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Synthesis and structural characterisation of monomeric Group 14 metal dialkyls MR_2 [R = $CPh(SiMe_3)(C_5H_4N\text{-}2)$ or $CH(SiMe_3)(C_9H_6N\text{-}8)$; M = Ge, Sn or Pb]

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A series of heavier main Group 14 metal dialkyls MR_2 [$R = R^1 = CPh(SiMe_3)(C_5H_4N\text{-}2)$, M = Ge **1** or Sn **2**; $R = R^2 = CH(SiMe_3)(C_9H_6N\text{-}8)$, M = Sn **3** or Pb **4**] has been synthesized by the reaction of 2 equivalents of the appropriate lithium reagents LiR(tmen) (tmen = $Me_2NCH_2CH_2NMe_2$) with $GeCl_2$(diox) (diox = 1,4-dioxane), $SnCl_2$ or $Pb[N(SiMe_3)_2]_2$ in diethyl ether solution. Crystal structure analysis has shown that compounds **1**–**4** are monomeric with the *N*-functionalized alkyl ligands R^1 or R^2 bonded to the metal centre in a C,N-chelate fashion and the geometry around the metal is pyramidal, consistent with a stereoactive lone pair at the metal.

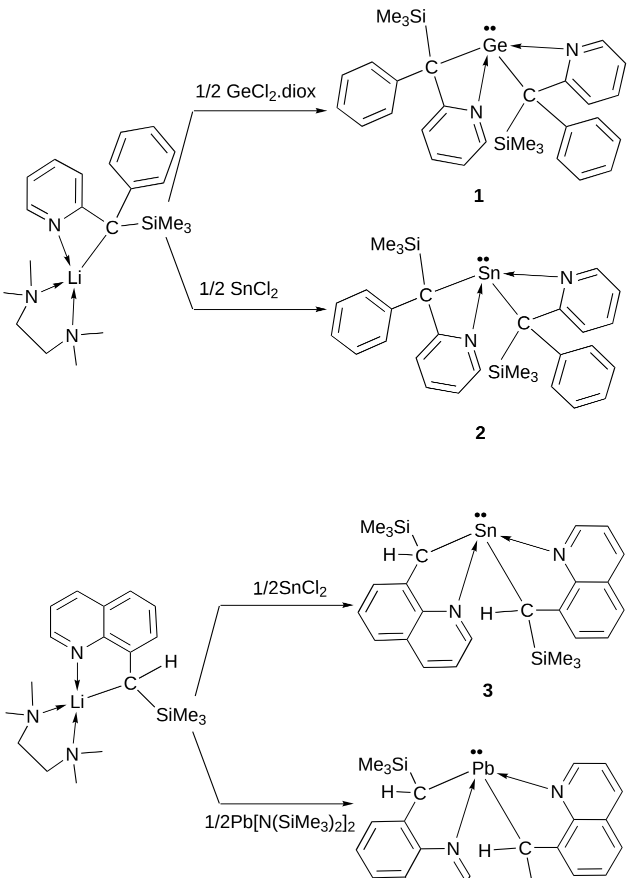
Organometallic chemistry of bivalent Group 14 metal compounds has become an active research area in the past two decades. It has been realized that these carbene analogues MR_2 can be stabilized by incorporating sterically hindered substituents on the metal. Lappert and co-workers[1–4] reported the first examples of stable metal dialkyls $[M\{CH(SiMe_3)_2\}_2]$ (M = Ge, Sn or Pb) and structural studies have found that the tin and germanium alkyls exist as dimers with a M–M interaction in the solid state and a monomer–dimer equilibrium in solution at ambient temperature. Among the three heavier metals, the numbers of structurally characterized compounds reported are in the order Sn > Ge ≫ Pb. In contrast, thermally stable organolead(II) compounds structurally characterised are scarce. Examples of monomeric Group 14 metal compounds are: $Ge[CH(SiMe_3)_2][C(SiMe_3)_3]$,[5] $M[C(SiMe_3)_2C_5H_4N\text{-}2]_2$ (M = Ge[6] or Sn[7]), $SnC(SiMe_3)_2(CH_2)_2C(SiMe_3)_2$,[8] $Pb[Si(SiMe_3)_3]_2$,[9] $M(C_6H_3R_2\text{-}2,6)_2$ (M = Ge, Sn or Pb; R = 2,4,6-$Me_3C_6H_2$),[10] $M(C_6H_2Bu^t_3\text{-}2,4,6)_2$ (M = Ge[11] or Sn[12]) and $M[C_6H_2(CF_3)_3\text{-}2,4,6]_2$ (M = Sn or Pb).[13,14] Some of these related compounds exist as dimers with M–M interactions (distances in parentheses) in the solid state such as $\{Sn[Si(SiMe_3)_3]_2\}_2$ (2.825 Å), $\{Ge[Si(SiMePr^i_2)_3]_2\}_2$,[15] $\{Ge[Si(SiPr^i_3)_3]_2\}_2$ (2.267 Å),[15] $[Ge(C_6H_3Et_2\text{-}2,6)_2]_2$[16] and $[Ge(C_6H_3Pr^i_2\text{-}2,6)_2]_2$ (3.301 Å).[17]

