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ARTICLE

Novel amino propyl substituted organo tin compounds

Johann Pichler, Ana Torvisco, Patrick Bottke, Martin Wilkening, and Frank Uhlig

Abstract: In this work, a new synthetic pathway yielding unprotected amino propyl tin compounds is described. For this purpose, mono stannanes with different substitution patterns are used. In a first step, tin hydrides are deprotonated using lithium diisopropyl amide and mixed with an electrophile containing a protected amine in the ω-position. After deprotection via acidic hydrolysis, the desired amino propyl tin compounds are obtained in high yield and purity. The thermal reaction behavior of the amino propyl tin hydrohalide intermediates containing one aromatic residue at the central tin atom is also investigated. For this purpose, amino propyl tin hydrohalides are heated under vacuum until the aromatic hydrocarbon is liberated. This thermal treatment leads to so far unknown tin halides containing an amino propyl side chain. For all of these substances detailed liquid ^{1}H, ^{13}C, and ^{119}Sn-nuclear magnetic resonance (NMR) data were obtained, and in one case solid state NMR is also conducted. Regarding solids, single crystal X-ray analysis is performed. Some derivatization reactions with these new substances are demonstrated, especially the synthesis of an amino propyl tin carboxylate, which might be very interesting for biological, pharmaceutical, or technical processes.

Key words: organotin, aminopropyl, protecting group, monostannane, solution and solid sate solid-state NMR study.

Résumé : Cette étude décrit une nouvelle voie de synthèse conduisant à la formation de composés d'aminopropylétain non protégés. On utilise pour cela des monostannanes selon différents modes de substitution. Dans un premier temps, ces hydrures d'étain sont déprotonés au moyen du diisopropylamidure de lithium et mélangés avec un électrophile comportant une amine protégée en position ω. Après déprotection par hydrolyse acide, les composés d'aminopropylétain désirés sont obtenus avec un rendement et une pureté élevés. Le comportement thermoréactif des hydrohalogénures d'aminopropylétain intermédiaires, qui contiennent un résidu aromatique situé sur l'atome d'étain central, a été également étudié. Pour cela, les hydrohalogénures d'aminopropylétain sont chauffés sous vide jusqu'à ce que l'hydrocarbure aromatique soit libéré. Ce traitement thermique conduit à la formation d'halogénures d'étain, inconnus jusqu'à aujourd'hui, comportant une chaîne latérale aminopropylique. Pour toutes ces substances, des données détaillées ont été obtenus par résonnance magnétique nucléaire (RMN) ^{1}H, ^{13}C et ^{119}Sn, en phase liquide. Une analyse par RMN à l'état solide a été également réalisée pour l'une des substances étudiées. Dans le cas de solides, une analyse par cristallographie aux rayons X a été effectuée. Certaines réactions de dérivatisation avec ces nouvelles substances sont mises en évidence, en particulier la synthèse d'un carboxylate d'aminopropylétain dont l'application à des procédés biologiques, pharmaceutiques ou techniques pourrait s'avérer intéressante. [Traduit par la Rédaction]

Mots-clés : organoétain, aminopropyle, groupe protecteur, monostannane, étude par RMN en solution et à l'état solide.

Introduction

In organosilicon chemistry, compounds with amino propyl groups are very well known (e.g., AMMO (3-(trimethoxysilyl)propane-1-amine), AMEO (3-(triethoxysilyl)propane-1-amine), AAMS (*N*-(2-aminoethyl)-3-aminopropyltrimethoxysilane)). They are commonly used for so-called silyl-terminated polyurethanes (STPU) in modern construction.[1–9] However, much less is known about compounds that involve the heavier group 14 elements. For this reason, we decided to investigate organo-tin compounds containing amino propyl groups. These types of substances should provide new applications in polymer science, catalysis, and biological activity. The first attempts to synthesize such compounds were made in 1955 by Gilman, who described the synthesis of triphenyl-γ-*N*,*N*-diethylaminopropyltin.[10] Twenty years later, a *N*,*N*-dimethylamino derivative was synthesized by Lequan.[11] Van der Kerk succeeded in the synthesis of triphenylaminopropyltin as the first real amino propyl compound, also checking for antifungal properties of this substance.[12,13] Using an electrochemical procedure, Smith was able to show that hexakis(γ-aminopropyl)ditin and tetrakis(γ-aminopropyl)tin as fully aminopropylated derivatives were accessible in 1967.[14,15] In 1979, Weichmann described the synthesis and derivatization of amino ethyltin compounds.[16] Different aryl and alkyl substituents on the tin atom were used, and also typical derivatization reactions with the amino nitrogen were demonstrated. However, no further investigations were performed on any of these compounds. This is perhaps due to the drawbacks of the synthetic procedures used so far. The compounds synthesized by Gilman, Lequan, and later on also by Jurkschat and co-workers[17] were made via simple salt-elimination reactions, but it was impossible to remove the substituents from the nitrogen afterwards, and thus no further reactions were possible, with the exception of quarternization,[10] salt-formation,[18] and possibly oxidation leading to *N*-oxides. Van der Kerk established a hydrostannylation reaction with unsaturated hydrocarbons to form the tin carbon bond.[12] Unfortunately, this reaction gives different regioisomers of the desired product, and in addition only activated double bonds (e.g., acrylnitrile, allylacetate) tend to react with the Sn–H

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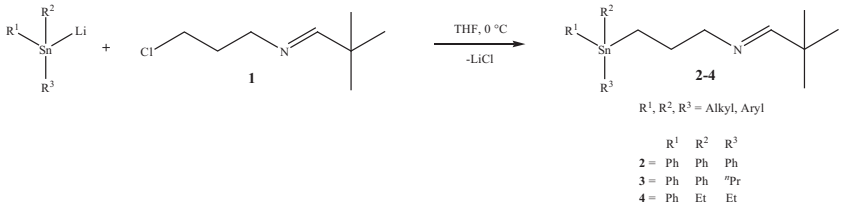
Scheme 1. Alkylation of (*E*)-*N*-(3-chloropropyl)-2,2-dimethylpropan-1-imine (**1**) with lithium stannides.



moiety, as shown by our own experiments[19] as well as by Pham.[20] The electrochemical approach of Smith leads to product mixtures and only persubstituted tin compounds, which are also not desirable since introduction of other substituents at the tin atom is difficult.[15] Finally, the C_2-spacer in Weichmann's procedure[16] tends to undergo Grob-fragmentation[21] even at low temperatures, thus the practical use of these compounds is limited. Therefore, we decided to investigate a new approach for the synthesis of such amino propyl tin compounds. We also studied the thermochemical properties of our compounds in comparison with those of Weichmann.[16] Finally, we also demonstrate some derivatization reactions on these new substances.

