2,4,6)$_2$ (M′ = Sn or Pb) [7], $Sn[N(SiMe_3)_2]_2$ [22], $Sn[N(H)C_6H_2Bu^t{}_3$-2,4,6]$_2$ [23], $Ge[\overline{NC(Me)_2(CH_2)_3C}Me_2]_2$ [24] and $Ge[CH(SiMe_3)_2][C(SiMe_3)_3]$ [25]. The crystalline hydrocarbyls $Sn(Cl)R$, $Sn[N(SiMe_3)_2]R$, SnR_2 ($R = C(SiMe_3)_2C_5H_4N$-2) [26] and $M[C_6H_2(CF_3)_3$-2,4,6]$_2$ (M = Sn [27] or Pb [28]) are also monomeric, but the pyridylalkyls have three- or four-coordinate tin, whilst in the fluoro complexes there are close intermolecular $Sn \cdots F$ contacts.

We have long been interested in using such bulky ligands X^- to achieve the synthesis of these and related MX_2 complexes and to study their chemistry [29]; see other parts of this series [30]. Such two-coordinate complexes MX_2 are highly coloured, thermochromic (being colourless at low temperatures) and low melting. They have been described as carbene analogues, since they are diamagnetic and exhibit the angular V-shaped geometry expected for a singlet electronic ground state, in which the metal atom possesses a stereochemically active lone pair of electrons (rather than having a linear triplet structure). The colour of the complexes has been attributed to a metal-centered electronic transition.

We now report the X-ray characterisation of two examples involving sterically demanding amido ligands, $Ge[N(SiMe_3)_2]_2$ (**1**) and $Sn[\overline{NC(Me)_2(CH_2)_3C}Me_2]_2$ (**2**). For the low melting complex **1** [22] we have previously reported electron diffraction data [22b], and also electronic, IR, NMR and He(I) photoelectron spectra for **1** and **2** and related compounds [22a, 24, 31, 32].

Experimental

General procedures

Pentane was freshly distilled from sodium under a dinitrogen atmosphere; dissolved dioxygen was removed by repeated freeze–degassing cycles before use. $GeCl_2$(1,4-dioxane) [16] and the lithium reagents $Li\overline{NC(Me)_2(CH_2)_3C}Me_2$ [33] and $LiN(SiMe_3)_2$ [17] were prepared as described elsewhere. Anhydrous $SnCl_2$ (Aldrich) was freed from moisture by stirring with $(CH_3CO)_2O$ for *c.* 16 h, followed by filtration, washing with dry Et_2O, and removal of residual solvents *in vacuo*. All manipulations were carried out under an atmosphere of pure argon, using a high vacuum manifold and conventional Schlenk techniques. Melting points (sealed capillary under Ar) are uncorrected. ^1H and ^{13}C NMR spectra were recorded at 305 K at 100 and 25.16 MHz, respectively, using a JEOL PFT 100 spectrometer. The ^{119}Sn NMR chemical shift data (δ relative to $SnMe_4$ at δ 0) were recorded at 93.27 MHz on a Bruker AC250SY instrument.

Synthesis of $Sn[\overline{NC(Me)_2(CH_2)_3C}Me_2]_2$ (2)

