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Stable heterocyclic (Schiff base) divalent Group 14 element species M–O-Schiff base-O (M = Ge, Sn, Pb)

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Abstract

The synthesis and characterization of new stable divalent germanium, tin and lead homoleptic species L_2M [L_2 = 2,2′-*N*,*N*′-bis(salicylidene)ethylenediamine, M = Ge (**1**), Sn (**2**), Pb (**3**); (*R*,*R*)-(−)-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamine, M = Ge (**4**), Sn (**5**), Pb (**6**) and *N*-methyl-2,2′-imino-bis(8-hydroxyquinoline), M = Ge (**7**), Sn (**8**)] are described. Compounds **1**–**8** were obtained in good yields by alcoholysis of the M–N bonds of the divalent precursors $[(Me_3Si)_2N]_2M$ by diols with bis(salicylidene)diamine and 2,2′-imino-bis-quinoline structures. They have been isolated as solids at ambient temperature and are monomeric. NMR, IR and UV spectra are suggestive of N···M intramolecular coordination. The chemistry of **1**–**8** is illustrated through their reactions with iodine and 1,2-benzoquinones. The X-ray structure of the L_2Sn-quinone adduct reveals a distorted octahedral coordination geometry around tin with remarkably short Sn–N distances. Various R–CH=O insertion reactions into the M–O bonds of **1**–**8** and M–O cleavage reactions with organic acids and acyl halides are also described; they provide a convenient procedure for the generation of new heteroleptic divalent species. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Germylene; Stannylene; Plumbylene; Schiff base

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1. Introduction

The study of divalent species of elements of Group 14 has been the subject of considerable scrutiny over the last few years [1]. As a general rule, when these species contain unfunctionalized organic ligands they undergo rapid oligomerization and polymerization. Sterically demanding substitutents have been used to prevent the aggregation, but the ligand backbone may also play an important role in improving stability. Thus, various kinetically and/or thermodynamically stabilized divalent germanium, tin and lead compounds have been isolated in a monomeric state [2]. Following our studies on the $(ArO)_2M$ species (Ar = 2,4,6-$[(CH_3)_2NCH_2]_3C_6H_2$; M = Ge, Sn, Pb) stabilized by dynamic intramolecular N···M···N coordination [3–5], we report in this paper the full details of the syntheses and properties of new bivalent heterocyclic species M–O–SB–O using ONNO tetradentate Schiff bases (SB) as ancillary ligands [HO–SB–OH = -*N*,*N*′-bis(salicylidene)ethylenediamine ($SalenH_2$), (*R*,*R*)-(−)-*N*,*N*′-bis(3,5-di-*tert*-butyl-salicylidene)-1,2-cyclohexanediamine ($BSalchH_2$) and *N*-methyl-2,2′-imino-bis(8-hydroxyquinoline) ($MeNquinH_2$)]. Some preliminary aspects of this work have been communicated earlier [6]. Although Salen ligand complexes of transition metals have been studied for more than 50 years [7], complexes of tetravalent Group 14 metals with these ligands have aroused interest only in the past 20 years and several complexes have been isolated [8–10,12a]. However, few papers have described Schiff base complexes of divalent Group 14 species and none with germanium [11,12b–14].

2. Results and discussion

2.1. Synthesis of the divalent species M–O–SB–O (M = Ge, Sn, Pb)

The classical nucleophilic substitution of metal halides by sodium alkoxides was our initial approach to

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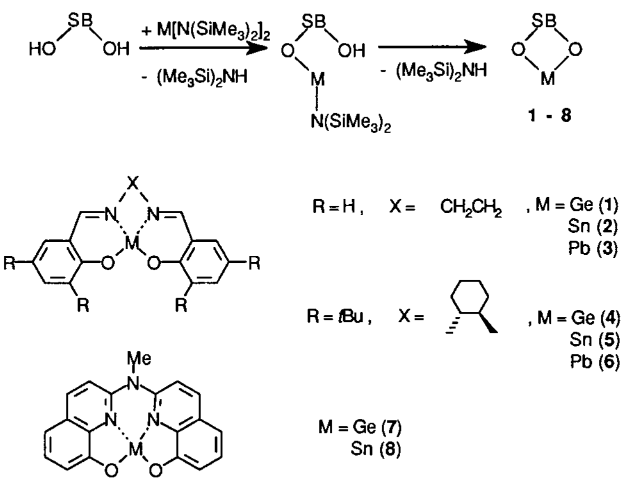
the synthesis of compounds **1** and **2**. Addition of a methanol solution of $GeCl_2 \cdot 1,4$-dioxane or of $SnCl_2$ to a solution of the sodium salt of $SalenH_2$, prepared in situ by the reaction of the diphenol $SalenH_2$ with sodium methoxide in anhydrous methanol under nitrogen, resulted in the formation in good yield (> 65%) of the desired compounds **1** or **2** as yellow solids (Eq. (1)).

$$MCl_2 + SalenNa_2 \rightarrow (Salen)M + 2NaCl \qquad (1)$$

Compounds **1** and **2** are barely soluble in non-polar or aprotic solvents and the difficulties encountered during purification (separation from NaCl) led us to explore alternative methods of preparing the divalent species **1**–**8**. The extreme sensitivity of the Group 14 metal–nitrogen bond to alcoholysis prompted us to carry out the reactions of Lappert's divalent species $M[N(SiMe_3)_2]_2$ [15] with the Schiff base diols $SB(OH)_2$ in pentane (Scheme 1). The reactions of the tin and lead compounds $M[N(SiMe_3)_2]_2$ with HO–SB–OH were nearly instantaneous and led to **2**, **3**, **5**, **6** and **8** in high yield. In contrast, in case of germanium (**1**, **4** and **7**), the reactions were complete only after 6 h at room temperature (r.t.). It was possible to characterize by ^1H-NMR spectroscopy the intermediate heteroleptic germylene $[HO–SB–Ge–N(SiMe_3)_2]$ in which only a single Ge–N bond reacts (case of **1**) (Scheme 1), if displaced disilylamine is not removed in order to force the equilibrium to the right.

These compounds are soluble (**1**, **2**, **4**, **5**, **7** and **8**) or barely so (**3** and **6**) in polar and protic solvents and poorly soluble (**1**, **2**, **4** and **5**) or insoluble in non-polar and aprotic solvents. All are unreactive towards dry oxygen in the solid state. In solution, in the presence of air and traces of moisture, and even when the solids are exposed to ambient (moist) air, oxidative hydrolysis to a tetravalent species occur and the protonated ligand is released.



Scheme 1.

2.2. Physicochemical and structural studies of the divalent species M–O–SB–O (M = Ge, Sn, Pb)

As a result of the low solubility or insolubility in benzene of compounds **3**, **6**, **7** and **8**, cryoscopic molecular-weight determinations were performed only for **1**, **2**, **4** and **5**; they showed that these species are monomeric in benzene solution. Compounds **1**–**8** have been characterized by ^1H-, ^{13}C-NMR, UV, IR and mass spectroscopy and also by ^{119}Sn-NMR spectroscopy for the stannylenes **2**, **5** and **8**. NMR, IR and UV spectroscopic data are reported in Table 1.

The ^1H-NMR spectra of compounds **1**–**6** showed δ values of the methine proton between 7.89 and 8.22 ppm. In most, the signal was a broad singlet and the peaks of the aromatic protons were complicated relative to those of the corresponding HO–SB–OH compounds. The signals for CH=N were shifted slightly downfield from those of the free ligand, while the aromatic signals shifted very slightly upfield. For compounds **1**–**3**, the signal corresponding to NCH_2 hydrogens appeared as a large massif. These phenomena are thought to be associated with the presence of $N \rightarrow M$ intramolecular coordination in these molecules. It is noteworthy that temperature does not appreciably affect the spectra (25–130°C).