Results and discussion

For the synthesis of the desired amino propyltin compound (**2–4**) using our procedure, the nucleophilic tin species needs to be generated first. Different procedures for the generation of nucelophilic tin species are given in the literature. In the simplest case, triorganotin halides are treated with alkali metals[22] in ethereal solvents or hexaorgano-distannanes with alkali metals,[23] or organo lithium reagents[23] in ethers. This strategy usually requires reaction times up to 48 h with reflux. In many cases, naphthalene is needed as a catalyst in amounts up to 10 mol%. If different substituents are present at the tin atom, these harsh conditions and long reaction times lead to product mixtures via exchange reactions of the organic residues at the tin atoms.[24] In fact, only in the case of Ph_6Sn_2 is this reaction suitable for the generation of anionic tin species, since the reaction proceeds within 4 h without any catalyst and gives only one product instead of inseparable product mixtures. In contrast to the aforementioned procedure, the deprotonation of tin hydrides is an alternative route. Since pure tin hydrides can easily be synthesized[25,26] and the deprotonation reaction is a very fast reaction, product mixtures can be avoided. For this task, different reagents are mentioned in the literature and mostly all strong bases can be used.[27–29] However, lithium diisopropyl amide (LDA) was shown to be the reagent of choice for this reaction, since it is commercially available, easy to handle, and leads to excellent stannide yields even in cases where other reagents failed completely.[30,31] Tin hydrides (**16–18**) treated with LDA at 0 °C give yellow to red solutions of the desired anion. These solutions are stable at this temperature for several hours. To avoid side reactions, the solutions are used immediately after preparation. The stannide solution is then added to the electrophile, which already contains the amino group synthon (Scheme 1).

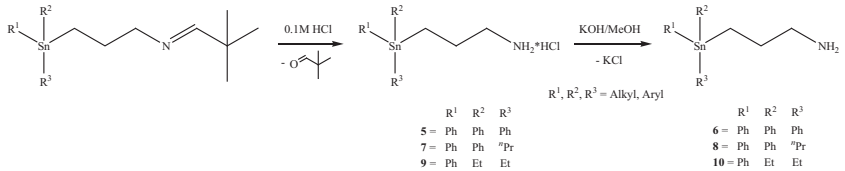
Since the commercially available α,ω-chloroaminopropyl hydrochloride contains active hydrogen, a protection group is necessary to avoid unwanted side reactions. Unfortunately, protection groups for amino groups, which are commonly used in organic chemistry, cannot be used in this case,[32] since, most likely, the reaction conditions for the deprotection step would also break the tin–carbon bonds within the molecule. Therefore, we introduced the imino derivative **1**, which enables us to synthesize our target compounds in very high yields. Compound **1** is completely stable under the basic conditions of the coupling reaction with the tin anion. Thus, neither elimination reactions at the chlorine carbon nor nucleophilic attack at the carbonyl analog imino carbon was detected, and only the desired salt elimination occurs, leading to usually pure products according to ^{1}H-NMR in yields >90%, without any purification steps being necessary. The crucial step of deprotection was easily achieved by using diluted aqueous solutions of HCl in equimolar amounts. By doing so, the imine is hydrolyzed, and the liberated aldehyde was removed together with the water under vacuum. The labile Sn–C bond remains untouched under these conditions and leads to an almost quantitative transformation into the corresponding aminopropyltin hydrochlorides, which can be isolated as an oily liquid (**9**) or amorphous solids (**5**, **7**). However, if concentrated HCl is used for the deprotection reaction chlorination at the tin atom also occurs. As the final step, the aminopropyltin compound is liberated from its hydrochloride by subsequent treatment with an equimolar amount of KOH in MeOH, followed be evaporation of the solvent and extraction of the product with CH_2Cl_2 (Scheme 2).

According to ^{1}H-NMR, the yields of clean product (**6, 8, 10**) are again almost quantitative, which can be easily accomplished by recrystallization or distillation if necessary. Weichmann[16] reported that heating of his aminoethyltin hydrohalides leads to the liberation of ethane and the nitrogen residue via a Grob type fragmentation[21] (Scheme 3) instead of a the expected protodearylation reaction at the tin atom.

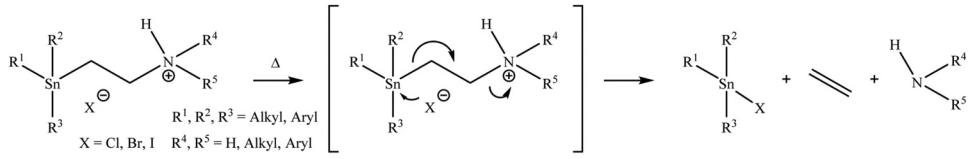
For this reason we also investigated the thermal reactivity of the aminopropyltin hydrohalides. Hydrochloride (**11**), -bromide (**12**), and -iodide (**13**) derivatives of **10** were synthesized by aqueous hydrolysis of **4** with the desired aqueous hydrohalide acid. The diethylphenyl substitution pattern was chosen to suppress rearrangement reactions as well as oligo substitution at the tin atom, so that in an ideal case only Grob fragmentation and (or) protodearylation of the phenyl group could occur (Scheme 4).