Solid $Li\overline{NC(Me)_2(CH_2)_3C}Me_2$ (3.84 g, 26.1 mmol) was added slowly to a stirring suspension of $SnCl_2$ (2.47 g, 13.0 mmol) in pentane (*c.* 80 ml). After *c.* 0.25 h, a pale pink colour developed which became intensely red after stirring overnight. The reaction mixture was filtered to remove precipitated lithium chloride, the filtrate concentrated by removal of solvent *in vacuo*, and cooled to −78 °C. Very dark red crystals of **2** formed (m.p. 44–48 °C), which were separated from the supernatant liquid by decantation, and dried *in vacuo*. Yield 2.26 g (43%). *Anal.* Found: C, 53.7; H, 8.6; N, 6.5. Calc. for $C_{18}H_{36}N_2Sn$: C, 54.1; H, 9.0; N, 7.0%. Molecular weight (cryoscopy, C_6H_6): found: 425; monomer requires 399; parent ion (P^+) in EI mass spectrum. ^1H NMR (C_6D_{12}): δ 1.64 (CH_3, 12H); 1.23 (CH_2, 4H); 0.48 (CH_2, 2H). ^{13}C NMR (C_6D_6): δ 34.41 (CH_3), $^1J(C\text{–}H) = 43.73$ Hz; 57.95 (β-C); 43.25 (γ-CH_2), $^1J(C\text{–}H) = 51.02$ Hz; 19.17 (δ-CH_2), $^1J(C\text{–}H) = 51.02$ Hz. ^{119}Sn NMR (pentane + C_7D_8): δ 749. IR (cm^{-1}, Nujol mull): $\nu_{as}(MN_2)$ 375w.

Synthesis of $Ge[\overline{NC(Me)_2(CH_2)_3C}Me_2]_2$ (3) (see also ref. 34)

Solid $Li\overline{NC(Me)_2(CH_2)_3C}Me_2$ (2.87 g, 19.5 mmol) was added slowly to a stirring suspension of $GeCl_2$(1,4-dioxane) (2.26 g, 9.8 mmol) in pentane (*c.* 50 ml). An orange colour slowly developed over *c.* 3 h. After stirring overnight, the reaction mixture was filtered to remove precipitated lithium chloride, concentrated *in vacuo*, and cooled to −78 °C. Orange crystals of **3** (m.p. 68–71 °C) slowly formed, were separated from the supernatant solution, and dried *in vacuo*. Yield 2.33 g (68%). *Anal.* Found: C, 61.0; H, 10.1. Calc. for $C_{18}H_{36}GeN_2$: C, 61.2; H, 10.2%. Molecular weight (cryoscopy, C_6H_{12}): found: 386; monomer requires 353; P^+ in EI mass spectrum. ^1H NMR (C_6D_6): δ 1.61 (CH_3, 12H); 1.12 (CH_2, 4H); 0.35 (CH_2, 2H). ^{13}C NMR (C_6D_6): δ 32.76 (CH_3), $^1J(C\text{–}H) = 48.08$ Hz; 55.81 (β-C); 40.83 (γ-CH_2), $^1J(C\text{–}H) = 57.69$ Hz; 16.92 (δ-CH_2), $^1J(C\text{–}H) = 57.69$ Hz. IR (cm^{-1}, Nujol mull): $\nu_{as}(MN_2)$ 385w.

X-ray structural determinations

A summary of the crystal and collection data for compounds **1** and **2** is given in Table 1. Crystals of **1** were removed from the Schlenk tube under a stream of N_2 and immediately covered with a layer of hydrocarbon oil. A suitable crystal was selected, attached to a glass fibre on a mounting pin and immediately placed in the low temperature N_2 stream. The crystals of **2** were mounted in sealed glass capillary tubes. An absorption correction was applied to **1** by using the method described in ref. 36*. No corrections were made for absorption in the case of **2**. Refinement was by full

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*The program obtains absorption tensors from $F_o - F_c$ differences [36b].

TABLE 1. Summary of crystal data and intensity collection for $Ge[N(SiMe_3)_2]_2$ (**1**) and $Sn[\overline{NC(Me)_2(CH_2)_3C}Me_2]_2$ (**2**)