The ^{119}Sn-NMR spectra of **2**, **5** and **8** exhibited singlets at -554 (-564 [12b]) ($CDCl_3$), -524 (C_6D_6) and -446 (DMSO-d_6) ppm, respectively, which fall within the range of shift values corresponding to four-coordinate Sn(II) compounds.

The IR spectra of **1**–**3** showed strong absorption bands at 1640–1620 cm^{-1}, which can be attributed to the $\nu_{C=N}$ stretching frequency. The observed shift of 5–20 cm^{-1} of these bands compared with those of the free ligands is consistent with the donation of the nitrogen lone pair of the azomethine group to the central atom.

The UV–vis spectra of **1**–**3** in DMF are also characteristic of such complexes with a ONNO tetradentate Schiff base ligand. In addition, of the characteristic bands of the free ligand, new absorption maxima were observed at 354, 366 and 379 nm, respectively. As previously observed for Group 14 metal divalent species donor complexes, these bands were shifted to shorter wavelengths compared with those of divalent species of Group 14 metals [16] that are not electronically stabilized.

2.3. Chemical reactivity of the divalent species M–O–SB–O (M = Ge, Sn, Pb)

The divalent compounds prepared in this study show limited M(II) reactivity undergoing oxidative addition adduct formation and M–O bond cleavage. Germylenes

Table 1
Spectroscopic data for compounds **1**–**8**

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
NMR (δ, ppm)								
^{1}H								
CH=N	8.10 (s)	8.11 (s)	8.22 (s)	7.89 (s)	7.90 (s)	8.14 (s)		
CH_3–N							3.78 (s)	3.80 (s)
CH_2	3.84 (br)	3.89 (br)	3.72 (br)					
*t*Bu				1.32 (s)	1.41 (s)	1.26 (s)		
				1.36 (s)	1.43 (s)	1.48 (s)		
				1.38 (s)	1.85 (s)			
				1.44 (s)	1.87 (s)			
Ar	6.50–7.40 (m)	6.50–7.37 (m)	6.44–7.50 (m)	6.92 (m)	6.96 (m)	6.86 (m)	6.96–7.60 (m)	6.90–7.50 (m)
				7.52 (m)	7.75 (m)	7.48 (m)		
^{13}C								
CH=N	167.02	166.99	163.61	166.61	160.56	161.06		
					167.20	167.34		
CH_2	54.81	55.59	58.88					
*t*Bu				30.17	30.31	29.95		
				31.48	30.43	32.015		
				32.47	31.79	33.83		
				33.18	31.85	35.53		
Ar	117–135	116.22	96.52	118.51	117.00	121.54		
	160.61	124.10	109.79	126.53	117.50	127.72		
		133.80	131.00	126.97	136.90	128.14		
		134.92	133.83	136.79	142.76	128.90		
				140.14	162	142.37		
				158.8	164			
^{119}Sn		−554.7			−524.5			−445.8
UV (DMF, λ nm) [a]	354	366	379					
IR (KBr, Nujol, cm^{-1})	1630	1636	1625					

[a] ϵ values have not been calculated due to the particular sensitivity of **1**–**3** to hydrolysis.

and stannylenes are known to insert into a carbon–halogen σ bond and to add to electron-poor or electron-rich 1,3-dienes and oxadienes [1]. Compounds **1**–**8** do react with iodine, but all attempts to effect a reaction with alkyl halides, dienes and conjugated carbonyl compounds failed (Scheme 2). The absence of this characteristic reactivity of the free divalent species is attributable to N···M intramolecular coordination. The equivalence of the aryl, methine and methylene resonances in ^{1}H-NMR spectra of the diiodide products **9**–**11** is indicative of a *trans* attachment of the iodine atoms.

With 1,2-quinones facile heterocyclization reactions were observed under very mild conditions (Scheme 2). These reactions are similar to those observed for various divalent Group 14 species and probably proceed by single-electron transfer [3–5,17–19].

Single crystals of **13**·CH_3CN suitable for X-ray structure analysis were obtained from acetonitrile. Fig. 1 shows the solid-state structure of **13** together with the numbering scheme.

The CH_3CN molecule is omitted for clarity. Relevant bonds distances and angles for **13** are given in Table 2. The tin atom has a distorted octahedral coordination geometry. The oxygen atoms of the quinone moiety are situated at axial and equatorial positions, whereas the ONNO atoms of the salen ligand occupy three equatorial and one axial position. The distortion of the octahedral coordination around tin originates from the chelating salen ligand, in which there is a considerable torsion of 40° along the atoms N(1)–C(8)–C(9)–N(2), and more probably from the constraints imposed by the five-membered ring Sn(1)–O(3)–C(17)–C(18)–O(4). The σ Sn–O distances of 2.007(3), 2.010(3), 2.026(2) and 2.029(2) Å correspond well with bond lengths found in other tin compounds, a typical Sn–O distance in the SnO_4N_2 system being around 2.02 Å [20]. The Sn←N distances of 2.174(3) and 2.191(3) Å are remarkably shorter than those observed in various other Sn(IV) systems with Sn←N donor acceptor bonds (> 2.37 Å) [21].

M–O bond cleavage reactions in **1**–**8** by organic acids and acid chlorides lead to new heteroleptic, acyclic divalent products. Thus, **2** reacts with trifluoroacetic acid, trifluoromethanesulfonic acid and acetyl chloride to yield the corresponding heteroleptic divalent species **17**, **18** and **19** (Scheme 3). Compounds **1**–**8** are also precursors of new heterocyclic divalent species, their M–O bond being very reactive towards activated organic carbonyl compounds.

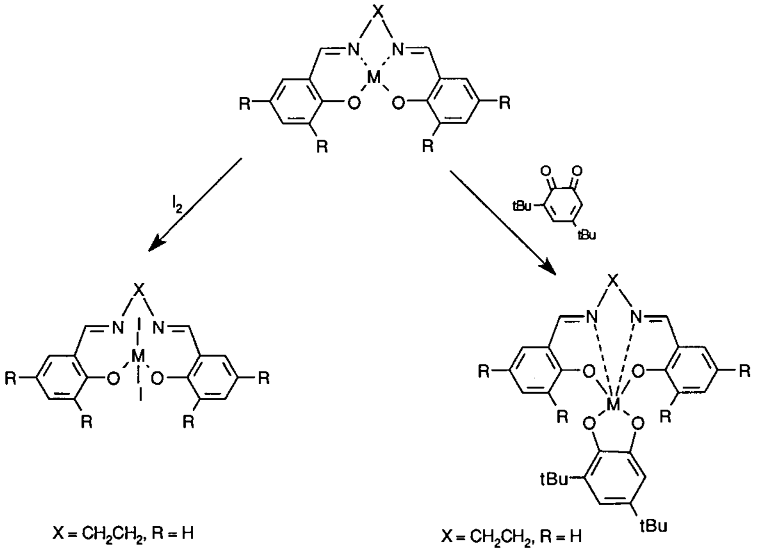
Such reactions have in particular been studied in the case of **2**, which reacts rapidly with chloral at r.t. to give almost quantitatively the 1,2 adduct **20**, which is stable at r.t. The rate of these insertion reactions, which are slightly faster when carried out in acetonitrile rather than in chloroform, depends on the nature of the aldehyde (propionaldehyde and benzaldehyde are respectively, very slightly reactive or unreactive toward **2**). It is noteworthy that the rate of these insertion reactions into **2** is slower than the rates of the insertions of the same aldehydes into the M–O bonds of various M(IV) compounds [22]. This suggests that the intramolecular coordination N···Sn hinders the nucleophilic attack of the carbonyl oxygen of the aldehyde on the tin in the first step of these reactions (Scheme 3).

