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Novel triphenyltin substituted derivatives of heavier alkaline earth metals

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Abstract

The synthesis and characterization of a family of novel alkaline earth metal stannides, in addition to tri- and pentastannanes are described. $[Ba(18\text{-crown-}6)(HMPA)_2][SnPh_3]_2$ (**4**), $[Ca(18\text{-crown-}6)(HMPA)_2][Sn(SnPh_3)_3]_2$ (**5**), and $[Sr(18\text{-crown-}6)(HMPA)_2][Sn(SnPh_3)_3]_2$ (**6**) were synthesized by insertion of the corresponding alkaline earth metals into the tin–tin bond of hexaphenyldistannane. $Ph_3SnSnPh_2SnPh_3$ (**7**), and $Sn(SnPh_3)_4$ (**8**) became available by treating **4** with diphenyldichlorostannane. All compounds were studied by NMR spectroscopy, and X-ray crystallography. The stannanes **7** and **8** were also characterized by elemental analysis. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Alkaline earth metal stannides; Stannanes; ^{119}Sn-NMR spectroscopy; Structure elucidation

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1. Introduction

Alkali metal stannides are well established starting materials for tin–element coupling reactions. Accordingly, alkali metal–tin derivatives have received significant attention [1–4]. In contrast, little is known about the corresponding alkaline earth metal derivatives, despite the well documented use of magnesium compounds in Wurtz-type tin chemistry [5,6].

Well characterized alkaline earth metal stannides are to the best of our knowledge limited to $Ca(THF)_4(SnMe_3)_2$ (**1**), synthesized and structurally characterized in 1996 by Westerhausen [7]. Compound **1** became available by treating hexamethyldistannane with elemental calcium Eq. (1).

$$Me_3Sn\text{–}SnMe_3 + Ca \rightarrow \underset{\mathbf{1}}{Ca(THF)_4[SnMe_3]_2} \quad (1)$$

Since magnesium stannides are important intermediates in the formation of silicon-tin moieties [6], and calcium stannides have been shown to be effective polymerization initiators [8], we were interested to explore the chemistry of the heavy alkaline earth metals calcium, strontium, and barium with hexaphenyldistannane. This paper describes the results of this work, including the reaction of the calcium, strontium, and barium stannides with hydrochloric acid and chlorostannanes.

2. Results and discussion

2.1. Synthesis

Alkali and alkaline earth metal stannides can be synthesized by reductive insertion of the alkaline earth metals into the tin–tin bond of hexaorganodistannanes, as shown previously with the synthesis of $Ca(THF)_4(SnMe_3)_2$ [7]. Westerhausen reports extended reaction times (3 days), probably due to the limited calcium surface area in this heterogeneous reaction. Significant reduction of reaction time in this synthetic scheme can be achieved by dissolving the alkaline earth metals and the distannanes in dry, liquid ammonia Eq. (2). The main products in this reaction are alkaline earth metal stannides $M^{II}[SnPh_3]_2$ (**2**–**4**), isolated as colorless solids.

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$$Ph_3Sn\text{–}SnPh_3 + M^{II} \rightarrow M^{II}[SnPh_3]_2 \qquad (2)$$

2, $M^{II} = Ca$; **3**, $M^{II} = Sr$; **4**, $M^{II} = Ba$

Treatment of the crude reaction mixture of the stannides **2**–**4** with a solution of anhydrous HCl in diethylether resulted in the formation of a precipitate containing alkaline earth metal dichlorides, and a solution consisting of various tin derivatives, identified by ^{119}Sn-NMR as Ph_3SnCl (~ 70%), $Ph_3SnSnPh_3$ (~ 25%, unreacted starting material), and trace amounts of $SnPh_4$ Eq. (3).

$$M^{II}(SnPh_3)_2 \xrightarrow[\text{HCL}]{\text{excess}} M^{II}Cl_2 + 2Ph_3SnCl \qquad (3)$$

The formation of the triphenyltinchloride via triphenyltinhydride proves the formation of compounds **2**–**4**.

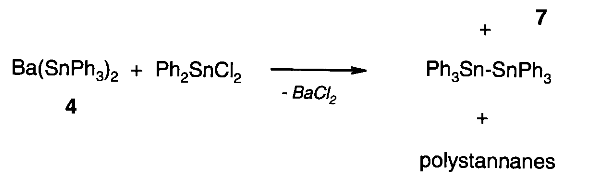
The addition of 18-crown-6 and HMPA (hexamethyl phosphoric triamide) to a DME (dimethoxyethane) solution of barium stannide resulted in the isolation and crystallographic characterization of $[Ba(18\text{-crown-}6)(HMPA)_2][SnPh_3]_2$ (**4**).