	1	2
Formula	$C_{12}H_{36}N_2Si_4Ge$	$C_{18}H_{36}N_2Sn$
Formula weight	393.4	399.2
Crystal system	orthorhombic	monoclinic
a (Å)	16.632(4)	10.796(2)
b (Å)	20.323(5)	14.388(2)
c (Å)	13.148(3)	12.930(2)
β (°)		97.40(1)
U (Å^3)	4444(2)	1991.6
Z	8	4
D_c (g cm^{-3})	1.176	1.33
Space group	*Pccn*	$P2_1/c$
Sample size (mm)		0.4×0.25×0.15
Absorption correction	yes	none
Temperature (K)	130	295
Radiation	Cu Kα	Mo Kα
Wavelength (Å)	1.54178	0.71069
μ (cm^{-1})	39.13	12.8
Scan speed	variable	variable
Background counts	50% of total scan time at each end	25% of total scan time at each end
2θ limits (°)	0.0–115.0	4–40
Unique reflections	2997	1963
Reflections $\|F^2\| > 3\sigma(F^2)$		1345
Reflections $F > 4.0\sigma(F)$	2258	
R	0.059	0.038
R_w	0.062	0.051
Index ranges	$0 \leq h \leq 18$ $0 \leq k \leq 22$ $0 \leq l \leq 14$	$0 \leq h \leq 10$ $0 \leq k \leq 13$ $-12 \leq l \leq 12$
Diffractometer	Siemens R3m/V	Enraf-Nonius CAD-4
Programme system used	Siemens SHELXTL PLUS	SHELXS-86 [35] and Enraf-Nonius SDP-Plus package
Structure solution	direct methods	heavy atom
Refinement method	full matrix least-squares	full matrix least-squares

matrix least-squares with anisotropic thermal parameters for non-hydrogen atoms. For **1**, hydrogen atoms were included in the riding model with fixed U_{iso} of 0.055 Å^2, whilst for **2**, the hydrogen atom positions were freely refined except for H(3B) which became unstable and had to be fixed, and all hydrogen thermal parameters were fixed at $U_{iso} = 1.3\ U_{eq}$ for the parent atom. The atomic coordinates of the non-hydrogen atoms are presented in Tables 2 and 3.

Results and discussion

We have previously reported the preparation of $Ge[N(SiMe_3)_2]_2$ (**1**) [22a] and $Sn[\overline{NC(Me)_2(CH_2)_3C}Me_2]_2$ (**2**) [31], but only in the case of **1** were full synthetic details indicated. The procedures for **2** and the analogous germanium complex $Ge[\overline{NC(Me)_2(CH_2)_3C}Me_2]_2$ (**3**) [31, 33, 34] are now given.

The amides **1**–**3** were synthesized according to eqns. (1) and (2) [22a, 31, 34]. In each case, reaction was accompanied by a change from colourless to orange or red; the products were low-melting solids and were extremely soluble in a range of hydrocarbons. Crystals of **1** were obtained by cooling a molten sample (60 °C) of the compound to room temperature over a period of 4 h. Those of **2** were obtained by recrystallization from pentane solution at −78 °C.

$$GeCl_2(1,4\text{-dioxane}) + 2LiNR_2 \longrightarrow Ge(NR_2)_2 + 2LiCl + 1,4\text{-dioxane} \quad (1)$$

$NR_2 = N(SiMe_3)_2$ (**1**) or $N\overline{C(Me)_2(CH_2)_3C}Me_2$ (**3**)

$$SnCl_2 + 2Li\overline{NC(Me)_2(CH_2)_3C}Me_2 \longrightarrow Sn[\overline{NC(Me)_2(CH_2)_3C}Me_2]_2 + 2LiCl \quad (2)$$

Although ether was a satisfactory solvent for the preparation of **1** with $LiN(SiMe_3)_2$, attempts to employ

TABLE 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$) for $Ge[N(SiMe_3)_2]_2$ (1)