These divalent Group 14 element species can also act as precursors of various stable doubly bonded derivatives O–SB–O–M=Y (Y = N–SiMe$_3$, S, Se) and organometallic complexes O–SB–O–M=M′L$_n$ [M′L$_n$ = W(CO)$_5$, Cr(CO)$_5$] or O–SB–O–M=Mn(Cp(CO)$_2$. These chemical properties and various ligand transfer reactions with BF$_3$·Et$_2$O, Cp$_2$TiCl$_2$, Cl$_2$Ni·DPPE and *t*BuPCl$_2$ will be reported in future publications.

3. Experimental

3.1. General procedures

All manipulations were performed under an inert atmosphere of nitrogen or argon using standard Schlenk and high-vacuum-line techniques. Dry, oxygen-free solvents were employed throughout. All solvents were distilled from sodium benzophenone or P$_2$O$_5$ before use. ^{1}H-NMR spectra were recorded on a Bruker AC 80 spectrometer operating at 80 MHz (chemical shifts are reported in ppm relative to internal Me$_4$Si) and ^{13}C spectra on a AC 200 MHz spectrometer; the multiplicity of the ^{13}C-NMR signals was determined by the APT technique. ^{1}H- decoupled ^{119}Sn-NMR spectra were recorded on a Bruker AC 200 or 400 MHz (chemical shifts are reported in ppm relative to external Me$_4$Sn).^{19}F spectra were recorded on a Bruker AC 80 spectrometer (chemical shifts are reported in ppm relative to external CF$_3$COOH). Mass spectra under electron impact (EI) or chemical ionization (CH$_4$) conditions at 70 and 30 eV were obtained on Hewlett–Packard 5989 and Nermag R10-10H spectrometers. IR and UV spectra were recorded on Perkin–Elmer 1600 FT-IR and Lambda-17 spectrophotometers. Melting points were taken uncorrected on a Leitz Biomed hotplate microscope apparatus. Elemental analyses (C, H,



X = CH$_2$CH$_2$, R = H
M = Ge **9**
Sn **10**
Pb **11**

X = CH$_2$CH$_2$, R = H
M = Ge **12**
Sn **13**
Pb **14**

X = (R,R)-C$_6$H$_{10}$, R = tBu
M = Ge **15**
Sn **16**

Scheme 2.

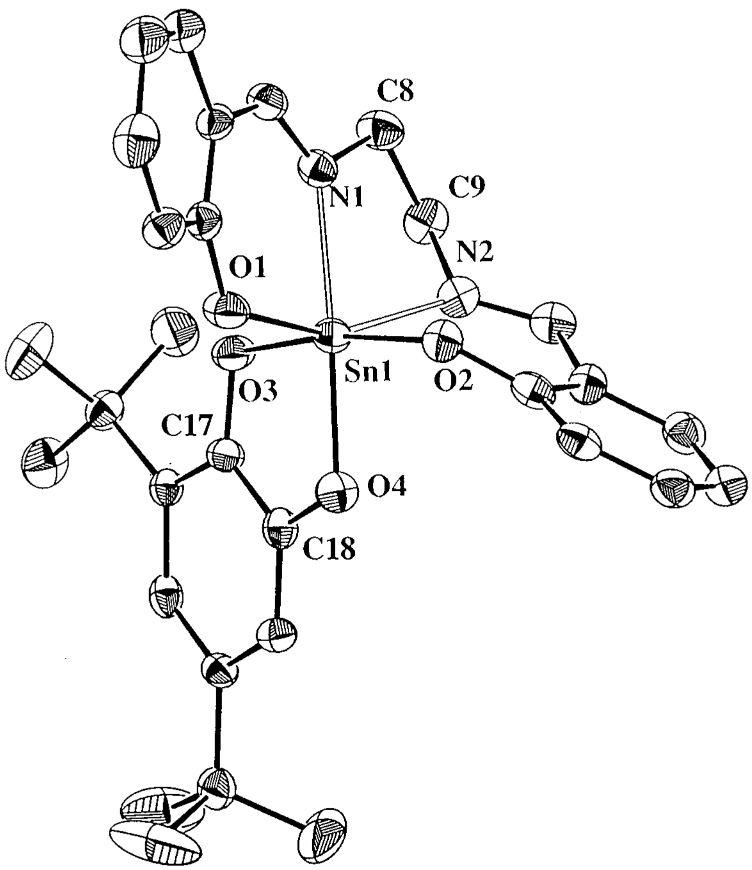


Fig. 1. Solid-state structure of **13**. Atoms are represented by thermal ellipsoids at the 50% probability level.

N) were performed at the Microanalysis Laboratory of the Ecole Nationale Supérieure de Chimie de Toulouse.

*3.2. [[2,2′-[1,2-Ethanediylbis[(nitrilo)-methylidyne]]bis[phenolato]](2-)]germanium (II) (**1**)*

To a solution of (Salen)H$_2$ (2.00 g, 7.45 mmol) in methanol (30 ml) was added a solution of 14.90 mmol of MeONa in methanol with stirring at r.t. The solution was stirred for 1 h after which time a solution of GeCl$_2$·1,4-dioxane (1.73 g, 7.45 mmol) in 20 ml of methanol was added with stirring. The reaction mixture was stirred at r.t. for 2 h. The volatiles were removed in vacuo. The residue was extracted with 3 × 50 ml of toluene. Concentration in vacuo gave a pale yellow powder of impure **1** (1.70 g) (traces of (Salen)H$_2$).

A solution of bis[bis(trimethylsilyl)amino]germanium-(II) (7.95 g, 20.20 mmol) in 50 ml of pentane was added to a stirred suspension of (Salen)H$_2$ (5.42 g, 20.20 mmol) in 40 ml of pentane. The mixture was stirred at r.t. for 12 h. A pale yellow precipitate appeared which was separated by filtration. Washing with pentane and drying in vacuo afforded pure **1** (5.63 g, 82%).

1: m.p. 170–180°C (dec.). ^{1}H-NMR (CDCl$_3$): 3.60–4.18 (m, 4H, CH$_2$), 6.50–7.40 (m, 8H, Ar), 8.10 (s, 2H, CH=N). ^{13}C-NMR (CDCl$_3$): 54.81 (CH$_2$), 117–135 (CH$_{Ar}$), 160.61 (C$_{quat}$–O), 167.02 (CH=N). MS: *m*/*z* 340 [M]$^{•+}$. UV (DMF): λ_{max} 354 nm. IR (KBr, Nujol, cm^{-1}): $\nu_{C=N}$ 1630. Anal. Calc. for $C_{16}H_{14}GeN_2O_2$: C, 56.71; H, 4.16; N, 8.27. Found: C, 56.89; H, 3.98; N, 8.16%.

*3.3. [[2,2′-[1,2-Ethanediylbis[(nitrilo)-methylidyne]]bis[phenolato]](2-)]-tin(II) (**2**)*

Following the procedure of the preceding preparation, impure **2** (2.44 g) was obtained from (Salen)H$_2$ (2.50 g, 9.32 mmol), MeONa (18.64 mmol) and SnCl$_2$ (1.77 g, 9.32 mmol).