We have recently reported the synthesis of a series of thermally stable transition-metal alkyls containing *N*-functionalized alkyl ligands including FeR_2 and CoR_2.[18,19] In this paper, we describe the preparation and structural characterization of some Group 14 metal dialkyls containing the *N*-functionalised alkyl ligands $[CPh(SiMe_3)(C_5H_4N\text{-}2)]^-$ (R^1) and $[CH(SiMe_3)(C_9H_6N\text{-}8)]^-$ (R^2).

Results and Discussion

Synthesis of compounds 1–4

Main Group 14 metal dialkyls MR_2 [$R = R^1 = CPh(SiMe_3)(C_5H_4N\text{-}2)$, M = Ge **1** or Sn **2**; $R = R^2 = CH(SiMe_3)(C_9H_6N\text{-}8)$, M = Sn **3** or Pb **4**] were prepared in good yields by the reaction of 2 equivalents of the appropriate lithium reagents LiR(tmen) (tmen = $Me_2NCH_2CH_2NMe_2$), with $GeCl_2$(diox) (diox = 1,4-dioxane), $SnCl_2$ or $Pb[N(SiMe_3)_2]_2$ in diethyl ether solution (Scheme 1). These compounds have been characterized by elemental analysis, spectroscopic methods and crystal structure analysis. Like the transition-metal analogues, the stability of compounds **1**–**4** is attributed to the sterically hindered *N*-functionalized alkyl ligands $^-R^1$ and $^-R^2$. The germanium dialkyl $Ge[CPh(SiMe_3)(C_5H_4N\text{-}2)]_2$ **1** was isolated as an orange crystalline solid with good solubility in solvents such as ether, toluene and tetrahydrofuran (thf). It is noteworthy that the attempted preparation of the similar compound $Ge[C(SiMe_3)_2(C_5H_4N\text{-}2)]_2$ from the reaction of $Li[C(SiMe_3)_2(C_5H_4N\text{-}2)](Et_2O)$ and $GeCl_2$(diox) at −78 °C has been reported



Scheme 1

Table 1 Selected bond distances (Å) and angles (°) for compounds GeR^1_2 **1** and SnR^1_2 **2**

	1 (M = Ge)	**2** (M = Sn)		**1** (M = Ge)	**2** (M = Sn)
M–C(1)	2.135(4)	2.329(4)	M–N(1)	2.313(4)	2.446(5)
M–C(16)	2.109(4)	2.333(4)	M–N(2)	2.313(4)	2.417(4)
C(1)–Si(1)	1.907(4)	1.896(4)	C(16)–Si(2)	1.907(4)	1.894(4)
C(1)–C(2)	1.495(6)	1.498(6)	C(2)–N(1)	1.337(5)	1.345(5)
C(16)–C(17)	1.498(6)	1.609(6)	C(17)–N(2)	1.331(5)	1.337(5)
C(1)–M–N(1)	64.2(1)	59.7(1)	C(16)–M–N(2)	64.1(1)	60.3(1)
N(1)–M–N(2)	145.8(1)	137.1(1)	C(1)–M–C(16)	105.4(1)	103.6(1)
C(1)–M–N(2)	95.4(1)	92.2(1)	C(16)–M–N(1)	93.8(1)	93.3(1)
C(2)–C(1)–M	92.7(2)	93.8(2)	C(17)–C(16)–M	93.8(2)	92.0(2)
C(1)–C(2)–N(1)	111.8(4)	113.4(4)	C(16)–C(17)–N(2)	112.3(4)	113.9(4)
C(2)–N(1)–M	91.2(2)	92.9(3)	C(17)–N(2)–M	89.9(3)	93.0(3)

to be unsuccessful and it was suggested that the germanium compound produced was thermally unstable.[7] However, a very recent paper described the successful synthesis and characterization of this germanium compound.[6] The first example of a stable germylene $Ge[CH(SiMe_3)_2]_2$ was prepared by the reaction of $MgCl[CH(SiMe_3)_2]\cdot Et_2O$ with $GeCl_2(diox)$.[4]

Tin(II) dialkyls $Sn[CPh(SiMe_3)(C_5H_4N\text{-}2)]_2$ **2** and $Sn[CH(SiMe_3)(C_9H_6N\text{-}8)]_2$ **3** were isolated as red crystalline solid in good yields (79, 85%). Compound **2** is more soluble in most hydrocarbon solvents than **3** which is only soluble in toluene and thf. The reactivity of **3** has been briefly communicated recently.[20,21] It reacts with elemental chalcogen to form stannane chalcogenones $R_2Sn{=}E$ (E = S, Se or Te) and forms Lewis acid–base adducts with tin(II) dihalides.