Atom	x	y	z	U_{eq}[a]
Ge	4194(1)	4795(1)	1739(1)	34(1)
N(1)	4123(3)	3944(3)	2289(4)	24(2)
N(2)	3355(3)	5289(3)	2302(4)	28(2)
Si(1)	4055(1)	3770(1)	3591(1)	27(1)
Si(2)	4390(1)	3329(1)	1422(1)	27(1)
Si(3)	2345(1)	5038(1)	2375(1)	29(1)
Si(4)	3613(1)	6117(1)	2454(1)	32(1)
C(1)	4177(4)	4534(4)	4355(5)	37(2)
C(2)	4879(4)	3209(4)	3996(5)	37(3)
C(3)	3100(4)	3350(4)	3954(5)	37(2)
C(4)	3781(4)	2572(4)	1660(6)	43(3)
C(5)	5489(4)	3138(4)	1456(5)	36(2)
C(6)	4164(4)	3596(4)	104(5)	45(3)
C(7)	2182(4)	4229(4)	1724(5)	38(2)
C(8)	1684(4)	5629(4)	1684(6)	42(3)
C(9)	1962(4)	5014(4)	3707(5)	39(3)
C(10)	3471(5)	6601(4)	1260(6)	52(3)
C(11)	3034(5)	6507(4)	3513(6)	51(3)
C(12)	4697(4)	6177(4)	2801(6)	44(3)

[a] Equivalent isotropic U_{eq} defined as one third of the trace of the orthogonalised U_{ij} tensor.

TABLE 3. Atomic coordinates ($\times 10^4$) for $Sn[\overline{NC(Me)_2(CH_2)_3C}Me_2]_2$ (2)

Atom	x	y	z
Sn	1418.3(5)	469.4(4)	3202.4(5)
N(1)	595(6)	−863(4)	3139(5)
N(2)	3058(6)	435(4)	2498(5)
C(1)	−758(8)	−930(6)	2785(6)
C(2)	−1463(9)	−1339(7)	3626(7)
C(3)	−900(9)	−2220(7)	4068(8)
C(4)	441(10)	−2075(6)	4469(7)
C(5)	1227(7)	−1680(6)	3659(7)
C(6)	−1300(8)	38(7)	2506(8)
C(7)	−1044(8)	−1505(7)	1767(7)
C(8)	1490(9)	−2443(7)	2884(9)
C(9)	2462(9)	−1383(7)	4242(8)
C(10)	3146(8)	38(7)	1440(6)
C(11)	3694(9)	770(7)	755(6)
C(12)	4877(9)	1206(7)	1233(8)
C(13)	4656(9)	1639(8)	2274(8)
C(14)	4171(7)	926(7)	3026(7)
C(15)	1841(10)	−172(7)	933(7)
C(16)	3907(10)	−847(7)	1454(8)
C(17)	5211(10)	260(8)	3454(8)
C(18)	3815(9)	1468(8)	3950(8)

the same solvent in the syntheses involving $Li\overline{NC(Me)_2(CH_2)_3C}Me_2$ gave low yields of poor quality material. Use of pentane is therefore recommended.

Molecular structures of compounds 1 and 2

The atomic coordinates and equivalent isotropic thermal parameters for the non-hydrogen atoms of **1** and **2** are given in Tables 2 and 3; selected intramolecular bond lengths and angles are presented in Tables 4 and 5. Figures 1 and 2 show projections of the molecular structures. Both crystalline complexes are monomeric and possess the expected bent geometry involving a stereochemically active lone pair of electrons. The amido ligands are staggered to reduce steric interaction between them. There are no close intermolecular bonding interactions between the tin or germanium atoms and neighbouring molecules. Cryoscopy had previously shown that **1** [22a] as well as **2** and the amides $Sn(NBu^t_2)_2$ (M = Ge or Sn) [24, 31] are monomeric in dilute cyclohexane solution.

Our major objective in determining the X-ray crystal structures of **1** and **2** was to allow a fuller comparison of the structural properties of monomeric divalent Group 14 amides in general to be made. Table 6 summarises relevant data in the solid state (X-ray diffraction) and gas phase (electron diffraction) for the series of compounds $M[N(SiMe_3)_2]_2$ and $M[\overline{NC(Me)_2(CH_2)_3C}Me_2]_2$.