Surprisingly, the analogous reaction with calcium and strontium led to the isolation and subsequent crystallographic characterization of the more complex alkaline earth metal stannides $[M^{II}(18\text{-crown-}6)(HMPA)_2][Sn(SnPh_3)_3]_2$ (**5**, $M^{II} = Ca$; **6**, $M^{II} = Sr$), formed concurrently with $SnPh_4$ Eq. (4).

$$M^{II}[SnPh_3]_2 + 6Ph_3Sn - SnPh_3$$
$$\rightarrow M^{II}[Sn(SnPh_3)_3]_2 + 6SnPh_4 \qquad (4)$$

5, $M^{II} = Ca$; **6**, $M^{II} = Sr$

The migration of phenyl and methyl groups in organotin chemistry has been well documented [9]. Examples include the reaction of elemental lithium with $SnPh_4$ in liquid ammonia, yielding $[Li(NH_3)_4][Sn(SnPh_3)_3].C_6H_6$ [4], or the treatment of either **1** [7] or $LiSnMe_3$ [10] with an excess of Sn_2Me_6. Phenyl migration has also been observed in related alkali metal derivatives. Wright et al. report on a triphenyllead derivative which decomposes within 12 h at room temperature [11]. The decomposition pathway seems to involve migration of a phenyl group under formation of $PbPh_4$ and elemental lead. Indeed, if solutions containing compounds **4**–**6** are kept at room temperature, the formation of a black powder, presumably tin, is observed. Colorless crystals obtained from these solutions contained $SnPh_4$.



Scheme 1. Reaction of **4** with diphenyldichlorostannane.

The reaction of **4** with diphenyldichlorostannane resulted in the formation of octaphenyltristannane (**7**), and hexaphenyldistannane (Scheme 1). The two products were separated by crystallization. The presence of $Ph_3SnSnPh_3$ can not only be explained by an incomplete reaction, but also as the result of a transmetallation process, under formation of $Ph_3SnSnPh_3$, $BaCl_2$ and polystannanes (Scheme 1).

Analogously, treatment of **5** or **6** with triphenylchlorostannane results in the formation of tetrakis[triphenylstannyl]stannane (**8**) Eq. (5)

$$M^{II}[Sn(SnPh_3)_3]_2 + 2Ph_3Sn\text{–}Cl \rightarrow \underset{\mathbf{8}}{Sn(SnPh_3)_4} + 2M^{II}Cl_2 \qquad (5)$$

5, $M^{II} = Ca$; **6**, $M^{II} = Sr$

Compounds **7** and **8** were obtained previously by either reacting diphenyldichlorostannane with lithium triphenylstannide; the reaction of lithiumstannides with $SnCl_4$; or treating triphenylchlorostannanes and $SnCl_4$ with elemental lithium. However, no crystallographic data were reported [12,13].

2.2. Structural descriptions/discussions

2.2.1. $[Ba(18\text{-crown-}6)(HMPA)_2][SnPh_3]_2$ (4): compound 4, depicted in Fig. 1, consists of separated cation and anions

The barium atom, located on a center of symmetry, is surrounded by one 18-crown-6 macrocycle, in addition to two HMPA molecules located in trans position to each other, resulting in an overall coordination number at barium of eight. The Ba–O (crown ether) distances range from 2.770(2) to 2.810(1) Å, while Ba–O (HMPA) distances are observed at 2.567(2) Å. The tin atom in the independent $SnPh_3$ anion is pyramidal with a sum of angles at Sn of 290.3°. There is no contact below 5 Å between cation and anions.

The comparison of structural features between **4** and **1**, indicates that both compounds contain triorganotin anions, but compound **1** displays cation-anion contacts, whereas **4** exhibits separated cation and anions. Several factors contribute towards the different ion association in compounds **1** and **4**. In compound **1**, only THF donors are available to saturate the metal center. THF is a relatively weak Lewis base compared to the multidentate crown ether, and the strong donor HMPA. Consequently, the formation of a separated cation in **1**, saturated with only THF is energetically not preferred over donation. In compound **4** however, solvation with the strong donors 18-crown-6 and HMPA is energetically preferred over a presumably weak alkaline earth metal–tin interaction. Another factor favoring the formation of separated rather than contact ions is the sterically more encumbered $[SnPh_3]^-$ in **4**, compared to the smaller $[SnMe_3]^-$ [7].

