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Monomeric 1,4,2,3,5λ^2-Diazadisilastannolidines and -Plumbolidines

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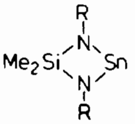
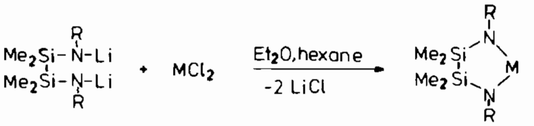
Like many other metal amides [1], tin(II) and lead(II) amides are monomeric in solution and thermally stable if *N*-trimethylsilyl-groups are present [2]. In contrast with non-cyclic derivatives, there are only a few cyclic tin(II) or lead(II) amides which have been characterized unambiguously as monomeric in solution [3]. The crystal structure of compound **1** shows that it can also exist as a monomer in the solid state [4], and it is regarded as a monomer in solution. Considering the rich chemistry of **1** [3a, 5], other cyclic Sn(II)– or Pb(II)–amides are of interest.



1

(R = t-Bu, monomeric in solution [3b])
(R = i-Pr, dimeric in solution [3b])

To our knowledge the ligand –(R)N–SiMe$_2$–SiMe$_2$–N(R)– has not been used for stabilizing carbene analogues or similarly unstable species, although various other heterocyclic compounds are known [6]. The ring strain in 1,4,2,3,5λ^2-diazadisilastannolidines, **2**, or -plumbolidines, **3**, would be reduced with respect to **1**, and organyl groups other than t-Bu might be tolerated without changing the solution structure. In this letter, we report the synthesis of the compounds **2** and **3**, according to eqn. 1.

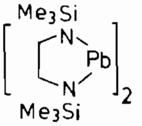


(1)

R	i-Pr	s-Bu	t-Bu		t-Oct	
M	Sn	Sn	Sn	Pb	Sn	Pb
	2a	**2b**	**2c**	**3c**	**2d**	**3d**

The compounds **2d**, **3d** are oily red liquids, **2c**, **3c** are orange crystalline solids, **2b** is an orange liquid and **2a** is a pale yellow solid. They are thermochromic, becoming redder on heating, like other Sn(II) or Pb(II)–amides [2, 3]. Purification by distillation (**2a–c**) (10^{-2}–10^{-3} torr) leads to some decomposition, in particular for **2d** and for the lead compounds **3c, d**. The compounds **2** and **3** are extremely sensitive towards oxygen and moisture; they decompose slowly on standing in daylight and the lead amides react vigorously with CH_2Cl_2. For many purposes the compounds **2** and **3** are sufficiently pure when the reaction solution (eqn. (1)) is filtrated and the solvent is removed.

The monomeric structure of the compounds **2** and **3** can be established by ^{119}Sn and ^{207}Pb NMR spectroscopy [7]. Relevant NMR data are given in Table I. The criterion of ^{119}Sn- and ^{207}Pb-chemical shifts becomes readily apparent, by comparison with δ ^{119}Sn of **2** (R = Et) which is dimeric (δ ^{119}Sn = +208(28 °C), +253(80 °C)) and with δ ^{207}Pb of a dimeric lead(II) amide **4**.



4

δ ^{207}Pb = +403(28 °C)

A detailed discussion of the spectroscopic data (NMR, UPS) of **1**, **2** and noncyclic Sn(II)– and Pb(II)–amides together with molecular orbital calculations will be presented elsewhere.

Experimental

All compounds were handled in a dry N_2 atmosphere. The synthesis of the 1,2-bis(alkylamino)-1,1,2,2-tetramethyldisilanes and the dilithiation has been performed according to the literature [8].