As expected, there is a trend towards increasing metal–nitrogen bond lengths in the amides of the heavier metals, both in the solid and vapour phase. Comparing the X-ray diffraction data for the amides of tin and germanium, progressively larger bond lengths are found in the order $NR_2 = N(H)C_6H_2Bu^t_3$-2,4,6 [23]

TABLE 4. Intramolecular distances (Å) and angles (°) with e.s.d.s. in parentheses for $Ge[N(SiMe_3)_2]_2$ (1)

(a) Bonds			
Ge–N(1)	1.878(5)	Ge–N(2)	1.873(5)
N(1)–Si(1)	1.751(5)	N(1)–Si(2)	1.749(5)
N(2)–Si(3)	1.757(5)	N(2)–Si(4)	1.749(6)
Si(1)–C(1)	1.859(7)	Si(1)–C(2)	1.862(7)
Si(1)–C(3)	1.866(7)	Si(2)–C(4)	1.869(8)
Si(2)–C(5)	1.869(7)	Si(2)–C(6)	1.855(7)
Si(3)–C(7)	1.873(8)	Si(3)–C(8)	1.865(8)
Si(3)–C(9)	1.865(7)	Si(4)–C(10)	1.867(8)
Si(4)–C(11)	1.869(8)	Si(4)–C(12)	1.863(7)
(b) Angles			
N(1)–Ge–N(2)	107.1(2)	Ge–N(1)–Si(1)	124.4(3)
Ge–N(1)–Si(2)	113.0(3)	Si(1)–N(1)–Si(2)	120.7(3)
Ge–N(2)–Si(3)	125.3(3)	Ge–N(2)–Si(4)	112.2(3)
Si(3)–N(2)–Si(4)	120.5(3)	N(1)–Si(1)–C(1)	110.7(3)
N(1)–Si(1)–C(2)	110.8(3)	C(1)–Si(1)–C(2)	106.1(3)
N(1)–Si(1)–C(3)	113.4(3)	C(1)–Si(1)–C(3)	109.7(3)
C(2)–Si(1)–C(3)	105.9(3)	N(1)–Si(2)–C(4)	110.0(3)
N(1)–Si(2)–C(5)	112.4(3)	C(4)–Si(2)–C(5)	110.8(3)
N(1)–Si(2)–C(6)	110.4(3)	C(4)–Si(2)–C(6)	106.7(3)
C(5)–Si(2)–C(6)	106.3(3)	N(2)–Si(3)–C(7)	111.6(3)
N(2)–Si(3)–C(8)	110.4(3)	C(7)–Si(3)–C(8)	104.9(3)
N(2)–Si(3)–C(9)	112.6(3)	C(7)–Si(3)–C(9)	110.9(3)
C(8)–Si(3)–C(9)	105.8(3)	N(2)–Si(4)–C(10)	112.3(3)
N(2)–Si(4)–C(11)	111.5(3)	C(10)–Si(4)–C(11)	109.8(4)
N(2)–Si(4)–C(12)	109.2(3)	C(10)–Si(4)–C(12)	107.1(4)
C(11)–Si(4)–C(12)	106.7(3)		

TABLE 5. Intramolecular distances (Å) and angles (°) with e.s.d.s. in parentheses for $Sn[\overline{NC(Me)_2(CH_2)_3C}Me_2]_2$ (2)