The lead(II) dialkyl $Pb[CH(SiMe_3)(C_9H_6N\text{-}8)]_2$ **4** was prepared by the reaction of $LiR^2(tmen)$ with $Pb[N(SiMe_3)_2]_2$ and isolated as a red crystalline solid by fractional crystallization. Attempted alkylation reaction of $LiR^2(tmen)$ with $PbCl_2$ led to reduction to lead metal. Compound **4** is more stable in the solid state, slowly decomposing to lead metal at room temperature in solution. The more lipophilic compound $M[N(SiMe_3)_2]_2$ (M = Ge, Sn or Pb) has been used as the starting material for the synthesis of compounds such as SnR_2 respectively.[22,23]

The ^{119}Sn NMR spectra of compounds **2** and **3** exhibited singlet peaks at δ 156.18 and 141.73 respectively, comparable to the peak at δ 141.0 of the related *N*-functionalized tin dialkyl $Sn[C(SiMe_3)_2(C_5H_4N\text{-}2)]_2$.[7] The ^{207}Pb NMR spectrum of **4** displayed a singlet signal at δ 1981 upfield when compared with those of other lead(II) dialkyls with monodentate ligands $Pb[2,4,6\text{-}(F_3C)_3C_6H_2]_2$[14] (δ 4878) and $Pb(C_6H_3R_2\text{-}2,6)_2$ (R = mesityl) (δ 3870).[10]

Crystal structures

Crystal structure determinations of compounds **1**–**4** have shown that the anionic ligands R^1 and R^2 are bonded in a *trans* C,N-chelate fashion with a co-ordination number of four for the metal centres. All of the four structures show a square-pyramidal geometry consistent with a stereoactive lone pair at the metal. In contrast, the structures of the transition-metal analogue $[Fe\{C(SiMe_3)_2(C_5H_4N\text{-}2)\}_2]$ is tetrahedral and $[CoR^1_2]$ and $[CoR^2_2]$ are square planar. Dimeric structures with interligand bridges were also found for the compounds $[\{M[CH(SiBu^tMe_2)(C_5H_4N\text{-}2)]_2\}_2]$ (M = Co or Fe).[18] The crystal structures of **1**–**4** with selected bond distances and angles are shown in Figs. 1–3 and Tables 1 and 2.

The structures of compounds **1** and **2** are similar. The four atoms bonded to the metal make a least-squares base plane from which deviations of N(1), N(2), C(1), C(16) atoms are about ±0.3072 and ±0.276 Å respectively. The Ge and Sn atoms occupy the apex with a lone pair of electrons and are 0.982 and 1.170 Å from the base plane and 0.211, 0.029 and 0.281, 0.49 Å out of the pyridine planes, respectively. The nearest Ge · · · Ge and Sn · · · Sn distances are 9.21 and 5.531 Å, respectively, which rule out the possibility of M · · · M interaction as found in $\{M[CH(SiMe_3)_2]_2\}_2$ (M = Ge or Sn).[1–4] The unit-cell packings of **1** and **2** are similar but quite different from that of $Sn[C(SiMe_3)_2(C_5H_4N\text{-}2)]_2$.[7] It is noteworthy that the dihedral angles between two phenyl planes in **1** and **2** are 8.2 and 15.6° respectively, and suggest that there are some intramolecular π–π interactions in these complexes. The average bite angle C–M–N and the bite distance C · · · N are 64.2, 2.350 and 60.0°, 2.383 Å respectively in **1** (M = Ge) and **2** (M = Sn). The dihedral angles between the pyridyl and phenyl planes from the same ligand are 60.7 and 120.4°, respectively.

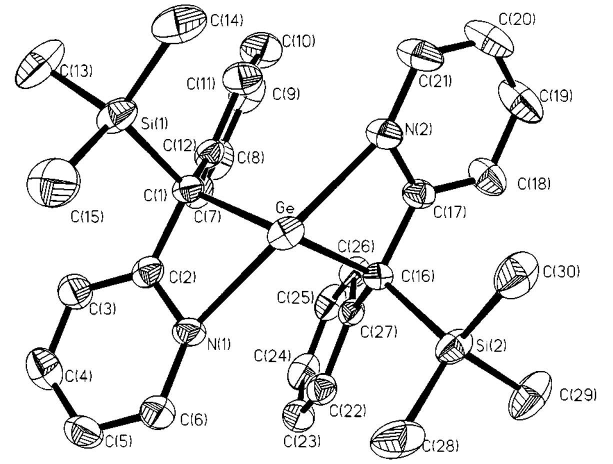


Fig. 1 Perspective drawing of compound **1** with the atomic numbering scheme. Thermal ellipsoids are shown at the 35% probability level and hydrogen atoms have been omitted. Compound **2** has a similar molecular structure