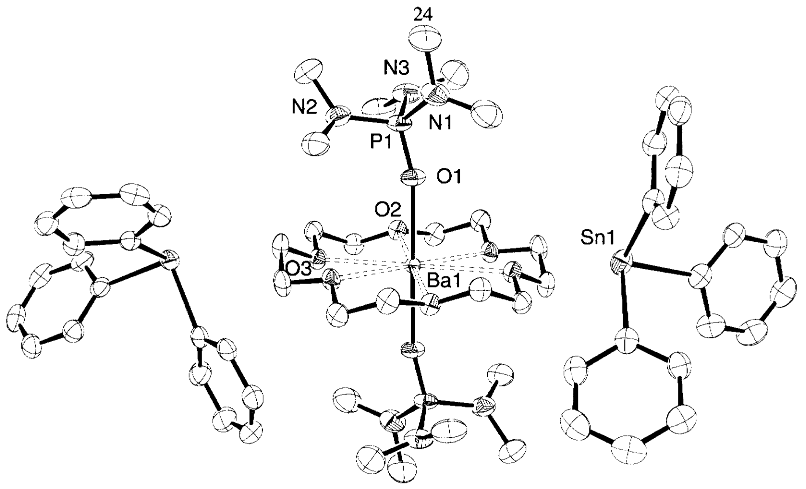


Fig. 1. Crystal structure of **4** with anisotropic displacement parameters depicting 30% probability. The hydrogen atoms have been omitted for clarity.

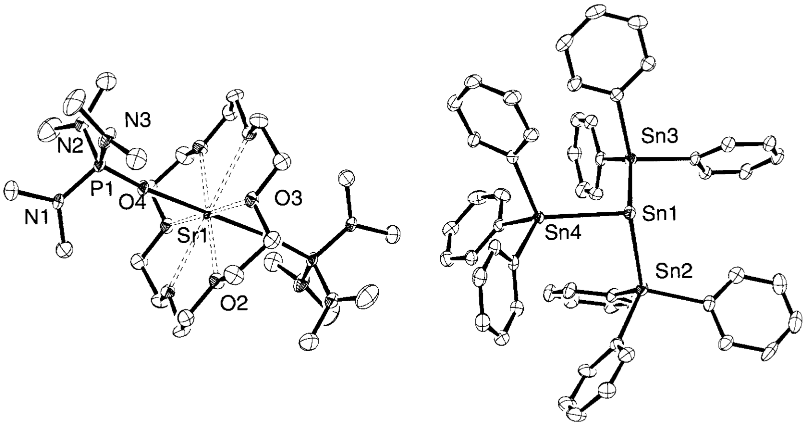


Fig. 2. Crystal structure of **5** with anisotropic displacement parameters depicting 30% probability. The hydrogen atoms have been omitted for clarity.

The $[SnPh_3]^-$ anion (sum of angles 290.3°) exhibits a significant distortion from tetrahedral geometry, closely related to the separated $[K(18\text{-crown-6}][SnPh_3]$ [2b], with a sum of angles at Sn of 291.5°. A similarly narrow angle, was observed for $[K\eta^6(C_6H_5Me)_3\text{-}Sn(CH_2\text{-tBu})_3]$ [14] (average C–Sn–C angles of 91.7°), and $Li(PMDTA)SnPh_3$ [2a] ($PMDTA = (Me_2NCH_2CH_2)_2NMe$) (average C–Sn–C angles of 96.1°). This significant pyramidal geometry in the triorganotin unit, has been explained by a high p-character in the tin-carbon bond, affected by the differences in energy between the s and p orbitals [15]. Consequently, the lone pair, and tin–alkali metal bond possesses high s-character· explaining the similar geometries between the separated and contact species (Table 1).

*2.2.2. $[M^{II}(18\text{-crown-6})(HMPA)_2][Sn(SnPh_3)_3]_2$, **5** ($M^{II}$ = Ca) and, **6** (M^{II} = Sr)*

Compounds **5** and **6** are isomorphous. Accordingly, their structural features are very similar and will be described together. Fig. 2 depicts the complete structure of compound **5**, while Fig. 3 shows one of the stannide anions.