(a) Bonds			
Sn–N(1)	2.111(6)	Sn–N(2)	2.093(6)
N(1)–C(1)	1.477(10)	N(1)–C(5)	1.476(10)
N(2)–C(10)	1.498(10)	N(2)–C(14)	1.482(10)
C(1)–C(2)	1.524(13)	C(1)–C(6)	1.536(13)
C(1)–C(7)	1.551(12)	C(2)–C(3)	1.487(13)
C(3)–C(4)	1.488(14)	C(4)–C(5)	1.539(14)
C(5)–C(8)	1.537(14)	C(5)–C(9)	1.506(12)
C(10)–C(11)	1.541(13)	C(10)–C(15)	1.506(13)
C(10)–C(16)	1.514(14)	C(11)–C(12)	1.484(13)
C(12)–C(13)	1.529(15)	C(13)–C(14)	1.549(14)
C(14)–C(17)	1.526(14)	C(14)–C(18)	1.517(14)
(b) Angles			
N(1)–Sn–N(2)	109.7(2)	Sn–N(1)–C(1)	117.8(5)
Sn–N(1)–C(5)	112.5(4)	C(1)–N(1)–C(5)	118.0(6)
Sn–N(2)–C(10)	124.3(5)	Sn–N(2)–C(14)	118.0(5)
C(10)–N(2)–C(14)	117.3(6)	N(1)–C(1)–C(2)	111.6(6)
N(1)–C(1)–C(6)	110.2(7)	N(1)–C(1)–C(7)	112.3(7)
C(2)–C(1)–C(6)	107.9(7)	C(2)–C(1)–C(7)	109.7(7)
C(6)–C(1)–C(7)	104.8(7)	C(1)–C(2)–C(3)	112.7(8)
C(2)–C(3)–C(4)	110.2(8)	C(3)–C(4)–C(5)	114.3(8)
N(1)–C(5)–C(4)	109.9(7)	N(1)–C(5)–C(8)	112.6(7)
N(1)–C(5)–C(9)	109.2(7)	C(4)–C(5)–C(8)	110.1(7)
C(4)–C(5)–C(9)	107.2(7)	C(8)–C(5)–C(9)	107.6(7)
N(2)–C(10)–C(11)	109.8(7)	N(2)–C(10)–C(15)	107.9(7)
N(2)–C(10)–C(16)	114.0(7)	C(11)–C(10)–C(15)	107.1(7)
C(11)–C(10)–C(16)	109.5(8)	C(15)–C(10)–C(16)	108.2(8)
C(10)–C(11)–C(12)	115.0(7)	C(11)–C(12)–C(13)	108.4(8)
C(12)–C(13)–C(14)	112.7(8)	N(2)–C(14)–C(13)	110.3(7)
N(2)–C(14)–C(17)	112.5(8)	N(2)–C(14)–C(18)	109.5(7)
C(13)–C(14)–C(17)	110.5(8)	C(13)–C(14)–C(18)	107.2(8)
C(17)–C(14)–C(18)	106.6(8)		

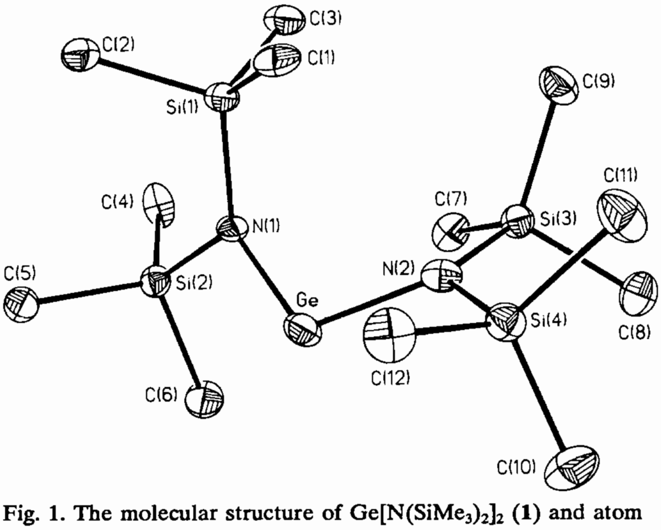

Fig. 1. The molecular structure of $Ge[N(SiMe_3)_2]_2$ (1) and atom numbering scheme.