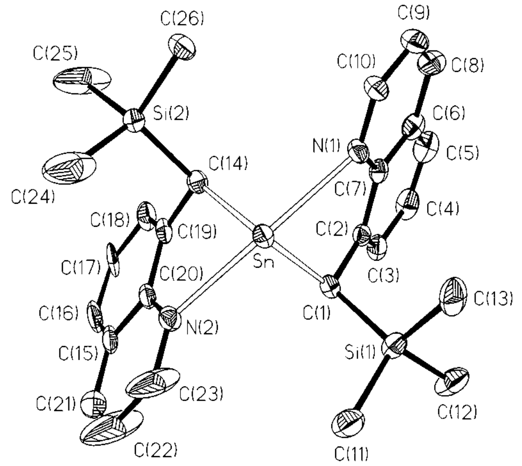


Fig. 2 Perspective drawing of compound **3** with the atomic numbering scheme. Thermal ellipsoids are shown at the 35% probability level

Table 2 Selected bond distances (Å) and angles (°) for SnR^2_2 **3** and PbR^2_2 **4**

	3 (M = Sn)	**4** (M = Pb)		**3** (M = Sn)	**4** (M = Pb)
M–C(1)	2.274(4)	2.342(3)	M–N(1)	2.524(3)	2.584(3)
M–C(14)	2.252(4)	2.329(3)	M–N(2)	2.487(3)	2.600(3)
C(1)–Si(1)	1.864(4)	1.838(3)	C(14)–Si(2)	1.871(4)	1.910(4)
C(1)–C(2)	1.500(6)	1.521(4)	C(14)–C(19)	1.497(6)	1.486(5)
C(2)–C(7)	1.420(6)	1.446(5)	C(19)–C(20)	1.424(6)	1.414(4)
C(7)–N(1)	1.372(6)	1.362(5)	C(20)–N(2)	1.362(6)	1.396(5)
C(1)–M–N(1)	71.8(1)	71.0(1)	C(14)–M–N(2)	72.6(1)	69.2(1)
N(1)–M–N(2)	148.4(1)	146.5(1)	C(1)–M–C(14)	94.7(1)	93.2(1)
C(1)–M–N(2)	86.7(1)	86.2(1)	C(14)–M–N(1)	86.1(1)	87.5(1)
C(2)–C(1)–M	111.1(3)	111.1(2)	C(19)–C(14)–M	111.4(3)	114.3(2)
C(1)–C(2)–C(7)	120.3(4)	120.6(3)	C(14)–C(19)–C(20)	119.4(4)	119.3(3)
C(2)–C(7)–N(1)	117.7(4)	118.1(3)	C(19)–C(20)–N(2)	118.3(4)	118.2(3)
C(7)–N(1)–M	110.2(2)	111.1(2)	C(20)–N(2)–M	110.5(3)	110.5(2)

Table 3 Selected structural data for some monomeric bivalent Group 14 metal compounds

Compound	M–C/Å	M–N/Å	C–M–C/°	Ref
M = Ge				
1 $Ge[CPh(SiMe_3)(C_5H_4N-2)]_2$	2.135(4)	2.313(4)	105.4(1)	This work
$Ge[CH(SiMe_3)_2]_2$[a]	2.038(15)	—	107(2)	4
$Ge[CH(SiMe_3)_2][C(SiMe_3)_3]$	2.067(4), 2.012(6)	—	111.3(2)	5
$Ge[C(SiMe_3)_2(C_5H_4N-2)]_2$	2.127(4)	2.273(3)	112.5(2)	6
$Ge(C_6H_3R_2-2,6)_2$[b]	2.033	—	114.4(2)	10
M = Sn				
2 $Sn[CPh(SiMe_3)(C_5H_4N-2)]_2$	2.329(4)	2.446(5)	103.6(1)	This work
3 $Sn[CH(SiMe_3)(C_9H_6N-8)]_2$	2.274(4)	2.524(3)	94.7(1)	This work
$Sn[CH(SiMe_3)_2]_2$[a]	2.22(2)	—	97(2)	4
$Sn[2,4,6-(F_3C)_3C_6H_2]_2$	2.281(5)[c]	—	98.3(1)	13
$Sn(C_6H_3R_2-2,6)_2$[b]	2.225(5)	—	114.7(2)	10
$Sn[C(SiMe_3)_2(C_5H_4N-2)]_2$	2.35(2)	2.42(2)	116.7(2)	7, 24
$Sn[1-C_{10}H_6(NMe_2)-8]_2$	2.231(9)[c]	2.567(8)	93.8(5)	25
$Sn[C_6H_3(CH_2NMe_2)_2-2,6]Cl$	2.158(8)	2.564(8)	95.0(3)	26
M = Pb				
4 $Pb[CH(SiMe_3)(C_9H_6N-8)]_2$	2.336(3)[c]	2.592(3)	93.2(1)	This work
$Pb[2,4,6-(F_3C)_3C_6H_2]_2$	2.366(4)[c]	—	94.5(1)	14
$Pb(C_6H_3R_2-2,6)_2$	2.334(12)	—	114.5(6)	10

[a] Gas phase structure. [b] R = Mesityl. [c] Average.