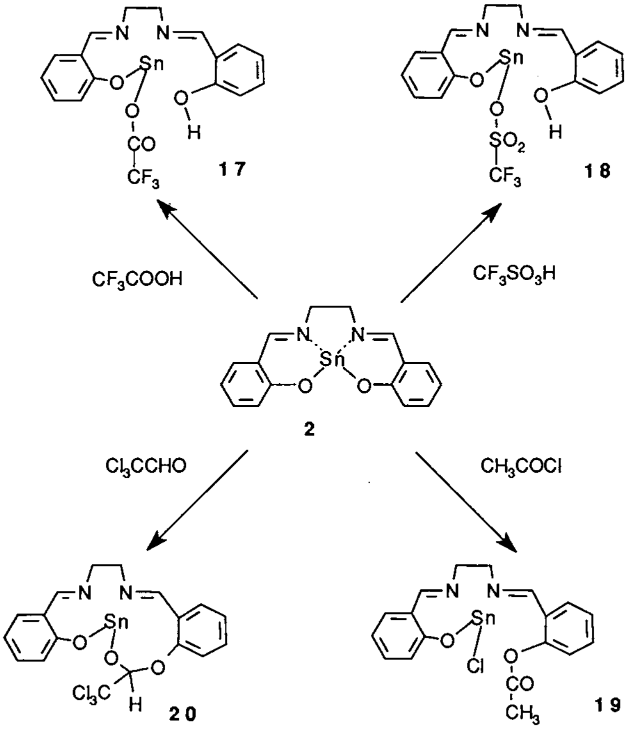
To a suspension of (Salen)H$_2$ (4.64 g, 17.29 mmol) in pentane (30 ml) was added a solution of bis-[bis(trimethylsilyl)amino]tin(II) (7.60 g, 17.29 mmol) in 50 ml of pentane. The mixture was stirred at r.t. for 10 h. Filtration followed by drying in vacuo afforded **2** (5.53 g, 83%) as a bright yellow powder.

2: m.p. 255–260°C (dec.). ^{1}H-NMR (CDCl$_3$): 3.88 (m, 4H, CH$_2$), 6.51–7.37 (m, 8H, Ar), 8.11 (s, 2H, CH=N). ^{13}C-NMR (CDCl$_3$): 55.59 (CH$_2$), 116.22 (CH$_{Ar}$), 124.10 (CH$_{Ar}$), 133.80 (CH$_{Ar}$), 134.92 (CH$_{Ar}$),

Table 2
Selected bond lengths (Å) and angles (°) for **13**

Bond lengths	
Sn(1)–O(1)	2.007(3)
Sn(1)–O(4)	2.010(3)
Sn(1)–O(3)	2.026(2)
Sn(1)–O(2)	2.029(2)
Sn(1)–N(2)	2.174(3)
Sn(1)–N(1)	2.191(3)
Bond angles	
O(1)–Sn(1)–O(4)	101.60(11)
O(1)–Sn(1)–O(3)	97.34(11)
O(4)–Sn(1)–O(3)	82.43(10)
O(1)–Sn(1)–O(2)	89.77(10)
O(4)–Sn(1)–O(2)	89.14(10)
O(3)–Sn(1)–O(2)	169.90(9)
O(1)–Sn(1)–N(2)	156.70(11)
O(4)–Sn(1)–N(2)	100.52(11)
O(3)–Sn(1)–N(2)	92.72(11)
O(2)–Sn(1)–N(2)	83.33(11)
O(1)–Sn(1)–N(1)	86.46(11)
O(4)–Sn(1)–N(1)	165.81(11)
O(3)–Sn(1)–N(1)	84.99(11)
O(2)–Sn(1)–N(1)	102.68(11)
N(2)–Sn(1)–N(1)	73.50(12)

166.99 (CH=N). ^{119}Sn{^{1}H}-NMR ($CDCl_3$): − 554.7. MS: *m*/*z* 386 $[M]^{\bullet +}$. UV (DMF) λ_{max} 366 nm. IR (KBr, Nujol, cm^{-1}): $\nu_{C=N}$ 1636. Anal. Calc. for $C_{16}H_{14}N_2O_2Sn$: C, 49.92; H, 3.67; N, 7.28. Found: C, 50.12; H, 3.82; N, 7.31%.



Scheme 3.

[[2,2′-[1,2-Ethanediylbis[(nitrilo)-methylidyne]]bis[phenolato]](2-)]-lead(II) (3)

A solution of bis[bis(trimethylsilyl)amino]lead(II) (1.80 g, 3.40 mmol) in 20 ml of pentane was added to a stirred suspension of (Salen)H_2 (0.91 g, 3.40 mmol) in 20 ml of pentane. After stirring for 16 h at r.t., filtration gave **3** (1.46 g, 91%) as a bright yellow powder.

3: m.p. > 300°C (dec.). ^{1}H-NMR (DMSO-d_6): 3.73 (m, 4H, CH_2), 6.44–7.50 (m, 8H, Ar), 8.22 (s, 2H, CH=N). ^{13}C-NMR (DMSO-d_6): 58.88 (CH_2), 96.52 (CH_{Ar}), 96.56 (C_q), 97.52 (C_q), 109.79 (CH_{Ar}), 109.79 (CH_{Ar}), 131.00 (CH_{Ar}), 133.83 (CH_{Ar}), 163.61 (CH=N). UV (DMF) λ_{max} 379 nm. IR (KBr, Nujol, cm^{-1}): $\nu_{C=N}$ 1625. Anal. Calc. for $C_{16}H_{14}N_2O_2Pb$: C, 40.59; H, 2.98; N, 5.92. Found: C, 40.91; H, 3.02; N, 6.11%.

3.5. [[2,2′-[1,2-Cyclohexanediylbis[(nitrilo)-methylidyne]]bis[4,6-bis(1,1-dimethylethyl)phenolato]]-(2-)]-germanium(II) (4)

Using the same procedure as in the preceding preparation, **4** was obtained from $[(Me_3Si)_2N]_2Ge$ (0.36 g, 0.92 mmol) and (BSalch)H_2 (0.50 g, 0.92 mmol). Yield: 0.45 g, 80%.

4: m.p. 180–190°C (dec.). ^{1}H-NMR (C_6D_6): 1.32 (s, 9H, *t*Bu), 1.36 (s, 9H, *t*Bu), 1.38 (s, 9H, *t*Bu), 1.44 (s, 9H, *t*Bu), 1.20–2.10 (m, 8H, CH_2), 2.90–2.98 (m, 2H, CH), 6.92 (m, 2H, Ar), 7.52 (m, 2H, Ar), 7.89 (s, 2H, CH=N). ^{13}C-NMR (C_6D_6): 30.17 (*t*Bu), 31.48 (*t*Bu), 32.47 (*t*Bu), 33.18 (*t*Bu), 72.14 (CH), 118.51 (CH_{Ar}), 126.53 (CH_{Ar}), 136.79 (CH_{Ar}), 140.14 (CH_{Ar}), 158.8 (C_q–O), 166.61 (CH=N). MS: *m*/*z* 618 $[M]^{\bullet +}$. Anal. Calc. for $C_{36}H_{52}GeN_2O_2$: C, 70.03; H, 8.49; N, 4.54. Found: C, 70.23; H, 8.62; N, 4.48%.

3.6. [[2,2′-[1,2-Cyclohexanediylbis[(nitrilo)-methylidyne]]bis[4,6-bis(1,1-dimethylethyl)phenolato]]-(2-)]-tin(II) (5)

$[(Me_3Si)_2N]_2Sn$ (0.24 g, 0.54 mmol) in pentane solution (20 ml) was added to a stirred suspension of (BSalch)H_2 (0.30 g, 0.54 mmol) in 30 ml of pentane. The mixture was stirred at r.t. for 16 h. Filtration afforded **5** as a bright yellow powder, which was washed with pentane and dried in vacuo (0.29 g, 82%).