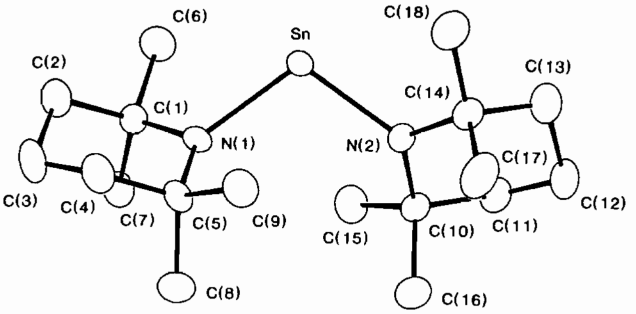

Fig. 2. The molecular structure of $Sn[\overline{NC(Me)_2(CH_2)_3C}Me_2]_2$ (2) and atom numbering scheme.

$< N(SiMe_3)_2 < \overline{NC(Me)_2(CH_2)_3C}Me_2$. Although the relative basicities of the ligands must have some influence, the general trend reflects the different steric demands of the ligands. The primary amido moiety is clearly less bulky than the two secondary groups; evidence for the larger bulk of $\overline{NC(Me)_2(CH_2)_3C}Me_2$ with respect to $N(SiMe_3)_2$ rests on X-ray structural data on $[Li\{\mu\text{-}N(SiMe_3)_2\}]_3$ ($<$N–Li–N′$>$ 147(3)°) and $[Li\{\mu\text{-}\overline{NC(Me)_2(CH_2)_3C}Me_2\}]_4$ ($<$N–Li–N′$>$ 168.5(4)°) [33], N–M–N′ angles in the corresponding Ge(II) and Sn(II) amides (*vide infra*), and is also provided by photolysis experiments involving the bisamides [22, 38]. Whilst $Sn[N(SiMe_3)_2]_2$ yielded the persistent Sn(III)-centred radical $^{\bullet}Sn[N(SiMe_3)_2]_3$ [38], no corresponding $^{\bullet}Sn[\overline{NC(Me)_2(CH_2)_3C}Me_2]_3$ species was observed, the only radical detected by ESR spectroscopy being $^{\bullet}\overline{NC(Me)_2(CH_2)_3C}Me_2$ [22a]. Presumably, there is insufficient space for three $^{-}NC(Me)_2(CH_2)_3CMe_2$ ligands to coordinate to a tin atom.

The N–M–N′ angles decrease in the sequence Ge > Sn > Pb. This is consistent with Bent's rule, which predicts that in the complexes where the electronegativity difference between metal and ligand is greatest (i.e. in the case of the lead compound), the non-bonding electrons of the metal atom possess greatest s-character. The N–M–N′ angle is also influenced by the bulk of the ligands; the crystalline amides $M[\overline{NC(Me)_2(CH_2)_3C}Me_2]_2$ have larger N–M–N′ angles than $M[N(SiMe_3)_2]_2$ (M = Ge or Sn); $Sn[N(H)C_6H_2Bu^t{}_3\text{-}2,4,6]_2$ has a considerably small~~er~~ angle (89.6(6)°).

In each of the complexes, the sum of the bond angles about the nitrogen atoms closely approximates to 360°, implying a planar geometry at nitrogen. In the case of the bis(trimethylsilyl)amides, this may be due to interactions of π-character between N and Si, but because the planarity is retained in the bis(tetramethylpiperidinato) complexes, some degree of π-bonding between nitrogen and Ge or Sn may be implicated; planar geometries at N in metal amides are the rule rather than the exception [39].