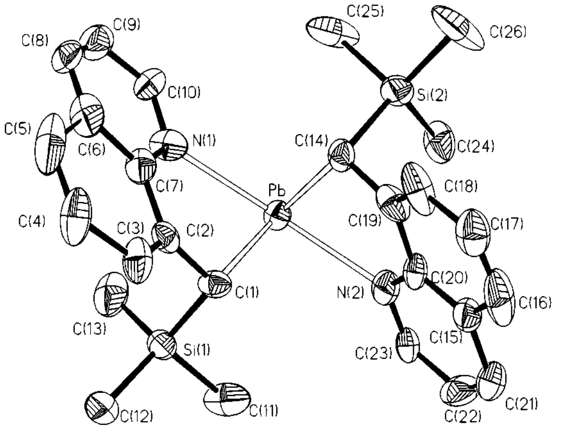


Fig. 3 Perspective drawing of compound **4**. Details as in Fig. 2

In the structures of compounds **3** and **4** the four coordinating atoms make a least-squares plane from which deviations of atoms N(1), N(2), C(1) and C(14) are about ±0.426 and ±0.4401 Å respectively. The Sn atom in **3** is 1.11 Å from the base plane, slightly shorter than the value of 1.17 Å in compound **2**, while in **4** the Pb atom is 1.1770 Å from this base plane. The nearest Sn · · · Sn and Pb · · · Pb distances are 6.168 and 10.541 Å respectively which also rules out the existence of any bonding between them. In compounds **3** and **4** the *C,N*-chelate forms a five-membered ring, which has less ring strain than the four membered ring in **1** and **2**. This is supported by comparison of the values of the average bite angle C–M–N and C · · · N distances of alkyl ligands $^-R^1$ and $^-R^2$. The values in **3** and **4** are 70.3, 2.851 and 72.2°, 2.816 Å respectively which are larger than those in **1** and **2**. The sum of the angles subtended at the metal centres in **1**–**4** are 317.4, 305.5, 317.2 and 314.3° respectively, consistent with the presence of a stereochemically active lone pair of electrons.

Selected structural data for compounds **1**–**4** and some Group 14 element carbene analogues are shown in Table 3. Within a homologous series, the metal–carbon distances of the bivalent Group 14 metal compounds vary according to the size of the metal atoms. For metal dialkyls, the metal–carbon distances are dependent on the degree of the substitution at the α-carbon of the ligands. For example, the M–C_α distance of 2.274(4) Å in **3** is shorter than the corresponding distance of 2.329(4) Å in **2**. In addition, the steric and electronic effects due to the coordination of the electron-donating nitrogen atoms also lead to elongation of the M–C distances. In contrast, the gas-phase structures of $M[CH(SiMe_3)_2]_2$ (M = Ge or Sn) have comparatively longer M–C_α distances.

It is noteworthy that compounds **1**–**4** obtained are racemic

Table 4 Selected X-ray crystallographic data for compounds **1**–**4**

	1	**2**	**3**	**4**
Molecular formula	$C_{30}H_{36}GeN_2Si_2$	$C_{30}H_{36}N_2Si_2Sn$	$C_{26}H_{32}N_2Si_2Sn$	$C_{26}H_{32}N_2PbSi_2$
M	553.4	599.5	547.4	635.9
Colour and habit	Golden prism	Golden grain	Dark red prism	Red prism
Crystal size/mm	0.20 × 0.22 × 0.32	0.28 × 0.38 × 0.42	0.38 × 0.36 × 0.32	0.20 × 0.20 × 0.60
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/n$ (no. 14)	$P2_1/c$ (no. 14)	*P*1 (no. 2)	*Pb*1
a/Å	18.246(2)	17.756(4)	10.553(2)	10.602(1)
b/Å	9.984(1)	10.080(2)	16.095(3)	16.024(1)
c/Å	18.246(2)	18.865(4)	16.192(3)	16.307(1)
α/°			79.26(3)	79.55(1)
β/°	115.76(1)	114.89(3)	86.09(3)	85.71(1)
γ/°			87.01(3)	86.39(1)
U/Å^3	2993.8(15)	3063(1)	2693.6(9)	2713.3(3)
Z	4	4	4	4
D_c/g cm^{-3}	1.232	1.300	1.350	1.557
μ/mm^{-1}	1.123	0.93	1.053	6.321
$2\theta_{max}$/°	55	52	52	52
Unique data measured	6043	5368	12 218	6880
No. observed reflections	4587	4011	7575	6880
No. variables, *p*	203	317	560	560
R	0.041	0.042	0.0437	0.0749
R′	0.088	0.043	0.0513	0.0816