1,4-Dialkyl-2,2,3,3-tetramethyl-1,4,2,3,5λ^2-stannolidines and -plumbolidines

A freshly prepared suspension of the dilithiated bis(amino)disilane (eqn. (1)) (8 mmol) in 50 ml of ether/hexane (1:1) is cooled to −78 °C. After adding $SnCl_2$ (1.5 g, 8 mmol) or $PbCl_2$ (2.22 g, 8 mmol) and warming to room temperature, stirring is continued for 2 h. Hexane and ether are removed *in vacuo*; 20 ml of hexane are added again, and evaporation (*in vacuo*) of the filtrated clear solution leaves the compounds **2** and **3** in >90% yield. Fractional distillation gives pure **2a** (boiling point (b.p.) 71 °C/10^{-2} torr), **2b** (b.p. 76 °C/10^{-2} torr), **2c** (b.p. 70 °C/10^{-2} torr), **3c** (b.p. 89 °C/10^{-3} torr).

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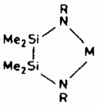
0020-1693/86/$3.50

TABLE I. ^{13}C, ^{29}Si, ^{119}Sn and ^{207}Pb NMR Data[a] of 1,4,2,3,5λ^2-Diazadisilastannolidines (**2**) and -Plumbolidines

	M	R	δ ^{13}C (SiMe)	δ ^{13}C (R)			δ ^{29}Si	δ M[b] (^{119}Sn, ^{207}Pb)
2a	Sn	i-Pr	2.1 (45.0) [9.0]	49.9(CH) [42.3]	32.4(CH_3) [39.9]		–2.6 [n.o.]	+708[c]
2b	Sn	s-Bu[d]	2.1 (47.3)	56.1(CH) [35.4] 30.6(CH_3) [35.4]	38.0(CH_2) [39.4] 12.2(CH_3)		–2.5 [26.3]	+705
2c	Sn	t-Bu	5.4 (44.6) [8.2]	57.7(C) [22.4][e]	38.5(CH_3) [43.7]		–4.4 [21.2]	+760
3c	Pb	t-Bu	9.3 (43.5)	57.5(C) [22.4][e]	40.1(CH_3) [31.0][e]		+7.3 [27.1][e]	+4900
2d	Sn	t-Oct[f]	6.6 (44.6) [8.2]	62.2(C) [20.0] 33.0(C)	64.3(CH_2) [46.5] 32.8(CH_3)	37.7(CH_3) [20.1]	–5.9 [19.4]	+785
3d	Pb	t-Oct[f]	9.6 (43.7)	61.8(C) [15][e] 32.8(C)	64.6(CH_2) [47.4][e] 32.8(CH_3)	40.1(CH_3) [25.5][e]	+4.3 [n.o.][e]	+4930

[a] Bruker WP 200-FT NMR spectrometer in C_6D_6, 27–28 °C, *ca.* 10% *w*/*v*; δ $^{13}C(C_6D_6)$ = 128.0 relative to Me_4Si; δ ^{29}Si, δ ^{119}Sn and δ ^{207}Pb relative to external Me_4Si, Me_4Sn and Me_4Pb, respectively. Coupling constants $^1J(^{29}Si^{13}C)$ in parentheses and $J(M^{13}C)$, $J(M^{29}Si)$ (M = ^{119}Sn, ^{207}Pb) in square brackets. [b] Broad resonances, owing mainly to partially relaxed scalar coupling $^1J(M^{14}N)$; $\Delta\nu 1/2$ (^{119}Sn) *ca.* 400–500 Hz and $\Delta\nu 1/2$ (^{207}Pb) *ca.* 800–1000 Hz. [c] Measured in C_7D_8 at +105 °C; $^1J(^{119}Sn^{14}N)$ = 190 ± 10 Hz. [d] Separate resonances for the two diastereomers (*SS*- and *RS*-configurations) are not resolved. [e] The ^{207}Pb satellites are broadened; this is presumably the result of chemical shift anisotropy (CSA) relaxation of the ^{207}Pb nucleus. [f] t-Oct = $C(CH_3)_2–CH_2–C(CH_3)_3$.

Acknowledgements

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