Interestingly, although the metal–nitrogen bond lengths for the $^{-}N(SiMe_3)_2$ complexes are similar in both the solid and vapour phases, the N–M–N′ angles are considerably smaller in the vapour. We noted this previously in the case of $M[N(SiMe_3)_2]_2$ (M = Sn or Pb) [22b], and the same is now shown to be the case

TABLE 6. Selected structural parameters and colours of the monomeric complexes $M(NR_2)_2$ (M = Ge, Sn or Pb; R = $SiMe_3$ or $NR_2 = \overline{NC(Me)_2(CH_2)_3C}Me_2$) and $Sn[N(H)C_6H_2Bu^t{}_2\text{-}2,4,6]_2$

Complex	Colour	X-ray diffraction				Electron diffraction		References
		⟨M–N⟩ (Å)	N–M–N′ (°)	α^a (°)	β^b (°)	⟨M–N⟩ (Å)	N–M–N′ (°)	
$Ge[N(SiMe_3)_2]_2$ (**1**)	yellow	1.876(5)	107.1(2)	12.3	121	1.89(1)	101(1.5)	this work^c, 22b^d
$Ge[\overline{NC(Me)_2(CH_2)_3C}Me_2]_2$ (**3**)	orange	1.89(1)	111.4(5)	7.7	119			24^c, 37^c
$Sn[N(SiMe_3)_2]_2$	orange	2.09(1)	104.7(2)	11	123	2.09(1)	96	22b^d, 31^c
$Sn[\overline{NC(Me)_2(CH_2)_3C}Me_2]_2$ (**2**)	maroon	2.102(6)	109.7(2)	5.5	118			this work^c
$Sn[N(H)C_6H_2Bu^t{}_3\text{-}2,4,6]_2$	orange	2.025(10)	89.6(6)					23^c
$Pb[N(SiMe_3)_2]_2$	orange	2.24(2)	103.6(7)	8.5	126	2.20(2)	91(2)	22b^{c,d}
$Pb[\overline{NC(Me)_2(CH_2)_3C}Me_2]_2$	unstable							24

^{a}Angle α is the difference between the mean of the 'inner' M–N–Si or M–N–C angles and the mean of the 'outer' ones (see text). ^{b}Angle β is the mean value of the Si–N–Si or C–N–C angles. ^{c}X-ray. ^{d}Electron diffraction.

for M = Ge (**1**); the difference is *c.* 6° for Ge compared with *c.* 8.5° for Sn and *c.* 12.5° for Pb. Presumably, packing in the solid state of molecules having the gas phase structures would be very inefficient; the observed X-ray structures show that the relative conformation of the two ligands has changed, causing increased (intramolecular) steric repulsion between them, and a consequent increase in N–M–N′ bond angles, presumably in order to relieve intermolecular inter-ligand contacts. Such substantial differences between molecular structures in the gas and the crystal are likely to be general when bulky ligands are involved.

Another feature in the X-ray data of $M[N(SiMe_3)_2]_2$ (M = Sn or Pb) to which attention was drawn was that two of the M–N–Si angles are wider than the others by *c.* 10°. The corresponding angles in $Ge[N(SiMe_3)_2]_2$ (**1**) are Ge–N(1)–Si(1) and Ge–N(2)–Si(3) (mean angle *c.* 125°) and Ge–N(1)–Si(2) and Ge–N(2)–Si(4) (mean angle *c.* 113°); the difference between these values is *c.* 12°. In Table 6, the equivalent values are tabulated as α for all the complexes studied. The wider ('inner') angles correspond to the most crowded environments, in which the angles M–N–Si are on the side of the molecule opposite the lone pair. Increased steric demand in the case of **1** leads to a greater value of α compared with that in the analogous tin and lead complexes. This effect is also reflected in the M–N–C angles of the $M[\overline{NC(Me)_2(CH_2)_3C}Me_2]_2$ complexes (M = Ge or Sn). For the same reason, the mean Si–N–Si or C–N–C angles (given as β in Table 6) also decrease in the order Pb > Sn > Ge.

Supplementary material

Atomic coordinates, bond lengths and angles, and thermal parameters for compounds **1** and **2** have been deposited at the Cambridge Crystallographic Data Centre.

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