5: m.p. 230–232°C (dec.). ^{1}H-NMR (C_6D_6): 1.41 (s, 9H, *t*Bu), 1.43 (s, 9H, *t*Bu), 1.85 (s, 9H, *t*Bu), 1.87 (s, 9H, *t*Bu), 1.20–2.05 (m, 8H, CH_2), 2.90–2.98 (m, 2H, CH), 6.96 (m, 2H, Ar), 7.75 (m, 2H, Ar), 7.90 (s, 2H, CH=N). ^{13}C-NMR (C_6D_6): 30.31 (*t*Bu), 30.43 (*t*Bu), 31.79 (*t*Bu), 31.85 (*t*Bu), 63.43 (CH), 66.17 (CH), 117.00 (CH_{Ar}), 117.50 (CH_{Ar}), 136.90 (CH_{Ar}), 142.76 (CH_{Ar}), 162 (C_q–O), 164 (C_q–O), 160.56 (CH=N), 167.20 (CH=N). $^{119}Sn\{^1H\}$-NMR (C_6D_6): − 524.5. MS: *m/z* 664 $[M]^{\bullet +}$. Anal. Calc. for $C_{36}H_{52}N_2O_2Sn$: C, 65.17; H, 7.9; N, 4.22. Found: C, 65.31; H, 8.22; N, 4.12%.

3.7. [[2,2′-[1,2-Cyclohexanediylbis[(nitrilo)-methylidyne]]bis[4,6-bis(1,1-dimethylethyl)phenolato]]-(2-)]-lead(II) (**6**)

Using the same procedure as in the previous preparation, **6** was obtained from $[(Me_3Si)_2N]_2Pb$ (0.23 g, 0.43 mmol) and $(BSalch)H_2$ (0.24 g, 0.43 mmol) as a bright yellow powder (0.29 g, 88%).

6: m.p. 280–290°C (dec.). ^1H-NMR ($CDCl_3$): 1.26 (s, 18H, *t*Bu), 1.48 (s, 18H, *t*Bu), 1.20–2.05 (m, 8H, CH_2), 3.0–3.5 (m, 2H, CH), 6.86 (m, 2H, Ar), 7.48 (m, 2H, Ar), 8.14 (s, 2H, CH=N). ^{13}C-NMR (C_6D_6): 24.77 (CH_2), 25.25 (CH_2), 27.42 (CH_2), 29.95 (*t*Bu), 32.015 (*t*Bu), 33.83 (C_q), 35.53 (C_q), 66.87 (CH), 68.52 (CH), 121.54 (C_q), 127.72 (CH_{Ar}), 128.14 (CH_{Ar}), 128.90 (CH_{Ar}), 142.37 (C_q), 161.06 (CH=N), 167.34 (CH=N). MS: *m/z* 752 $[M]^{\bullet +}$. Anal. Calc. for $C_{36}H_{52}N_2O_2Pb$: C, 57.42; H, 6.97; N, 3.72. Found: C, 57.62; H, 7.13; N, 3.62%.

3.8. [[2,2′-(Methylimino)bis[8-quinolinato]]-(2-)]germanium(II) (**7**)

A pentane solution (20 ml) of $[(Me_3Si)_2N]_2Ge$ (0.25 g, 0.63 mmol) was added to a stirred suspension of $(MeNquin)H_2$ (0.20 g, 0.63 mmol) in 30 ml of pentane. The mixture was stirred at r.t. for 18 h. Filtration and drying in vacuo afforded **7** as a pale yellow powder (0.20 g, 82%).

7: m.p. 265–270°C (dec.). ^1H-NMR ($CDCl_3$): 3.78 (s, 3H, CH_3N), 6.96–7.60 (m, 8H, Ar). MS: *m/z* 389 $[M]^{\bullet +}$. Anal. Calc. for $C_{19}H_{13}GeN_3O_2$: C, 58.61; H, 3.37; N, 10.8. Found C, 58.91; H, 3.53; N, 11.12%.

3.9. [[2,2′-(Methylimino)bis[8-quinolinato]]-(2-)]tin(II) (**8**)

In a similar way, the reaction of $[(Me_3Si)_2N]_2Sn$ (0.26 g, 0.59 mmol) with $(MeNquin)H_2$ (0.19 g, 0.59 mmol) afforded **8** as a bright yellow powder (0.20 g, 78%).

8: m.p. 270–275°C (dec.). ^1H-NMR ($CDCl_3$): 3.80 (s, 3H, CH_3N), 6.90–7.5 (m, 8H, Ar). $^{119}Sn\{^1H\}$-NMR (DMSO-d_6): − 445.8. MS: *m/z* 435 $[M]^{\bullet +}$. Anal. Calc. for $C_{19}H_{13}N_3O_2Sn$: C, 52.58; H, 3.02; N, 9.68. Found: C, 52.81; H, 3.20; N, 9.82%.

3.10. Reaction of **1** with iodine

Iodine (0.12 g, 0.41 mmol) in 20 ml of pentane was added dropwise to a suspension of **1** (0.14 g, 0.41 mmol) in 20 ml of pentane. Immediately, the brown color of the mixture was discharged. The mixture was stirred at r.t. for 2 h. Filtration and drying in vacuo gave **9** as a bright red–orange powder (0.24 g, 92%).

9: m.p. 280–290°C (dec.). ^1H-NMR (DMSO-d_6): 4.23.(s, 4H, CH_2), 6.8–7.7 (m, 8H, Ar), 9.19 (s, 2H, CH=N). ^{13}C-NMR (DMSO-d_6): 50.35 (CH_2), 116.26 (C_q), 120.33 (CH_{Ar}), 120.88 (CH_{Ar}), 135.39 (CH_{Ar}), 138.01 (CH_{Ar}) 161.88 (C_q–O) 171.49 (CH=N). MS: *m/z* 467 $[M-I]^+$. Anal. Calc. for $C_{16}H_{14}GeI_2N_2O_2$: C, 32.42; H, 2.38; N, 4.73. Found: C, 32.53; H, 2.24; N, 4.63%.

3.11. Reaction of **2** with iodine

Using the same procedure as in the preceding preparation, **10** was obtained from **2** (0.25 g, 0.65 mmol) and iodine (0.17 g, 0.65 mmol). Yield: 0.39 g (93%).

10: m.p. 285–290°C (dec.). ^1H-NMR (DMSO-d_6): 4.21.(s, 4H, CH_2), 6.8–7.8 (m, 8H, Ar), 9.03 (s, 2H, CH=N). ^{13}C-NMR (DMSO-d_6) 50.67 (CH_2), 117.48 (C_q), 119.42 (CH_{Ar}), 122.54 (CH_{Ar}), 136.85 (CH_{Ar}), 137.39 (CH_{Ar}) 163.911 (C_q–O) 170.0 (CH=N). $^{119}Sn\{^1H\}$-NMR (DMSO-d_6): − 788.7. MS: *m/z* 513 $[M-I]^+$. Anal. Calc. for $C_{16}H_{14}I_2N_2O_2Sn$: C, 30.01; H, 2.21; N, 4.38. Found C, 30.13; H, 2.41; N, 4.23%.

3.12. Reaction of **3** with iodine

In a similar way, the reaction of **3** (0.16 g, 0.34 mmol) with iodine (0.09 g, 0.35 mmol) in THF, after 72 h of stirring, gave **11** (0.20 g, 80%).

11: m.p. > 300°C (dec.). ^1H-NMR (DMSO-d_6): 3.95 (s, 4H, CH_2), 6.3–7.6 (m, 8H, Ar), 8.46 (s, 2H, CH=N). Anal. Calc. for $C_{16}H_{14}N_2O_2Pb$: C, 26.38; H, 1.94; N, 3.85. Found: C, 26.63; H, 2.12; N, 3.73%.