Initially, compound **4** was treated with diluted HCl to yield the corresponding hydrochloride **9**. TGA/DSC/MS measurements were conducted on this substance to examine its thermal stability and to detect possible reaction products. According to these measurements, an exothermic decomposition reaction takes place between 120 and 150 °C, which is in the same region as stated in Weichmann's paper,[16] but in contrast to his findings, in our case benzene is liberated leading to 3-(chlorodiethylstannyl)propan-1-amine (**11**). To prove these findings, the thermal treatment of **9** was repeated in a preparative scale. In this case, the hydrochloride **9** was placed in a Schlenk tube equipped with a reflux condenser. While heating under vacuum, benzene was eliminated first, and the product distilled into the condenser at ~250 °C where it solidified. The solid residue was then recrystallized out of benzene to yield pure **11**. In the same way, the bromo- and iodo-derivatives (**12** and **13**) were also synthesized but without isolation of the hydrohalide intermediate. Compound **11** was converted by a salt metathesis into the fluoro-derivative **14** via reaction with KF in THF/acetone and into the corresponding acetate **15** with sodium acetate in methanol. However, for the synthesis of **14**, the addition of acetone in this Finkelstein type reaction could not be avoided, thus leading to formation of the corresponding acetone ketimine as a major side product (~40% according to ^{19}F-NMR) and lowering the yield of the whole reaction compared with the synthesis of (**15**). We tried to perform single crystal analysis on all

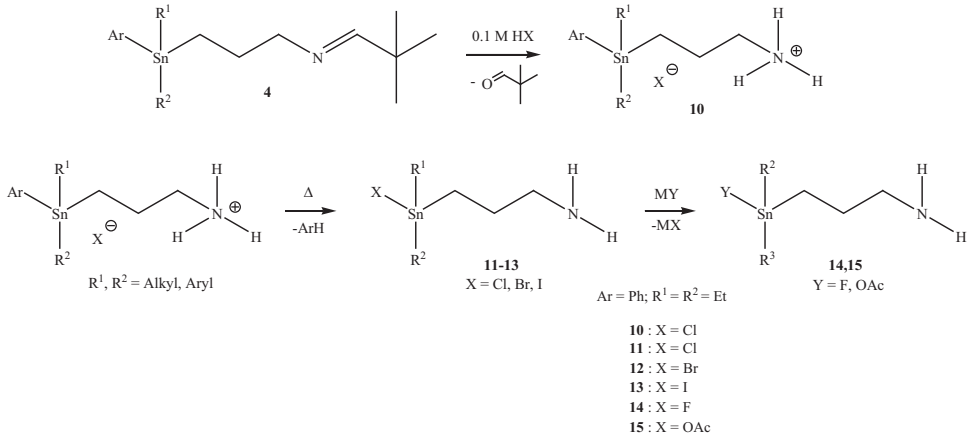
Scheme 2. Deprotection of aminopropyltin compounds via acidic hydrolysis.



Scheme 3. Grob fragmentation of aminoethyltin hydrochloride compounds.



Scheme 4. Thermally induced protodearylation of aminopropyltin hydrohalides and substitution reactions.



solid products in this investigation. However, in the case of the synthesized hydrohalides, it was not possible to grow suitable crystals even after several attempts of recrystallization. For the other solid compounds (**6, 11–15**), full X-ray data are provided. We also succeeded in the crystallization and mounting of the low melting point starting material triphenylstannane (**16**) (Fig. 1) as a rare example of a crystalline stannane.

In fact there are only two other examples known in the literature, both reported by our group. For **16**, the hydrogen at the tin atom was located in the difference map, and thus we are able to provide the first experimental Sn–H bond length (1.13(5) Å) measurement for monostannanes. However, it is not possible to compare the Sn–H bond length of **16** with the only other known tin monohydrides. In the case of 2,6-xylyl$_3$SnH,[34] the Sn–H was not reliably located in the difference map, which is a common problem with light atoms (hydrogen) located next to heavy atoms because of their poor scattering abilities. For mesityl$_2$SnH$_2$,[33] which is a dihydride, Sn–H bonds are in the average of 1.669(2) Å. The solid structure of **16** also shows interesting secondary interactions between a hydrogen atom of one aromatic ring forming an edge to face interaction (2.778 Å) with one of the phenyl substituents, and the hydrogen at the tin atom interacting with the aromatic π-system (3.092 Å) of a neighboring molecule (Fig. 1). In the crystal structure of **6** (Fig. 2), the tin atom in this case is in a tetrahedral environment. However, the tetrahedra is slightly distorted, and a weak dative interaction between the nitrogen lone pair and the central tin atom takes place (Fig. 2). The distance between Sn and N (2.740(1) Å) is longer than the sum of the ionic radii[35] but still within the sum of the van der Waals radii.[36] No secondary interactions or supramolecular structure motifs are observed for this substance. After exchange of one organic residue with an electronegative substituent, the environment around the tin atom changes dramatically. Also in Fig. 2, the iodo compound **13** is shown as a demonstrating example for comparison. For all the similar derivatives (**11–15**) stated in this paper, important bond lengths and angles can be found in Table 2.

In all these cases, the central tin atom is surrounded by a trigonal-bipyramidal environment with the electronegative substituents in apical positions. Interestingly, the Sn–N bond distances are of similar lengths (Table 2). The shortest Sn–N bond length is found in the iodo compound **13** with 2.330(3) Å, while the longest is 2.397(2) Å for the acetate **15**. For the halogen substituents (F, Cl, Br, I), the Sn–X bond length increases as the size of the halogen atom increases. The shortest bond length is found for fluoride **14** with 2.108(1) Å compared with 3.060(3) Å for the iodide **13**. Within this homologous row, the compounds crystallize in a different manner. Fluoride **14** and chloride **11**, as well as the acetate **15**, are found in a $P2_1/n$ space group in the monoclinic crystal lattice, whereas bromide **12** and iodide **13** are in the *Pbca* space group in the orthorhombic crystal lattice (Table 1). This might be due to two different supramolecular structures found for these substances. With the most electronegative elements (F, O, Cl), compared to Br and I, a different polymeric structure is formed by H-X interactions. For the first case, the supramolecular lattice of the chloro compound **11** is shown as an example and the iodo derivative **13** for the second case (Fig. 3).