Compounds **5** and **6** display separated ions. The alkaline earth metal cations are surrounded by one 18-crown-6 macrocycle and two HMPA donors, resulting in a coordination number of eight. A center of symmetry at the central metal generates half of the crown ether atoms in addition to the second HMPA donor. Consequently, only one $[Sn(SnPh_3)_3]^-$ anion is contained in each asymmetric unit. Metal–oxygen distances (crown ether) for **5** range from 2.589(4) to 2.735(4) Å, with significantly shorter calcium-oxygen (HMPA) distances (2.243(3) Å). Metal-oxygen (crown ether) interactions for **6** are in the range of 2.668(4)–2.736(4) Å, the Sr–O (HMPA) distances are observed at 2.428(4) Å. The $[Sn(SnPh_3)_3]^-$ anions exhibit central Sn atoms with three Sn–Sn linkages, observed between

Table 1
Selected bond lengths (Å) and angles (°) in compounds **4**–**8**

Compound	Sn–Sn (Å)	Sn–C (Å)	M-donor (Å)	Sn–Sn–Sn (°)	C–Sn–C(°)
4		2.231(3), 2.233(3), 2.240(2)	2.5674(17) [a] 2.7703(15) [b] 2.7785(15) [b] 2.8097(16) [b]		95.08(9), 96.20(9), 98.75(9)
5	2.8202(5), 2.8290(5), 2.8347(5)	2.157(5), 2.160(5), 2.161(5), 2.168(5), 2.173(5), 2.175(5), 2.176(5), 2.181(5), 2.192(5)	2.243(3) [a] 2.589(4) [b] 2.665(3) [b] 2.735(4) [b]	96.456(14) 97.434(14) 96.203(14)	98.8(2), 99.0(2), 100.2(2), 100.5(2), 100.7(2), 104.1(2), 105.8(2), 106.7(2), 106.9(2)
6	2.8108(8), 2.8301(8), 2.8358(8)	2.137(7), 2.146(7), 2.148(7), 2.158(6), 2.159(7), 2.163(6), 2.166(6), 2.173(7), 2.190(7),	2.428(4) [a], 2.668(4) [b] 2.688(4) [b] 2.735(4) [b]	95.71(2), 98.26(2), 98.30(2)	99.7(2), 101.0(2), 101.2(3), 101.4(2), 101.8(2), 103.6(3), 104.5(2), 104.6(3), 105.2(2),
7 [c]	2.7685(2), 2.7719(2), 2.7935 (2), 2.8030(3)	2.141(2), 2.141(3), 2.143(2), 2.145(2), 2.146(3), 2.147(2), 2.147(2), 2.147(3), 2.147(3), 2.148(3), 2.152(2), 2.152(2), 2.152(3), 2.157(2), 2.157(3), 2.163(2),		115.522(8), 117.583(7)	103.94(9), 104.80(10), 105.73(10), 106.05(10), 106.49(9), 106.85(9), 107.44(9), 107.89(10), 108.21(10), 108.70(10), 108.95(10), 109.16(10), 109.55(10), 111.111(10)
8	2.7983(6)	2.147(6)		109.5	107.2(2)

[a] HMPA.
[b] 18-crown-6.
[c] Two independent molecules.

2.8202(5) and 2.8347(5) Å in **5** and 2.8108(8) and 2.8358(8) Å in **6**. The central Sn atoms exhibit pyramidal geometry with angle sums of 290.1(1) (**5**) and 292.3(1)° (**6**).

The cations in compounds **4**–**6** are very similar: in both cases the metal is connected to crown ether and two HMPA donors. The comparison of metal-crown and metal-HMPA bond lengths shows a smooth trend consistent with the increase in the ionic radius (ionic radii CN = 8: Ca 1.26 Å, Sr 1.40 Å, Ba 1.56 Å) [16]. This specific cation coordination has been observed previously in [Sr(18-crown-6)(HMPA)$_2$][SMes*]$_2$ [17], (Mes* = 2,4,6-tBu$_3$C$_6$H$_2$), [Sr(18-crown-6)(HMPA)$_2$][SeMes*]$_2$ [18], and [Ba(18-crown-6)(HMPA)$_2$]-[SeMes*]$_2$ [19], where the strong cation-donor interaction affected the cation and anion separation. The [Sn(SnPh$_3$)$_3$]$^-$ anion has been observed previously as the product of a reaction involving SnPh$_4$ and elemental lithium in liquid ammonia, resulting in [Li(NH$_3$)$_4$][Sn(SnPh$_3$)$_3$] [4], or in the reaction of Ph$_2$SnCl$_2$ with elemental ytterbium, yielding [Yb(-DME)$_3$Cl]$_2$ [Sn(SnPh$_3$)$_3$]$_2$ [3]. Structural features of the lithium and ytterbium derivatives and **5** and **6** compare favorably: Sn–Sn distances in [Li(NH$_3$)$_4$][Sn(SnPh$_3$)$_3$] are observed between 2.817(1) and 2.834(2), with the ytterbium derivative displaying very similar values (**5** 2.8108(8), **6** 2.8358(8) Å). The Sn–Sn distances may also be compared with those in the Zintl ion Sn_4^{2-}. Not surprisingly, the dianion displays slightly longer Sn–Sn distances with an average of 2.96 Å [20]. The sum of tin–tin–tin angles in **5** is 290.09°, and 292.27° for compound **6**. These values agree well with the geometry observed for the tin center in **4**, and the closely related stannide derivatives mentioned above.