3.13. Reaction of **1** with 3,5-di-*tert*-butyl-1,2-benzoquinone

A solution of 3,5-di-*tert*-butyl-1,2-benzoquinone (0.07 g, 0.32 mmol) in 20 ml of pentane was added to a stirred suspension of **1** (0.11 g, 0.32 mmol) in 20 ml of pentane. The reaction mixture was stirred at r.t. for 3 h. Filtration, washing with pentane and drying in vacuo gave **12** (0.16 g, 88%) as a pale orange powder.

12: m.p. 230–240°C (dec.). ^1H-NMR ($CDCl_3$): 1.17 (s, 9H, *t*Bu), 1.21 (s, 9H, *t*Bu), 3.42–4.40 (m, 4H, CH_2), 6.51–7.51 (m, 10H, Ar), 8.15 (s, 2H, CH=N). ^{13}C-NMR ($CDCl_3$): 29.87 (*t*Bu), 31.90 (*t*Bu), 51.66 (CH_2), 54.92 (CH_2), 107.62 (CH_{Ar}), 112.11 (CH_{Ar}), 118.90 (CH_{Ar}), 122.25 (CH_{Ar}), 131.91 (CH_{Ar}), 136.00 (CH_{Ar}), 136.81 (CH_{Ar}), 164.03 (C_q–O), 164.84 (C_q–O), 165.93 (CH=N), 169.46 (CH=N). Anal. Calc. for $C_{30}H_{34}GeN_2O_4$: C, 64.44; H, 6.13; N, 5.01. Found: C, 64.65; H, 6.31; N, 4.92%.

3.14. Reaction of **2** with 3,5-di-*tert*-butyl-1,2-benzoquinone

3,5-Di-*tert*-butyl-1,2-benzoquinone (0.12 g, 0.54 mmol) in pentane solution (20 ml) was added dropwise to a stirred suspension of **2** (0.21 g, 0.54 mmol) in 20 ml of pentane. The reaction mixture was stirred at r.t. for 3 h. Filtration, followed by drying in vacuo, gave **13** (0.28 g, 85%) as an orange powder. Slow evaporation of an acetonitrile solution of **13** gave orange crystals of **13**·CH_3CN suitable for X-ray crystallography.

13: m.p. 218–220°C (dec.). ^{1}H-NMR ($CDCl_3$): 1.14 (s, 9H, *t*Bu), 1.21 (s, 9H, *t*Bu), 3.8 (m, 2H, CH_2), 4.3 (m, 2H, CH_2), 6.27 (m, 4H, Ar), 6.55–7.5 (m, 10H, Ar), 8.31 (s, 2H, CH=N). ^{119}Sn{^{1}H}-NMR ($CDCl_3$): − 591.7. MS: *m*/*z* 606 $[M]^{\bullet+}$. Anal. Calc. for $C_{30}H_{34}N_2O_4Sn$: C, 59.53; H, 5.66; N, 4.63. Found: C, 59.73; H, 5.71; N, 4.54%.

3.15. Reaction of **3** with 3,5-di-*tert*-butyl-1,2-benzoquinone

A solution of 3,5-di-*tert*-butyl-1,2-benzoquinone (0.11 g, 0.49 mmol) in 15 ml of THF was added dropwise to a suspension of **3** (0.23 g, 0.49 mmol) in 20 ml of THF. The reaction mixture was stirred at r.t. for 12 h. Filtration and drying in vacuo gave **14** (0.17 g, 89%) as a pale green powder.

14: m.p. > 300°C (dec.). ^{1}H-NMR (DMSO-d_6): 1.06 (s, 9H, *t*Bu), 1.24 (s, 9H, *t*Bu), 3.75 (s, 4H, CH_2), 6.27 (m, 4H, Ar), 6.53 (m, 4H, Ar), 7.04 (m, 2H, Ar), 8.25 (s, 2H, CH=N). Anal. Calc. for $C_{30}H_{34}N_2O_4Pb$: C, 51.93; H, 4.94; N, 4.04. Found: C, 52.02; H, 5.12; N, 3.93%.

3.16. Reaction of **4** with 3,5-di-*tert*-butyl-1,2-benzoquinone

3,5-Di-*tert*-butyl-1,2-benzoquinone (0.04 g, 0.19 mmol) in 10 ml of pentane was added dropwise to a stirred suspension of **4** (0.12 g, 0.19 mmol) in 15 ml of pentane. The mixture was stirred for 2 h. Filtration and drying in vacuo yielded **15** (0.15 g, 92%) as a pale orange powder.

15: m.p. 210–220°C (dec.). ^{1}H-NMR (C_6D_6): 1.25 (s, 9H, *t*Bu), 1.32 (s, 9H, *t*Bu), 1.38 (s, 9H, *t*Bu), 1.52 (s, 9H, *t*Bu), 1.57 (s, 9H, *t*Bu), 1.95 (s, 9H, *t*Bu) 1.20–2.03 (m, 8H, CH_2), 2.95 (m, 2H, CH), 6.82 (m, 1H, Ar), 7.04 (m, 1H, Ar), 7.11 (m, 1H, Ar), 7.16 (m, 1H, Ar), 7.69 (m, 1H, Ar), 7.84 (m, 1H, Ar), 7.90 (s, 2H, CH=N). Anal. Calc. for $C_{50}H_{72}GeN_2O_4$: C, 71.69; H, 8.66; N, 3.34. Found: C, 71.92; H, 8.83; N, 3.25%.

3.17. Reaction of **5** with 3,5-di-*tert*-butyl-1,2-benzoquinone

Using the same procedure as in the previous preparation, **16** was obtained from **5** (0.03 g, 0.04 mmol) and 3,5-di-*tert*-butyl-1,2-benzoquinone (0.01 g, 0.04 mmol). Yield: 0.03 g, 75%.

16: m.p. 220–230°C (dec.).^{1}H-NMR (C_6D_6): 1.26 (s, 9H, *t*Bu), 1.33 (s, 9H, *t*Bu), 1.39 (s, 9H, *t*Bu), 1.53 (s, 9H, *t*Bu), 1.58 (s, 9H, *t*Bu), 1.96 (s, 9H, *t*Bu) 1.20–2.05 (m, 8H, CH_2), 2.94 (m, 2H, CH), 6.86 (m, 1H, Ar), 7.01 (m, 1H, Ar), 7.08 (m, 1H, Ar), 7.14 (m, 1H, Ar), 7.67 (m, 1H, Ar), 7.83 (m, 1H, Ar), 7.88 (s, 2H, CH=N). ^{13}C-NMR (C_6D_6): 22.88 (C_q), 24.02 (C_q), 26.23 (C_q), 27.29 (C_q), 29.78 (C_q), 29,91 (*t*Bu), 30.64 (*t*Bu), 31.57 (*t*Bu), 31.61 (*t*Bu), 32.25 (CH_2), 34.44 (CH_2), 35.24 (CH_2), 61.76 (CH–N), 66.67 (CH–N), 109.92 (CH_{Ar}), 111.34 (CH_{Ar}), 129.66 (CH_{Ar}), 130.97 (CH_{Ar}), 131.56 (CH_{Ar}), 118.16 (Cq_{Ar}), 119.32 (Cq_{Ar}), 133.98 (Cq_{Ar}), 139.78 (Cq_{Ar}), 139.96 (Cq_{Ar}), 143.06 (Cq_{Ar}), 143.16 (Cq_{Ar}), 146.88 (Cq_{Ar}), 150.49 (Cq_{Ar}), 165.39 (Cq_{Ar}), 165.80 (Cq_{Ar}), 166.35 (CH=N), 169.63 (CH=N). ^{119}Sn{^{1}H}-NMR (C_6D_6): − 568.2. MS: *m*/*z* 884 $[M]^{\bullet+}$. Anal. Calc. for $C_{50}H_{72}N_2O_4Sn$: C, 67.95; H, 8.21; N, 3.17. Found: C, 68.12; H, 8.31; N, 2.95%.