In comparison to the 3-(halodiphenylstannyl)-*N*,*N*-dimethylpropan-1-amine compounds published by the group of Jurkschat,[16] all Sn–N distances are approximately 0.22 Å shorter, and the Sn–X distance 0.15 Å longer for our compounds, but the same trends are displayed. However, compared to 3-(iododimethylstannyl)-*N*,*N*-dimethylpropan-1-amine synthesized by Han, Sn–N (2.38(1) Å)

Fig. 1. Molecular structure of triphenylstannane (16) and its secondary H-π interactions in solid state (30% ellipsoids).

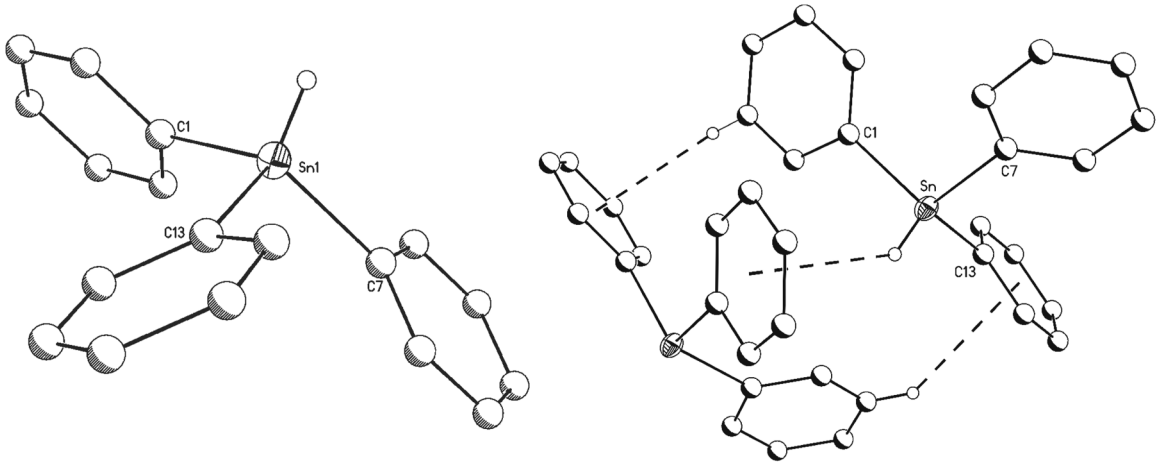


Fig. 2. Molecular structure of triphenylaminopopyltin (6) and of 3-(diethyiodolstannyl)propan-1-amine (13) (30% ellipsoids).

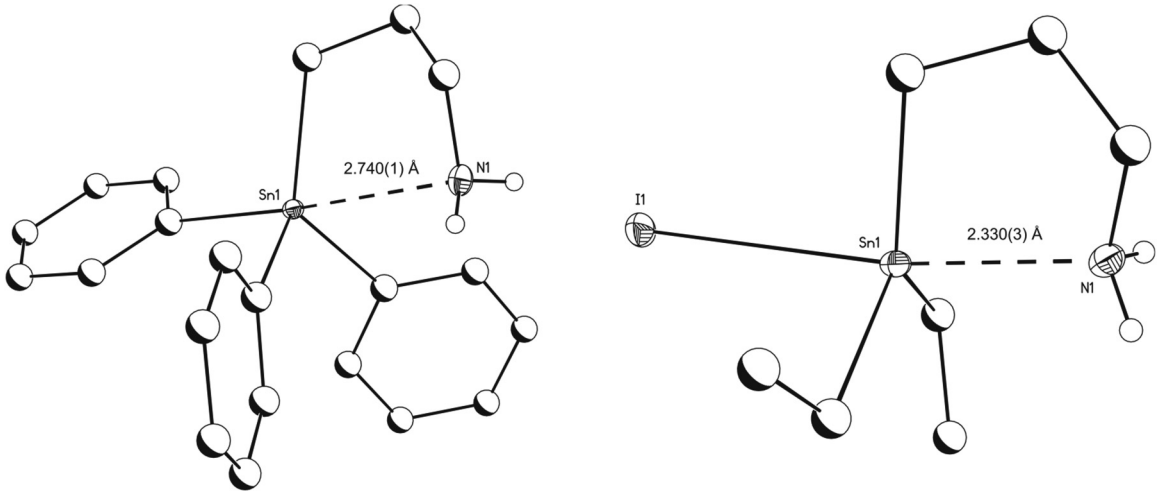


Table 1. Crystallographic data and details of measurements for compounds **6**, **11–16**.