mixtures of their (*RR*) and (*SS*) diastereoisomers, as confirmed by their ^{1}H and ^{13}C NMR spectra. Molecular models suggest that the (*RS*) and (*SR*) diastereoisomers are sterically unfavourable. Moreover, the crystal structure data of **1**–**4** have shown that only the (*RR*) and (*SS*) diastereoisomers are observed in the unit-cell packings and the (*RS*) or (*SR*) diastereoisomers are not found.

Experimental

General procedures

All manipulations were carried out under an inert atmosphere of dinitrogen or argon by standard Schlenk techniques or in a dinitrogen glove-box. Solvents were dried over and distilled from CaH_2 (hexane) and/or Na (Et_2O, toluene). The compound $SnCl_2$ (Aldrich) was used without further purification; $GeCl_2$(diox),[4] LiR^1(tmen)[27] and LiR^2(tmen)[20] were prepared according to the literature. Proton, ^{13}C, ^{119}Sn and ^{207}Pb NMR spectra were recorded at 250, 62.90, 186.50 and 104.63 MHz, respectively, using a Bruker WM-250 or ARX-500 instrument. All spectra were recorded in C_6D_6, and the chemical shifts δ are relative to $SiMe_4$ (^{1}H and ^{13}C), $SnMe_4$ (^{119}Sn) and $PbMe_4$ (^{207}Pb) respectively.

Preparations

GeR$^1_2$ 1. To a stirring solution of $GeCl_2$(diox) (0.75 g, 3.24 mmol) in diethyl ether (50 cm^3) was added dropwise a solution of LiR^1(tmen) 2.36 g, 6.48 mmol) in ether (60 cm^3) at 0 °C. The orange mixture was stirred at ambient temperature for 12 h. The insoluble solid was filtered off and the orange filtrate concentrated and cooled at −20 °C for 2 d to yield orange crystals of compound **1** (1.20 g, 67%), m.p. 190–192 °C (decomp.) (Found: C, 64.76; H, 6.46; N, 4.92. Calc. for $C_{30}H_{36}GeN_2Si_2$: C, 65.11; H, 6.56; N, 5.06%). EI mass spectrum: *m*/*z* 554 (M^+) and 314 ($[M - R^1]^+$). ^{1}H NMR (C_6D_6, 250 MHz): δ 0.27 (s, 18 H), 6.42–6.54 (m, 6 H), 6.72–6.75 (m, 2 H), 6.78–6.84 (m, 8 H) and 8.10 (dt, *J* = 5.2, 1.4 Hz, 2 H). ^{13}C NMR (C_6D_6, 62.90 MHz): δ −0.09, 52.47, 119.88, 121.48, 125.50, 126.57, 127.12, 127.25, 136.00, 144.06, 146.80 and 170.13.

SnR$^1_2$ 2. A solution of LiR^1(tmen) (0.63 g, 1.74 mmol) in diethyl ether (25 cm^3) was added slowly to a suspension of $SnCl_2$ (0.17 g, 0.88 mmol) in ether (30 cm^3) and stirred at ambient temperature for 6 h. The white precipitate was filtered off and the deep yellow filtrate concentrated and cooled at −20 °C for a few days, yielding reddish orange crystals of compound **2** (0.41 g, 79%), m.p. 155–160 °C (decomp.) (Found: C, 60.20; H, 6.00; N, 4.72. Calc. for $C_{30}H_{36}N_2Si_2Sn$: C, 60.11; H, 6.05; N, 4.67%). EI mass spectrum: *m*/*z* 600 (M^+); 360 ($[M - R^1]^+$) and 240 ($[R^1]^+$). ^{1}H NMR (C_6D_6, 250 MHz): δ 0.27 (s, 18 H), 6.36–6.41 (m, 2 H), 6.54 (d, *J* = 7.5, 4 H), 6.66 (t, *J* = 7.2, 2 H), 6.82 (m, 8 H) and 7.84 (d, *J* = 5.2 Hz, 2 H). ^{13}C NMR (C_6D_6, 62.90 MHz): δ 0.36, 55.76, 119.67, 120.88, 126.03, 127.05, 127.11, 136.06, 144.95, 146.63 and 170.79. ^{119}Sn NMR (C_6D_6, 186.50 MHz): δ 156.18 (s).