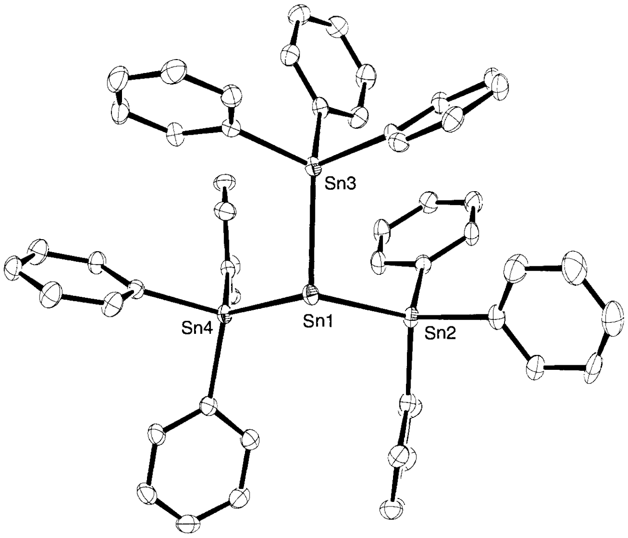


Fig. 3. The stannide anion in **5** illustrating the pyramidal geometry at the central Sn atoms. Anisotropic displacement parameters depict 30% probability. The hydrogen atoms have been omitted for clarity.

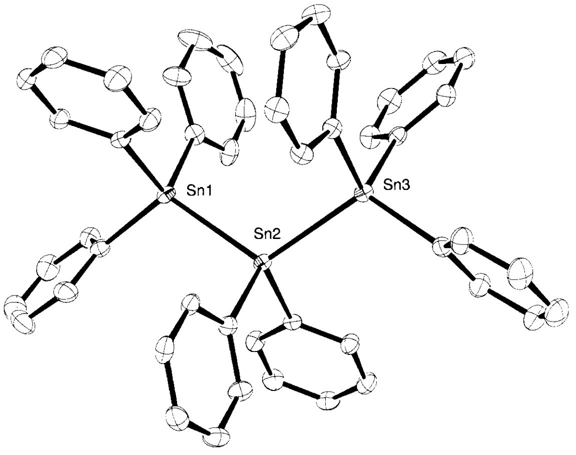


Fig. 4. Crystal structure of **7** with anisotropic displacement parameters depicting 30% probability. The hydrogen atoms have been omitted for clarity. Only one of the two independent molecules is shown.

2.2.3. Ph$_3$SnSnPh$_2$SnPh$_3$ (7)

Compound **7**, depicted in Fig. 4 crystallizes with two independent molecules in the asymmetric unit, of which only one is shown. The central tin backbone consists of three tin atoms, arranged in a zigzag chain. All tin centers are four coordinate: the outer ones with three Sn–Ph and one Sn–Sn contact, the central one with two Sn–Sn bonds and two Sn–Ph interactions. Tin–tin bond lengths are observed between 2.7685(2) and 2.830(3) Å, while tin-carbon distances are found between 2.141(2) and 2.163(2) Å. The tin atoms display approximate tetrahedral geometry with a tin–tin–tin angle of 115.522(8) and 117.583(7)° for the two independent molecules, carbon–tin–carbon angles between 103.94(9) and 111.11(10)°, and carbon-tin–tin angles between 110.59(7) and 115.68(7)°.

2.2.4. Sn(SnPh$_3$)$_4$ (8)

Compound **8**, shown in Fig. 5 crystallizes in the cubic space group P-43n. Only two of the tin atoms, in addition to one phenyl ring are contained in the asymmetric unit. The central tin atom is surrounded in an ideal tetrahedral fashion by four tin atoms, which are ligated by three phenyl groups, resulting in a tetrahedral geometry for all tin atoms. The tin–tin distance is observed at 2.7983(6) Å and the tin-carbon distances are observed at 2.147(6) Å.