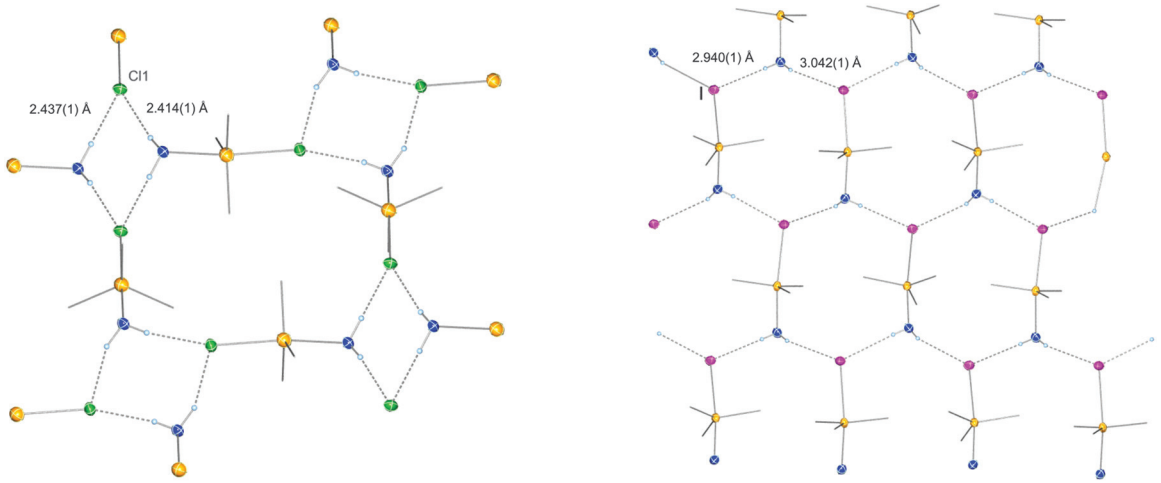
Compound	Ph_3SnH (**16**)	Ph_3SnA (**6**)	Et_2SnAF (**14**)	Et_2SnACl (**11**)	Et_2SnABr (**12**)	Et_2SnAI (**13**)	$Et_2SnAacetate$ (**15**)
Formula	$C_{18}H_{16}Sn$	$C_{21}H_{23}NSn$	$C_7H_{18}FNSn$	$C_7H_{18}ClNSn$	$C_7H_{18}BrNSn$	$C_7H_{18}INSn$	$C_9H_{21}NO_2Sn$
Fw (g mol^{-1})	351.00	408.09	253.91	270.36	314.82	361.81	293.96
a (Å)	10.2387(9)	7.9511(7)	8.3288(3)	8.0696(3)	12.4587(6)	12.6749(4)	7.7714(4)
b (Å)	17.0950(16)	7.7836(7)	11.1680(4)	12.6624(5)	12.3707(6)	13.3911(4)	13.4517(6)
c (Å)	8.6077(9)	14.6823(13)	10.9091(4)	11.1410(4)	14.1833(6)	13.7536(4)	11.9859(5)
α (°)	90	90	90	90	90	90	90
β (°)	99.248(5)	90.503(3)	103.136(1)	103.395(2)	90	90	101.381(2)
γ (°)	90	90	90	90	90	90	90
V (Å^3)	1487.0(2)	908.63(14)	988.17 (6)	1107.42(7)	2185.97(18)	2334.41(12)	1228.35(10)
Z	4	2	4	4	8	8	4
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic	Monoclinic
Space group	$P2_1/c$	$P2_1$	$P2_1/n$	$P2_1/n$	*Pbca*	*Pbca*	$P2_1/n$
d_{calc} (mg/m^3)	1.568	1.492	1.707	1.622	1.913	2.059	1.590
μ (mm^{-1})	1.70	1.41	2.54	2.49	5.94	4.78	2.06
T (K)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
2θ range (°)	2.0–25.0	2.6–28.3	2.7–27.1	2.5–36.8	2.7–27.1	2.7–28.3	3.1–27.1
Independent reflns	2619	4189	2169	1947	1921	2907	2702
No. of params	176	219	101	101	101	101	129
F(000)	696	412	504	536	1216	1360	592
R_{int}	0.089	0.023	0.018	0.069	0.024	0.031	0.022
R_1, wR_2 (all data)	0.0536, 0.1327	0.0206, 0.0393	0.0174, 0.0370	0.0308, 0.1132	0.0223, 0.0506	0.0231, 0.0532	0.0245, 0.0434
R_1, wR_2 (>2σ)	0.0475, 0.1236	0.0196, 0.0385	0.0148, 0.0353	0.0296, 0.1087	0.0212, 0.0500	0.0218, 0.0524	0.0189, 0.0415

Note: Mo Kα (λ = 0.71073 Å). $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_d|$; $wR_2 = [\Sigma_w(F_o^2 - F_2^2)^2/\Sigma_w(F_o^2)^2]^{1/2}$.

Table 2. Selected bond lengths and angles.

	Sn–$C_{(Ph)}$	Sn–$C_{(Et)}$	Sn–$C_{(amine)}$	Sn–X	Sn–N	N–H···X	N–Sn–X	N–Sn–$C_{(amine)}$	X–Sn–$C_{(amine)}$
Ph_3SnH (**16**)	2.144(4)								
$Ph_3Sn[(CH_2)_3NH_2]$ (**6**)	2.151(3) 2.194(3)$_{trans\ to\ the\ amine}$		2.145(3)		2.740(1)		175.81(11)	73.76(3)	
$Et_2Sn[(CH_2)_3NH_2]F$ (**14**)		2.144(2)	2.153(2)	2.108(1)	2.387(1)	2.027(2) 1.975(2)	170.59(11)	79.28(3)	91.38(2)
$Et_2Sn[(CH_2)_3NH_2]Cl$ (**11**)		2.149(3)	2.146(2)	2.623(1)	2.339(2)	2.414(1) 2.437(1)	170.30(11)	79.49(3)	90.81(2)
$Et_2Sn[(CH_2)_3NH_2]Br$ (**12**)		2.175(3)	2.151(3)	2.796(4)	2.347(3)	2.776(1) 2.853(1)	172.27(11)	79.89(3)	92.47(2)
$Et_2Sn[(CH_2)_3NH_2]I$ (**13**)		2.185(3)	2.152(3)	3.060(3)	2.330(3)	2.940(1) 3.042(1)	171.80(2)	80.43(3)	91.63(2)
$Et_2Sn[(CH_2)_3NH_2]$Acetate (**15**)		2.147(2)	2.150(2)	2.027(1)	2.397(2)	2.160(1) 2.332(1)	173.76(11)	78.88(3)	95.67(2)

Fig. 3. Supramolecular network formed by the fluoro (**14**) and chloro (**11**) (shown) derivatives as well as by the bromo (**12**) and iodo (**13**) (shown) derivatives respectively (30% ellipsoids). Values shown in Å.



as well as Sn–I (3.0567(6) Å) bond lengths are of the same length as in our compounds.[37] Along with Han,[37] we also observe a bond length longer than the sum of the ionic radii,[35] however this is only observed for iodo compound **13**. The other derivatives show shorter bond lengths. The large difference compared to Jurkschat's compounds might be an electronic effect of the aromatic rings at the tin atom. However, supramolecular structures were not mentioned.[16] This suggests that the ability for the formation of hydrogen bonds is very important for the properties of this certain type of molecule, at least in the solid state. With the fluoro-derivative **14** in hand, we also performed solid state ^{119}Sn and $^{119}Sn\{^{19}F\}$ CP MAS NMR experiments (Fig. 4) to eventually gain some insight into the bonding nature between the tin and the halogen atom in our compounds. With a $^1J(^{119}Sn\text{-}^{19}F)$ coupling constant of 1920 Hz, no tremendous change is observed compared to the coupling constant of 2069 Hz in a $CDCl_3$ solution.