3.18. Reaction of **2** with trifluoroacetic acid

To a suspension cooled to − 5°C of **2** (0.045 g, 0.12 mmol) in 5 ml of $CHCl_3$ was added dropwise a solution of acetyl chloride (0.013 g, 0.12 mmol) in $CHCl_3$ (5 ml). After stirring was continued at r.t. for 1 h, analysis of the mixture by ^{1}H-, ^{19}F- and ^{119}Sn-NMR revealed the formation of the heteroleptic stannylene **17**.

17: ^{1}H-NMR ($CDCl_3$): 3.77 (m, 2H, CH_2), 3.92 (m, 2H, CH_2), 6.70–7.34 (m, 8H, Ar), 8.13 (s, 1H, CH=N), 8.34 (s, 1H, CH=N) 13.22 (br, 1H, OH). ^{19}F-NMR ($CDCl_3$): − 0.41. ^{119}Sn{^{1}H}-NMR ($CDCl_3$): − 410.

3.19. Reaction of **2** with trifluoromethanesulfonic acid

Using the same conditions, the reaction of **2** (0.040 g, 0.10 mmol) with trifluoromethanesulfonic acid (0.015 g, 0.10 mmol) afforded **18**, characterized by ^{1}H-, ^{19}F- and ^{119}Sn-NMR.

18: ^{1}H-NMR ($CDCl_3$): 3.79 (m, 2H, CH_2), 3.93 (m, 2H, CH_2), 6.69–7.33 (m, 8H, Ar), 8.12 (s, 1H, CH=N), 8.35 (s, 1H, CH=N) 13.22 (br, 1H, OH).^{13}C-NMR ($CDCl_3$): 59.74 (CH_2), 117.02 (CH_{Ar}), 117.45 (CH_{Ar}), 118.74 (CH_{Ar}), 131.58 (CH_{Ar}), 132.49 (CH_{Ar}), 134.01 (CH_{Ar}), 134.96 (CH_{Ar}), 161.08 (C_q–O), 166.58 (CH=N), 167.48 (CH=N). ^{19}F-NMR ($CDCl_3$): − 3.34. ^{119}Sn{^{1}H}-NMR ($CDCl_3$): − 350.

3.20. Reaction of **2** with acetyl chloride

In a similar way, the reaction of **2** (0.05 g, 0.13 mmol) with trifluoroacetic acid (0.01 g, 0.13 mmol) afforded the corresponding compound **19**, analysed by ^{1}H- and ^{119}Sn-NMR.

19: ^{1}H-NMR (DMSO-d_6): 1.88 (s, 3H, CH_3), 4.21 (s, 4H, CH_2), 6.88–7.63 (m, 8H, Ar), 8.85 (s, 2H, CH=N). ^{119}Sn{^{1}H}-NMR (DMSO-d_6): − 633.6.

*3.21. Reaction of **2** with trichloroacetaldehyde*

Using the same operating conditions as in the previous preparation, addition at − 5°C of trichloroacetaldehyde (0.01 g, 0.10 mmol) on a suspension of **2** (0.03 g, 0.10 mmol) gave the expected product **20** characterized by ^{1}H- and ^{119}Sn-NMR.

20: ^{1}H-NMR ($CDCl_3$): 3.73–4.45 (m, 4H, CH_2), 5.30 (s, 1H, CH), 6.62–7.57 (m, 8H, Ar), 8.21 (s, 1H, CH=N), 8.27 (s, 1H, CH=N). ^{119}Sn{^{1}H}-NMR ($CDCl_3$): − 629.5.

*3.22. Summary of crystal data for **13**·CH_3CN*

$C_{32}H_{37}N_3O_4Sn$, $M = 646.34$, monoclinic, $P2_1/n$, $a = 16.015(2)$, $b = 10.011(1)$, $c = 18.777(2)$ Å, $\beta = 101.70(1)°$, $V = 2947.9(6)$ Å^3, $Z = 4$, ρ_c 1.456 Mg m^{-3}, $F(000) = 1328$, $\lambda = 0.71073$ Å, $T = 193(2)$ K, μ(Mo–K$_\alpha$) = 0.908 mm^{-1}, crystal size 0.6 × 0.5 × 0.3 mm, $2.22° < \Theta < 23.26°$, 29117 reflections (4224 independent, $R_{int} = 0.0429$) were collected at low temperature using an oil-coated shock-cooled crystal [23] on a STOE-IPDS diffractometer. The structure was solved by direct methods (SHELXS-97) [24] and 368 parameters were refined using the least-squares method on F^2 [25]. Largest electron density residue: 0.304 e Å^{-3}, R_1 (for $F > 2\sigma(F)$) = 0.028 and $wR_2 = 0.071$ (all data) with $R_1 = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$ and $wR_2 = (\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2)^{0.5}$.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 134619. Copies of the data can be obtained free of charge from The Director, CCDC, 12 Union Rd., Cambridge, CB2 1EX, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.com.ac.uk).

References

[1] (a) J. Barrau, G. Rima, Coord. Chem. Rev. Part I: 178–180 (1998) 593. (b) W.P. Neumann, Chem. Rev. 91 (1991) 311. (c) M.F. Lappert, R.S. Rowe, Coord. Chem. Rev. 100 (1990) 267. (d) J. Satgé, J. Organomet. Chem. 400 (1990) 121. (e) P. Jutzi, Adv. Organomet. Chem. 26 (1986) 217. (f) W. Petz, Chem. Rev. 86 (1986) 1099. (g) P.P. Gaspar, Silylenes, in: R.A. Moss, M. Jones (Eds.), Reactive Intermediates III, Wiley, New York, 1985, p. 333. (h) J. Satgé, Rev. Silicon, Germanium, Tin Lead Comp. 8 (1985) 291. (i) J. Satgé, Pure Appl. Chem. 56 (1984) 137. (j) M. Veith, O. Recktenwald, Top. Curr. Chem. 104 (1982) 1. (k) P. Rivière, M. Rivière-Baudet, J. Satgé, Compr. Organomet. Chem. 2 (1982) 478. (l) W.P. Neumann, in: M. Gielen, P. Harrison (Eds.), The Stannylene R_2Sn. The Organometallic and Coordination Chemistry of Ge, Sn, and Pb, Freund, Tel Aviv, 1978, p. 51. (m) O.M. Nefedov, S.P. Kolesnikov, A.I. Ioffe, J. Organomet. Chem. Libr. 5 (1977) 181. (n) J. Satgé, M. Massol, P. Rivière, J. Organomet. Chem. 56 (1973) 1.