2.3. Conclusion

This work was conducted to explore the chemistry of the heavy alkaline earth elements calcium, strontium, and barium in conjunction with stannide anions. Synthetic access to the target molecules was possible by reductive insertion, involving the reaction of the metals with hexaphenyldistannane in liquid ammonia. The major reaction products of these reactions were identified

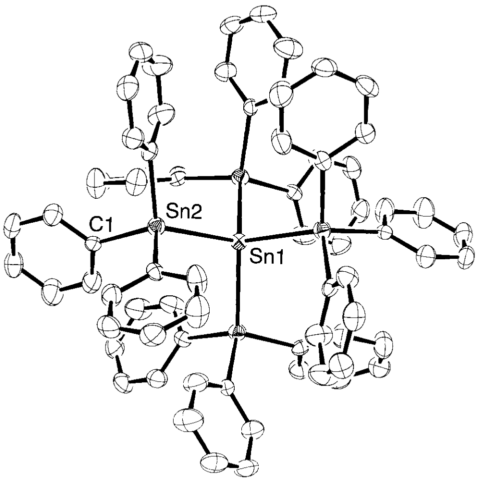


Fig. 5. Crystal structure of **8** with anisotropic displacement parameters depicting 30% probability. The hydrogen atoms have been omitted for clarity.

as $M(SnPh_3)_2$, by quenching the reaction mixture with anhydrous HCl and utilizing ^{119}Sn-NMR spectroscopy. Crystalline samples obtained after the addition of 18-crown-6 and HMPA indicated that phenyl migration had taking place, under formation of the more complex anions $Sn(SnPh_3)_3$ in addition to $SnPh_4$.

3. Experimental

3.1. General procedures

All reactions were performed under a purified nitrogen atmosphere by using modified Schlenk techniques and a Braun Labmaster 100 dry box. Toluene, DME, THF, and Et_2O were distilled just prior to use from a Na/K alloy followed by two freeze-pump-thaw cycles. Anhydrous ammonia (Matheson) was predried over sodium and condensed into the cooled (−78°C, dry ice/acetone) reaction mixtures. Commercially available strontium and barium metals were stored under mineral oil in a dry box, cut into small chunks and the remaining hydrocarbon oil was washed off with dry hexane. Calcium chips were used as received. Hexaphenyldistannane was prepared by published procedures [21]. HMPA was stirred over CaH_2 and distilled prior to use. Commercially available 18-crown-6 was dissolved in freshly distilled diethylether and stirred with finely cut sodium metal for one day. After filtration from excess metal, the crown was recrystallized at −20°C from hexanes and used as isolated. ^{1}H-(300 MHz) and ^{13}C (75 MHz)-NMR were recorded on a Bruker DPX-300 spectrometer. ^{119}Sn-(149.19 MHz) and ^{29}Si-NMR data (79.49 MHz) were collected using Bruker DRX 300 and DPX 400 spectrometers. Elemental analyses were obtained only for the non-metalated compounds, due to the extreme sensitivity of the alkaline earth metal stannides towards hydrolysis. For example, typical working time for mounting crystals was less than 10 min before decomposition occurred, even while the crystals were stored under a heavy hydrocarbon oil.

*3.2. General procedure for the synthesis of the alkaline earth metal stannides **2–6***

The synthetic procedures for compounds **4**, **5** and **6** were very similar. In the dry box Schlenk tubes were charged with either 0.3 g Ca (7.5 mmol), 0.3 g Sr (3.4 mmol) or 0.4 g Ba (3.0 mmol) and 0.7 g $(SnPh_3)_2$ (1 mmol). To these solids, 50 ml THF was added. The resulting mixtures were cooled to −78°C utilizing an acetone/dry-ice bath, whereupon approximately 10 ml of pre-dried liquid ammonia was condensed onto the reaction mixtures. The mixtures were refluxed for 6 h at −33°C (boiling point ammonia), where upon the initial blue color of the solution (unreacted metal in liquid NH_3), changed into a light gray, and then into reddish brown. After 6 h the solutions were gently warmed to room temperature upon which the ammonia evaporated. The remaining solvents were removed in vacuum, and the resulting light gray powder dissolved in a solution consisting of 60 ml dimethoxyethane (DME), 0.26 g 18-crown-6 (1.5 mmol) and 5 ml HMPA. The resulting solution was heated to a boil, and filtered hot through a Celite padded filter frit, resulting in a clear, pale green solution.