This suggests that at least the fluoro compound **14** is not present as an ionic compound, neither in the solid state nor in an apolar solution. Larger differences are observed for the chemical shifts than for the coupling constants. For ^{119}Sn with –34.8 ppm (solution) versus 74.2 ppm (s-st), a downfield shift is observed in the solid state. In the case of ^{19}F, an even larger downfield shift from –175.0 ppm in solution to 21.2 ppm in the solid state occurs. The large difference for the fluorine shifts, in particular, might be caused by the formation of the hydrogen bond network in the solid state, as shown by X-ray structure analysis (Fig. 3), an effect which should not be present in solution. Solution ^{119}Sn NMR data of the different halogenides (**11–14**) shows an unusual, narrow shift range of ~10 ppm starting at –25.5 ppm and ending at –34.8 ppm [Cl(–25.5) ~ Br(–25.9) > I(–30.7) > F(–34.8)]. In comparable compounds without donor atoms, a larger difference in the chemical shift is observed as well as a strong low-field shift. As an example, NMR data for the *n*-Bu_3SnX is given (X=Cl, Br, I) as follows: [Cl(152.0) > Br(138.5) > I(89.9)].[38] For X=F no solution NMR data is available due to insolubility. Additional NMR experiments on our compounds are currently ongoing. Defined amounts of donor molecules (e.g., THF, pyridine, HMPA) are added to the NMR solutions of **11,** and the changes in the NMR shifts as well as in the coupling constants are investigated and also VT-NMR studies conducted. The results will be published elsewhere.

Conclusion

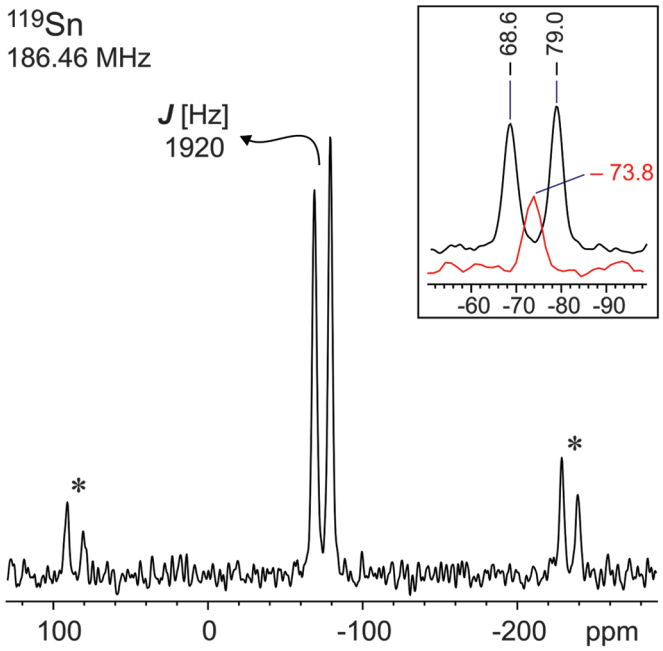
We were able to introduce a new versatile route to aminopropyl tin compounds in very good yields. We also first synthesized aminopropyl tin halides with acidic hydrogens present at the nitrogen atom via a so far unknown thermally induced proto dearylation reaction of aminopropyl tin hydrohalides. It was also possible to transform these compounds into the fluoride and acetate. For all of these substances a full set of NMR data and in the case of solid products also X-ray structures were obtained showing interesting structural properties differing form the so far literature known *N*,*N*-dimethylaminopropyl tin derivatives.

Experimental

Materials and methods

All moisture and air sensitive reactions were carried out under inert atmosphere using Schlenk techniques unless otherwise

Fig. 4. Solid-state ^{119}Sn MAS NMR spectrum of compound 14, which was recorded at a spinning speed of 30 kHz with the bearing gas at ambient temperature. Asterisks indicate spinning side bands. The magnification in the upper right corner includes the ^{119}Sn {^{19}F} CP MAS experiment (red), which proves that the coupling constant *J* [kHz] = 1.8 of the doublet in the Hahn-echo experiment [τ = 4 (131 μs @ 30 kHz)] (black) is a result of the ^{119}Sn - ^{19}F coupling. Please see the online version for colour.



stated. Nitrogen was used as inert gas and passed through molecular sieve of 4 Å and P_5O_{10} with moisture indicator (Sicapent® by Merck) to remove trace water. Solvents were stored over a drying agent (LAH in case of THF, P_5O_{10} for CH_2Cl_2, and $(MeO)_2Mg$ for methanol) under N_2 and distilled prior to use or taken directly from an Innovative Technology® solvent drying system (benzene, heptane). $CDCl_3$ was distilled over P_5O_{10} and stored under N_2. C_6D_6 was distilled over sodium and stored over a potassium mirror under N_2. All chemicals were used as received from various chemical suppliers without any further purification. Tin monohydrides (**16–18**) were synthesized from the corresponding tin chlorides according to the preparation method of Finholt,[25,26] using lithium aluminum hydride (LAH) in Et_2O. These tin chlorides were easily accessible with different aromatic and aliphatic substituents via various literature procedures. Kocheskov redistribution,[39] as well as hydro dearylation with HCl, and subsequent treatment with organometallic reagents (e.g., Grignard or organolithium reagents) yields the desired substitution patterns in the starting materials. However the synthesis of these substances is not stated in this paper and only spectroscopic data for the tin hydrides is provided. TGA/DSC/MS measurements were conducted on a TG-DSC STA 409 TASC 414/3C/3/F connected to a QMS 403 C by a capillary coupling (both by NETZSCH). Samples were measured in an Al crucible on a Pt sample carrier RG-2 in a temperature range of 35 °C to 540 °C with a ramp of 10 K/min under a He flow of 200 mL/min as inert gas. The following m/z values were tracked during the experiment: 2, 12, 14, 15, 16, 17, 18, 26, 30, 35, 38, 41, 44, 51, 59, 77, 78, 119. All elemental analyses were performed on a Heraeus VARIO ELEMENTAR EL analyzer. Melting points were determined with a STUART SCIENTIFIC SMP 10, no temperature corrections were applied.