SnR$^2_2$ 3. To a stirred suspension of $SnCl_2$ (0.27 g, 1.44 mmol) in diethyl ether (30 cm^3) was added dropwise a solution of LiR^2(tmen) (0.97g, 2.88 mmol) in ether (50 cm^3). The orange mixture was stirred for 16 h at ambient temperature. The solvent was then removed *in vacuo* and the residue extracted with toluene (50 cm^3). The insoluble solid was filtered off and the red filtrate concentrated and cooled at −20 °C for 1 d to yield red crystals of compound **3** (0.67 g, 85%), m.p. 225–226 °C (decomp.) (Found: C, 57.02; H, 5.91; N, 5.11. Calc. for $C_{26}H_{32}N_2Si_2Sn$: C, 57.05; H, 5.89; N, 5.12%). EI mass spectrum: *m*/*z* 548 (M^+) and 334 ($[M - R^2]^+$). ^{1}H NMR (C_6D_6, 250 MHz): δ 0.32 (s, 18 H), 1.17 (s, 2 H), 6.63 (dd, *J* = 8.2, 4.4, 2 H), 6.84 (d, *J* = 7.2, 2 H), 6.95 (dd, *J* = 8.0, 1.3, 2 H), 7.06 (t, *J* = 7.2, 2 H), 7.48 (dd, *J* = 8.3, 1.6, 2 H) and 8.67 (dd, *J* = 4.4, 1.7 Hz, 2 H). ^{13}C NMR (C_6D_6, 62.90 MHz): δ −0.24, 38.08, 129.44, 120.85, 128.79, 129.53, 130.96, 138.02, 146.45, 147.91 and 152.50. ^{119}Sn NMR (C_6D_6, 186.50 MHz): δ 141.73 (s).

PbR$^2_2$ 4. A solution of LiR^2(tmen) (3.60 g, 10.68 mmol) in toluene (50 cm^3) was added dropwise to a solution of $Pb[N(SiMe_3)_2]_2$ (2.82 g, 5.34 mmol) in toluene (30 cm^3) at −30 °C and in the absence of light. The reaction mixture was slowly raised to ambient temperature and stirred for 10 h. The black precipitate was filtered off and the filtrate concentrated. Orange-red crystalline compound **4** was obtained by fractional crystallization at −30 °C (2.21 g, 65%), m.p. 147–148 °C (decomp.) (Found: C, 49.07; H, 4.97; N, 4.40. Calc. for $C_{26}H_{32}N_2PbSi_2$: C, 49.11; H, 5.07; N, 4.40%). EI mass spectrum: *m*/*z* 636 (M^+), 422 ($[M - R^2]^+$) and 214 ($[R^2]^+$). ^{1}H NMR (C_6D_6, 250 MHz): δ 0.01 (s, $SiMe_3$, 18 H), 1.16 (s, $^2J_{HPb}$ = 52.1, 2 H), 6.64 (d, *J* = 6.8, 2 H), 6.69 (q, *J* = 4.2, 2 H), 6.75 (dd, *J* = 8.0, 1.2, 2 H), 7.19 (d, *J* = 7.8, 2 H), 7.49 (dd, *J* = 8.2, 1.7, 2 H) and 8.45 (dd, *J* = 4.3, 1.7 Hz, 2 H). ^{13}C NMR (C_6D_5, 62.90 MHz):

δ 0.33, 70.38, 119.87, 122.12, 126.76, 130.18, 136.70, 138.13, 148.23, 151.29 and 152.59. ^{207}Pb NMR (thf–C_6D_5, 104.63 MHz): δ 1981 (s).

X-Ray crystallography

Crystals of compounds **1** and **4** were grown from ether, those of **2** and **3** from ether–hexane and toluene respectively. X-Ray data were collected using single crystals sealed in capillaries under dinitrogen, and raw intensities were collected on a Siemens P4/PC four-circle diffractometer at 294 K for **1** and **2**, while raw intensities of **3** and **4** were collected on Siemens R3m/V and Rigaku RAXIS IIc diffractometers at 294 K respectively. The structures were solved by direct phase determination, and all non-hydrogen atoms were subjected to anisotropic refinement. The hydrogen atoms were generated geometrically (C–H bonds fixed at 0.96 Å) and allowed to ride on their respective parent atoms; they were assigned appropriate isotropic thermal parameters and included in the structure-factor calculations. Computations were performed using the Siemens SHELXTL PC program package[28] on a PC 486 computer, and anomalous dispersion corrections were incorporated.[29] The crystallographic data for **1**–**4** are shown in Table 4.