*3.2.1. Isolation of **4**, **5** and **6***

After storage of the solutions for a few days at −20°C colorless crystals, suitable for X-ray crystallography formed. ^{1}H-NMR for **4** (300.13 MHz, δ [ppm]): 2.60 (d, 36 H^3, $J_{PH} = 9.1$ Hz), 3.58 (24 H), 6.85 (dd, 12 H), 6.98 (t, 6 H), 7.21 (d, 12 H^1, $J_{Sn\text{-}H} = 40/38$ Hz). ^{119}Sn-NMR for **4** (111.90 MHz, δ [ppm]): −98.4. ^{1}H-NMR for **5** (300.13 MHz, δ [ppm]): 2.59 (d, 36 H^3, $J_{PH} = 9.2$ Hz), 3.48 (24 H), 7.02 (dd, 12 H), 7.49 (t, 6 H), 7.25 (d, 12 H^1, $J_{Sn\text{-}H} = 40/38$ Hz). ^{1}H-NMR for **6** (300.13 MHz, δ [ppm]): 2.65 (d, 36 H^3, $J_{PH} = 9.5$ Hz), 3.56 (24 H), 6.86 (dd, 12 H), 6.99 (t, 6 H), 7.21 (d, 12 H^1, $J_{Sn\text{-}H} = 41/39$ Hz).

Due to the very low solubility of **5** and **6** no ^{119}Sn-NMR data are available. Reliable elemental analyses could not be obtained, even when glove-box handling was attempted, due to the high moisture and oxygen sensitivity of all compounds reported. This is a well known problem in alkaline earth metal chemistry [22].

3.2.2. Reaction with HCl

The reactions described above were repeated, as described above, but after evaporation of the NH_3 at room temperature, the solution was quenched with 5 ml of a 1N HCl solution in diethylether, followed by

Table 2
Crystallographic data for compounds **4**–**8** [a]

Compound	**4**	**5**	**6**	**7**	**8**
Empirical formula	$C_{60}H_{90}BaN_6O_8P_2Sn_2$	$C_{132}H_{150}CaN_6O_8P_2Sn_8$	$C_{132}H_{150}N_6O_8P_2Sn_8Sr$	$C_{96}H_{80}Sn_6$	$C_{90}H_{96}Sn_5$
Formula weight	1460.04	3000.12	3047.66	1945.74	1771.12
Crystal shape	Colorless plate	Colorless plate	Colorless plate	Colorless block	Colorless cube
Crystal size (mm)	0.68 × 0.40 × 0.10	0.45 × 0.20 × 0.05	0.30 × 0.20 × 0.05	0.70 × 0.64 × 0.50	0.50 × 0.50 × 0.50
a (Å)	14.2205(2)	14.6442(5)	14.675(2)	10.2373(1)	15.5070(1)
b (Å)0	10.8190(1)	14.8981(5)	14.755(2)	19.6400(1)	
c (Å)	22.3361(2)	15.3800(6)	16.000(3)	22.0183(3)	
α (°)		98.589(1)	107.516(3)	76.389(1)	
β (°)	98.175(1)	100.570(1)	98.427(4)	79.238(1)	
γ (°)		94.254(1)	95.716(3)	74.988(1)	
V (Å^3)	3401.52(6)	3243.7(2)	3229.9(9)	4118.37(7)	3728.92(4)
Z	2	1	1	2	2
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	P-43n
D_{calc} (g cm^{-3})	1.426	1.536	1.567	1.569	1.577
Lin. abs. coeff. (mm^{-1})	1.400	1.633	2.009	1.836	1.697
Radiation	Mo–K$_\alpha$	Mo–K$_\alpha$	Mo–K$_\alpha$	Mo–K$_\alpha$	Mo–K$_\alpha$
T (K)	150	150	150	150	150
2θ Range (°)	3–57	3–57	3–57	2–57	3–57
Independent reflections (R_{int})	8050 (0.0143)	14453 (0.0394)	14274 (0.0559)	18346 (0.0153)	1548 (0.0268)
Parameters	359	736	710	920	66
R_1, wR_2 (all data)	0.0307, 0.0682	0.0800, 0.1118	0.1242, 0.1019	0.0340, 0.0557	0.0540, 0.1055
R_1, wR_2 (>2σ)	0.0278, 0.0668	0.0482, 0.0995	0.0678, 0.0877	0.0257, 0.0521	0.0476, 0.1016

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $wR_2 = \sqrt{\Sigma w\{(F_o)^2-(F_c)^2\}^2/\Sigma w\{(F_o)^2\}^2}$, $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $wR = \sqrt{\Sigma w||F_o|-|F_c||^2/\Sigma|F_o|^2}$.

removal of the volatiles in vacuum. The resulting solids were dissolved in diethylether, and filtered with the aid of a Celite padded filter frit, resulting in a clear pale yellow solution. The diethylether was removed, and the remaining solids examined by ^{119}Sn-NMR spectroscopy. ^{119}Sn-NMR (ppm): Ph_3SnCl (~ 70%, − 48.5 ppm), $Ph_3SnSnPh_3$ (25%, − 144.1 ppm), Ph_4Sn (~ 2–3%, − 128.4 ppm) and small unidentified signals at − 132.5 and 138.4 ppm.