NMR Spectroscopy

Solution ^{1}H (300.22 MHz), ^{13}C (75.50 MHz), and ^{119}Sn (111.92 MHz) NMR spectra were recorded on a Mercury 300 MHz spectrometer from Varian at 25 °C. Chemical shifts are given in parts per million (ppm) relative to TMS (δ = 0 ppm) regarding ^{13}C and ^{1}H, and relative to $SnMe_4$ in the case of ^{119}Sn. Coupling constants (*J*) are reported in Hertz (Hz). All NMR measurements were taken in $CDCl_3$, with exception of tin hydrides that were measured in C_6D_6 to avoid chlorination of the tin atom. For complete peak assignment, multinuclear NMR experiments were also carried out (H,H-COSY and C,H-HETCOR). Solid state high-resolution, i.e., magic angle spinning (MAS), ^{19}F and ^{119}Sn-NMR spectra were acquired using an Avance III NMR spectrometer (Bruker BioSpin) connected to a cryomagnet with a nominal field of 11.7 T. This resulted in resonance frequencies of 186.5 MHz for ^{119}Sn and 470.4 MHz for ^{19}F, respectively. A standard (double-resonance) 2.5 mm probe (Bruker), which can be operated at spinning speeds of up to 30 kHz, was used for the experiments. ^{119}Sn MAS NMR spectra were referenced to solid SnO_2, which shows its resonance signal at −604.3 ppm relative to the primary reference $SnMe_4$ (0 ppm). The spectra were recorded using a rotor-synchronized Hahn-echo pulse sequence (π/2-τ-π-τ-acquire; τ denotes the rotor period) and a standard cross-polarization (CP) pulse sequence, respectively. ^{119}Sn{^{19}F} CP MAS NMR was used with a flip-back pulse on the ^{19}F spins following data acquisition. Recycling delays of 600 s for the Hahn-echo experiment and 360 s for the CP experiment were used. The sample under investigation was used to set the Hartman–Hahn match under MAS conditions with the match optimized for a 30 kHz spinning speed. Processing of the data was carried out using TopSpin 3.1 software (Bruker) and MestReNova7 (Mestrelab research).

Crystal structure determination

All crystals suitable for single crystal X-ray diffractometry were removed from a Schlenk flask under a stream of N_2 and immediately covered with a layer of silicone oil. A single crystal was selected, mounted on a glass rod on a copper pin, and placed in the cold N_2 stream provided by an Oxford Cryosystems cryometer. XRD data collection was performed on a Bruker Apex II diffractometer with use of Mo Kα radiation (λ = 0.71073 Å) and a CCD area detector. Empirical absorption corrections were applied using SADABS.[40] The structures were solved with use of either direct methods or the Patterson option in SHELXS and refined by the full-matrix least-squares procedures in SHELXL.[41,42] Non-hydrogen atoms were refined anisotropically. Hydrogen atoms bonded to N1 for all compounds were located in a difference map and in some instances refined with distance restraints (SADI). Other hydrogen atoms were located in calculated positions corresponding to standard bond lengths and angles. In compound **16**, the hydrogen atom next to the heavy atom Sn was found on the difference Fourier map, however it should be noted that a common problem exists with locating light atoms (hydrogen) next to heavy atoms because of their poor scattering abilities. Multiple attempts to model disorder for the ethyl substituents in compound **12** resulted in unstable refinements. However the residual electron density was well below acceptable values. Compound **6** was twinned and was refined using the TWIN option in SHELXL, and the matrix (1 0 0 0 −1 0 0 0 −1 4) was applied. The contributions of the three twin components refined to 0.300(2)/0.857(2)/0.552(2).

(*E*)-*N*-(3-chloropropyl)-2,2-dimethylpropan-1-imine 1

In a 500 mL round-bottomed flask attached to a Dean–Stark trap and a N_2 supply, 3-chloropropan-1-amine hydrochloride (13 g, 0.10 mol/L, 1.0 equiv.), 2,2-dimethylpropanal (8.6 g, 0.10 mol/L, 1.0 equiv.), and KOH (5.6 g, 0.10 mol/L, 1.0 equiv.) were suspended in 250 mL of benzene. The suspension was heated under reflux until no more H_2O was generated. The solvent was distilled off under atmospheric pressure. Fractionation over a 20 cm Vigreux-collum under reduced pressure afforded (*E*)-*N*-(3-chloropropyl)-2,2-

dimethylpropan-1-imine (**1**) as colorless liquid (9.4 g, 58%). B.p.: 60 °C at 12 mbar (1 bar = 100 kPa). The product is stored under N_2 at –18 °C. ^{1}H-NMR δ: 7.48 (t, 1H, ^4J = 2.5, N = C*H*); 3.44 (t, 2H, ^3J = 12.9, CH_2CH_2Cl); 3.41 (td; 2H, ^3J = 14.1, CH_2N); 1.96 (p, 2H, $CH_2CH_2CH_2$); 0.98 (s, 9H, CH_3). ^{13}C-NMR δ: 173.3 (N = *C*H); 57.6 (N-*C*H_2); 42.6 (Cl-*C*H_2); 36.3 (*C* quart.); 33.2 ($CH_2CH_2CH_2$); 27.0 (3C, *C*H_3). Elemental analysis (calcd.): C: 58.2% (59.4%); H: 9.6% (10.0%); N: 8.9% (8.7%).