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References

1 D. E. Goldberg, P. B. Hitchcock, M. F. Lappert, K. M. Thomas, A. J. Thorne, T. Fjeldberg, A. Haaland and E. R. Schelling, *J. Chem. Soc., Dalton Trans.*, 1986, 2387.
2 P. J. Davidson, D. H. Harris and M. F. Lappert, *J. Chem. Soc., Dalton Trans.*, 1976, 2268.
3 P. B. Hitchcock, M. F. Lappert, S. J. Miles and A. J. Thorne, *J. Chem. Soc., Chem. Commun.*, 1984, 480.
4 T. Fjeldberg, T. Haaland, B. E. R. Schilling, M. F. Lappert and A. J. Thorne, *J. Chem. Soc., Dalton Trans.*, 1986, 1551.
5 P. Jutzi, A. Becker, H. G. Stammler and B. Neumann, *Organometallics*, 1991, **10**, 1647.
6 G. Ossig, A. Meller, C. Brönneke, O. Müller, M. Schäfer and R. Herbst-Irmer, *Organometallics*, 1997, **16**, 2116.
7 L. M. Engelhardt, B. S. Jolly, M. F. Lappert, C. L. Raston and A. H. White, *J. Chem. Soc., Chem. Commun.*, 1988, 336.
8 M. Kira, R. Yauchibara, R. Hirano, C. Kabuto and H. Sakurai, *J. Am. Chem. Soc.*, 1991, **113**, 7785.
9 K. W. Klinkhammer and W. Schwartz, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1334.
10 R. S. Simons, L. Pu, M. M. Olmstead and P. P. Power, *Organometallics*, 1997, **16**, 1920.
11 L. Lange, B. Meyer and W.-W. du Mont, *J. Organomet. Chem.*, 1987, 329, C17; P. Jutzi, H. Schmidt, B. Neumann and H.-G. Stammler, *Organometallics*, 1996, **15**, 741.
12 M. Weidenbruch, J. Schlaefke, A. Schäfer, K. Peters, H. G. von Schnering and H. Marsmann, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1846.
13 H. Grützmacher, H. Pritzkow and F. T. Edelmann, *Organometallics*, 1991, **10**, 23; H. Lay, H. Pritzkow and H. Grützmacher, *J. Chem. Soc., Chem. Commun.*, 1992, 260.
14 S. Brooker, J.-K. Buijink and F. T. Edelmann, *Organometallics*, 1991, **10**, 25.
15 M. Kira, T. Iwamoto, T. Maruyama, C. Kabuto and H. Sakurai, *Organometallics*, 1996, **15**, 3767.
16 J. T. Snow, S. Murakami, S. Masamune and D. J. Williams, *Tetrahedron Lett.*, 1984, **25**, 4191.
17 S. A. Batcheller, T. Tsumauraya, O. Tempkin, W. M. Davis and S. Massamune, *J. Am. Chem. Soc.*, 1990, **112**, 9394.
18 W.-P. Leung, H.-K. Lee, Z.-Y. Zhou and T. C. W. Mak, *J. Organomet. Chem.*, 1993, **462**, 7; W.-P. Leung, H.-K. Lee, L.-H. Weng, Z.-Y. Zhou and T. C. W. Mak, *Organometallics*, 1996, **15**, 1785.
19 W.-P. Leung, H.-K. Lee, L.-H. Weng, Z.-Y. Zhou and T. C. W. Mak, *J. Chem. Soc., Dalton Trans.*, 1997, 779.
20 W.-P. Leung, W.-H. Kwok, L. T. C. Law, Z.-Y. Zhou and T. C. W. Mak, *Chem. Commun.*, 1996, 505.
21 W.-P. Leung, W.-H. Kwok, F. Xue and T. C. W. Mak, *J. Am. Chem. Soc.*, 1996, **119**, 1145.
22 D. H. Harris and M. F. Lappert, *J. Chem. Soc., Chem. Commun.*, 1974, 895.
23 C. D. Schaeffer and J. J. Zuckermann, *J. Am. Chem. Soc.*, 1974, **96**, 7160.
24 B. S. Jolly, M. F. Lappert, L. M. Engelhardt, A. H. White and C. L. Raston, *J. Chem. Soc., Dalton Trans.*, 1993, 2653.
25 J. T. B. H. Jastrzebski, P. A. van der Schaaf, J. Boersma, G. van Koten, D. Heijdenrijk, K. Goubitz and D. J. A. de Ridder, *J. Organomet. Chem.*, 1989, **367**, 55.
26 J. T. B. H. Jastrzebski, P. A. van der Schaaf, J. Boersma, G. van Koten, M. C. Zoutberg and D. Heijdenrijk, *Organometallics*, 1989, **8**, 1373.
27 W.-P. Leung, L.-H. Weng, R.-J. Wang and T. C. W. Mak, *Organometallics*, 1995, **14**, 4832.
28 G. M. Sheldrick, *Crystallographic Computing 3*, eds. G. M. Sheldrick, C. Krieger and R. Goddard, Oxford University Press, New York, 1985, p. 175.
29 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974.

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