3.3. $Ph_3Sn–SnPh_2–SnPh_3$ (*7*)

A solution comprised of 0.086 g Ph_2SnCl_2 (0.25 mmol) in 25 ml THF was added dropwise to a cooled solution (− 60°C) of 0.37 g of **4** (0.25 mmol) dissolved in 50 ml THF. The resulting mixture was stirred for 4 h and then gently warmed to room temperature. The solvent was removed in vacuum and 100 ml of diethylether/*n*-hexane (1:1) were added. The mixture was filtered (G3) followed by removal of the solvent in vacuum. Colorless crystals were obtained from a 1:1 mixture of toluene and diethylether after storage for a few days at − 20°C. The colorless crystals are composed of a mixture of **7** and **8**, accordingly, no sharp melting point is observed (range 140–180°C). Compounds **7** and **8** can be manually separated under the microscope. **7**: M.p. 208–212°C. Elemental analysis: Anal. Found (calc.) C 60.1(59.3) H 3.95(4.18) ^{119}Sn-NMR: − 138.1 ppm ($SnPh_3$); − 230.7 ppm ($SnPh_2$); $^1J_{^{119}Sn-^{119/117}Sn} = 2875/2745$ cps; $^2J_{^{119}Sn-^{117}Sn} = 705$ cps.

3.4. $Sn(SnPh_3)_4$ (*8*)

Compound **8** can be synthesized in pure form by adding a solution containing 0.019 g Ph_3SnCl (0.05 mmol) dissolved in 25 ml THF dropwise to a cooled solution (− 60°C) of 0.15 g of **5** (0.05 mmol) in 50 ml THF. The reaction mixture was stirred for 4 h and then allowed to warm to room temperature. The solvent was removed in vacuum and 100 ml of diethylether/*n*-hexane (1:1) were added. The mixture was filtered (G3) and the solvent removed in vacuum. The resulting solid residue was recrystallized from a 1:1 mixture of toluene and diethylether. **8**: M.p. 302–308°C. Elemental analysis: Anal. Found (calc.) C 57.7(56.9) H 4.25(3.98). ^{119}Sn-NMR: − 135.51 ppm ($SnPh_3$); − 1092.4 ppm (Sn).

3.5. X-ray crystallographic studies

X-ray quality crystals for all compounds were grown as described in the experimental section. The crystals were removed from the Schlenk tube under a stream of N_2 and immediately covered with a layer of viscous hydrocarbon oil (Paratone N, Exxon). A suitable crystal was selected with the aid of a microscope, attached to a glass fiber, and immediately placed in the low temperature N_2 stream of the diffractometer [23]. Intensity data sets for all compounds were collected utilizing a Siemens SMART system, complete with 3-circle goniometer and CCD detector operating at −54°C. Each data set was collected at −123°C using a Cryojet low temperature device from Oxford Instruments and by employing graphite monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å). The data collections nominally covered a hemisphere of reciprocal space utilizing a combination of three groups of exposures, each with a different angle and each exposure covering 0.3° in ω. Crystal decay was monitored by repeating a set of initial frames at the end of the data collection and comparing the duplicate reflections, whereby no decay was observed for all compounds reported. An absorption correction was applied utilizing the program SADABS [24]. The crystal structures of all compounds were solved by Direct Methods, as included in the SHELXTL program package [25]. Missing atoms were located in subsequent difference Fourier maps and included in the refinement. The structures were refined by full-matrix least-squares refinement on F^2 (SHELXTL-93) [25]. Hydrogen atoms were placed geometrically and refined using a riding model, including free rotation of methyl groups. All compounds were refined with U_{iso} constrained at 1.2 (for non-methyl groups), and 1.5 (for methyl groups) times U_{eq} of the carrier C atom. The crystallographic programs used for structure refinement and solution were installed on a PC clone or a Silicon Graphics Indigo^2 R10000 High Impact. Scattering factors were those provided by the SHELX program [26]. All non-hydrogen atoms, with the exception of some disordered or restrained positions were refined anisotropically Table 2.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 137 003 for compound **4**, No. 137 004 for compound **5**, No. 137 005 for compound **6**, No. 137 006 for compound **7**, and No. 137 007 for compound **8**. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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