[2] For structurally characterized compounds for the last 5 years, see for example all and references therein: Ge: (a) W.-P. Leung, L.-H. Weng, W.-H. Kwok, Z.Y. Zhou, Z.Y. Zhang, T.C.W. Mak, Organometallics 18 (1999) 1482. (b) S. Benet, C.J. Cardin, D.J. Cardin, S.P. Constantine, P. Heath, M.G.B. Drew, H. Rashid, S. Teixeira, J.H. Thorpe, A.K. Todd, Organometallics 18 (1999) 389. (c) C.J. Cardin, D.J. Cardin, S.P. Constantine, M.G.B. Drew, H. Rashid, M.A. Convery, D. Frenske, J. Chem. Soc. Dalton Trans. (1998) 2749. (d) T. Hascall, A.L. Rheingold, I. Guzei, G. Parkin, Chem. Commun. (Cambridge) (1998) 101. (e) H. Schmidt, S. Keitemeyer, B. Neumann, H.-G. Stammler, W.W. Schoeller, P. Jutzi, Organometallics 17 (1998) 2149. (f) W.-P. Leung, W.-H. Kwok, L.-H. Weng, L.T.C. Law, Z.Y. Zhou, T.C.W. Mak, J. Chem. Soc. Dalton Trans. (1997) 4301. (g) J.E. Bender, M.M.H. Banaszak, J.W. Kampf, Organometallics 16 (1997) 2743. (h) H. Braunschweig, C. Drost, P.B. Hitchcock, M.F. Lappert, L.J.-M. Piersens, Angew. Chem. Int. Ed. Engl. 36(3) (1997) 261. (i) R.S. Simons, L. Pu, M.M Olmstead, P.P. Power, Organometallics 16 (1997) 1920. (j) G. Ossig, A. Meller, C. Brönneke, O. Müller, M. Schäfer, R. Herbst-Irmer, Organometallics 16 (1997) 2116. (k) H.V.R. Dias, Z. Wang, J. Am. Chem. Soc. 119 (1997) 4650. (l) M. Kira, T. Iwamoto, T. Maruyama, C. Kabuto, H. Sakurai, Organometallics 15 (1996) 3767. (m) P. Jutzi, H. Schmidt, B. Neumann, H.G. Stammler, Organometallics 15 (1996) 741. (n) N. Tokitoh, K. Manmaru, R. Okazaki, Chem. Lett. 9 (1995) 827. (o) N. Tokitoh, K. Manmaru, R. Okazaki, Organometallics 13 (1994) 167. Sn: (a)–(i). (p) B.G. Mc Burnett, A.J. Cowley, Chem. Commun. (Cambridge) (1999) 17. (q) C. Eaborn, P.B. Hitchcock, J.D. Smith, S.E. Szözerli, Organometallics 16 (1997) 5653. (r) C. Drost, P.B. Hitchcock, M.F. Lappert, L.J.-M. Piersens, Chem. Commun. (Cambridge) (1997) 1141. (s) M. Veith, C. Marthur, S. Marthur, V. Huch, Organometallics 16 (1997) 1292. (t) C. Janiak, R. Weinmann, F. Görlitz, Organometallics 16 (1997) 4933. (u) H.V.R Dias, W. Jin, Inorg. Chem. 35 (1996) 6546. (v) K.W. Klinkhammer, W. Schwartz, Angew. Chem. Int. Ed. Engl. 34 (1995) 1334. (w) C.M. Kuchta, G. Parkin, J. Am. Chem. Soc. 116 (1994) 8372. (x) M. Weidenbruch, J. Schlaefke, A. Schäfer, K. Peters, H.G. von Schnering, H. Marsmann, Angew. Chem. Int. Ed. Engl. 33 (1994) 1846. (y) M. Saito, N. Tokitoh, R. Okazaki, J. Am. Chem. Soc. 115 (1993) 2065. (z) D.A. Atwood, V.O. Atwood, A.H. Cowley, J.L. Atwood, E. Roman, Inorg. Chem. 31 (1992) 3871. Pb: (b), (g), (i), (q), (v). (aa) M. Stürmann, W. Saak, M. Weidenbruch, K.W. Klinkhammer, Eur. J. Inorg. Chem. (1999) 579. (ab) W.J. Evans, R.D. Clark, K.J. Forrestal, J.W. Ziller, Organometallics 18 (1999) 2401. (ac) N. Kano, N. Tokitoh, R. Okazaki, Organometallics 17 (1998) 1241. (ad) C.S. Weinert, I.A. Guzei, A.L. Rheingold, L.R. Sita, Organometallics 17 (1998) 498. (ae) M. Stürmann, M. Weidenbruch, K.W. Klinkhammer, F. Lissner, H. Marsmann, Organometallics 17 (1998) 4425. (af) N. Kano, N. Tokitoh, R. Okazaki, Organometallics 16 (1997) 4237. (ag) N. Tokitoh, N. Kano, K. Shibata, R. Okazaki, Organometallics 14 (1995) 3121.

[3] J. Barrau, G. Rima, T. El Amraoui, Organometallics 17 (1998) 607.

[4] J. Barrau, G. Rima, T. El Amraoui, J. Organomet. Chem. 561 (1998) 167.

[5] J. Barrau, G. Rima, T. El Amraoui, J. Organomet. Chem. 570 (1998) 163.

[6] D. Agustin, G. Rima, J. Barrau, Main Group Met. Chem. 20 (1997) 791.

[7] M.D. Hobday, T.D. Smith, Coord. Chem. Rev. 9 (1972) 311 and references therein.

[8] D.A. Atwood, Coord. Chem. Rev. 165 (1997) 267 and references therein.

[9] R.C. Mehrotra, G. Srivastava, B.S. Saraswat, Rev. Si, Ge Pb Pb Compd. 6 (1982) 171.

[10] F. Mucha, U. Böhme, G. Roewer, Chem. Commun. (Cambridge) (1998) 1289.

[11] D.A. Atwood, J.A. Jegier, K.J. Martin, D. Rutherford, J. Organomet. Chem. 503 (1995) C4.

[12] (a) A.M. Van den Bergen, R.J. Cozens, K.S. Murray, J. Chem. Soc. (A) (1970) 3060 and references therein. (b) A.M. Van den Bergen, J.D. Cashion, G.D. Fallon, B.O. West, Aust. J. Chem. 43 (1990) 1559.

[13] B.E. Afilaka, B.N. Ghese, Synth. React. Inorg. Met.-Org. Chem. 20 (1990) 951.

[14] F.P.R. Ewings, P.G. Harrison, A. Mongia, J. Organomet. Chem. 114 (1976) 35.

[15] M.J.S. Gynane, D.H. Harris, M.F. Lappert, P.P. Power, P. Rivière, M. Rivière-Baudet, J. Chem. Soc. Dalton Trans. (1977) 2004.

[16] W. Ando, H. Itoh, T. Tsumuraya, Organometallics 8 (1989) 2759.

[17] S. Kobayashi, S. Iwata, M. Abe, S.-I. Shoda, J. Am. Chem. Soc. 117 (1995) 2187.

[18] S. Kobayashi, S.-I. Shoda, S. Cao, S. Iwata, M. Abe, K. Yajima, K. Yagi, M. Hirashi, J. Macromol. Sci. Pure Appl. Chem. A31 (1994) 1835.

[19] S. Kobayashi, S. Iwata, M. Abe, S.-I. Shoda, J. Am. Chem. Soc. 112 (1990) 1625.

[20] C.E. Holloway, M. Melnik, Main Group Met. Chem. 21 (1998) 371 and references therein.

[21] J.T.B.H. Jastrzebski, G. Van Koten, Adv. Organomet. Chem. 35 (1993) 241 and references therein.

[22] J. Barrau, M. Massol, D. Mesnard, J. Satgé, Recl. Trav. Chim. Pays-Bas 92 (1973) 31.

[23] D. Stalke, Chem. Soc. Chem. Rev. 27 (1998) 171.

[24] G.M. Sheldrick, Acta Crystallogr. Sect. A 46 (1990) 467.

[25] SHELXL-97, Program for Crystal Structure Refinement, G.M. Sheldrick, University of Göttingen, Germany, 1997.