General procedure for alkylation of tin hydrides

A Schlenk tube is charged with LDA (2.3 g, 1.05 equiv.) dissolved in 50 mL THF. The desired tin hydride (20 mmol/L, 1.0 equiv.) was added dropwise at 0 °C under vigorous stirring. The slightly orange to red solution was stirred for another 5 min. In a second Schlenk tube electrophile (**1**) (3.2 g, 1.0 equiv.) was diluted in 25 mL THF and cooled to 0 °C. The freshly prepared stannide solution is then cannulaed dropwise on the electrophile solution under vigorous stirring. The cooling bath is removed and the solution is allowed to stir for an additional 10 min at RT. The solvent is then removed under reduced pressure, the residue suspended in 20 mL CH_2Cl_2 and stirred for 10 min at RT. The mixture is filtered through Celite®, washed 2 times with 10 mL CH_2Cl_2 and then the solvent pumped down again. The product is dried under oil vacuum at 50 °C for 2 h. The resulting colorless to slightly orange-red imines are oily liquids and usually pure according to ^{1}H-NMR but might be distilled under oil-vacuum if necessary.

(E)-2,2-dimethyl-N-(3-(triphenylstannyl)propyl)propan-1-imine 2

Slightly yellow oil. Yield: 94.3%. ^{1}H-NMR δ: 7.50–7.41 (m, 6H, *o*-Ph); 7.30 (s, 1H, N=C*H*); 7.29–7.23 (m, 9H, *m*,*p*-Ph); 3.29 (t, 2H, C*H*$_2$N); 1.91 (p, 2H, $CH_2CH_2CH_2$); 1.37 (t, 2H, C*H*$_2$Sn); 0.95 (s, 9H, C*H*$_3$). ^{13}C-NMR δ: 172.3 (N=*C*H); 138.8 (3C, ^1J(^{119}Sn-^{13}C) = 487, ^1J(^{117}Sn-^{13}C) = 465, *i*-Ph); 137.0 (6C, ^2J(^{119}Sn-^{13}C) = 36, ^2J(^{117}Sn-^{13}C) = 35, *o*-Ph); 128.8 (3C, ^4J($^{119/117}$Sn-^{13}C) = 11, *p*-Ph); 128.4 (6C, ^3J(^{119}Sn-^{13}C) = 49, ^3J(^{117}Sn-^{13}C) = 47, *m*-Ph); 64.7 (^3J(^{119}Sn-^{13}C) = 68, ^3J(^{117}Sn-^{13}C) = 65, N-*C*H_2); 35.9 (C-quart.); 27.7 (^2J($^{119/117}$Sn-^{13}C) = 19, $CH_2CH_2CH_2$); 27.0 (3C, *C*H_3); 8.1 (^1J(^{119}Sn-^{13}C) = 395, ^1J(^{117}Sn-^{13}C) = 377), *C*H_2Sn). ^{119}Sn-NMR δ: –99.5. Elemental analysis (calcd.): C: 65.5% (65.6%); H: 6.5% (6.6%); N: 3.0% (2.9%).

(E)-N-(3-(diphenyl(propyl)stannyl)propyl)-2,2-dimethylpropan-1-imine 3

Slightly orange oil. Yield: 91.3% ^{1}H-NMR δ: 7.63–7.54 (m, 4H, *o*-Ph); 7.51 (s, 1H, N=*CH*); 7.46–7.31 (m, 6H, *m*,*p*-Ph); 3.46 (t, 2H, C*H*$_2$N); 2.08–1.90 (m, 2H, $CH_2CH_2CH_2N$); 1.86–1.64 (m, 2H, $CH_2CH_2CH_3$); 1.45–1.20 (m, 4H, aliphatic); 1.14 (s, 9H, methyl); 1.09 (t, 3H, methyl). ^{13}C-NMR δ: 171.9 (N=*C*H); 140.0 (2C, *i*-Ph); 136.7 (4C, *o*-Ph); 128.3 (2C, *p*-Ph); 128.1 (4C, *m*-Ph); 64.8 (N-*C*H_2); 35.8 (C-quart.); 27.7 ($CH_2CH_2CH_2N$); 26.9 (3C, *C*H_3); 20.1 ($CH_2CH_2CH_3$); 18.8 ($CH_2CH_2CH_3$); 13.0 ($CH_2CH_2CH_3$); 7.4 ($CH_2CH_2CH_2N$). ^{119}Sn-NMR δ: –73.1.

(E)-N-(3-(diethyl(phenyl)stannyl)propyl)-2,2-dimethylpropan-1-imine 4

Colorless oil. Yield: 92.5% ^{1}H-NMR δ: 7.40–7.33 (m, 3H, *o*-Ph, N=C*H*); 7.28–7.16 (m, 3H, *m*,*p*-Ph); 3.26 (t, 2H, C*H*$_2$N); 1.82–1.65 (m, 2H, $CH_2CH_2CH_2N$); 1.32–0.75 (m, 21H, aliphatic). ^{13}C-NMR δ: 172.0 (N=*C*H); 141.1 (*i*-Ph); 136.5 (2C, *o*-Ph); 128.0 (*p*-Ph); 128.0 (2C, *m*-Ph); 65.1 (N-*C*H_2); 35.9 (C-quart.); 27.9 ($CH_2CH_2CH_2N$); 27.0 (3C, *C*H_3); 10.9 (2C, *C*H_2CH_3); 5.9 (*C*$H_2CH_2CH_2N$); 1.1 (2C, CH_2CH_3). ^{119}Sn-NMR δ: –34.3.

General procedure for hydrolysis of aminopropyl tin imines

A 250 mL round-bottomed flask is charged with the desired imine (10 mmol/L, 1.0 equiv.) and 50 mL THF. 1.0 equiv. of 0.1 N aqueous HX (X=Cl, Br, I) is added under stirring. The resulting milky suspension is completely evaporated on the rotavap at 50 °C. The resulting colorless to slightly orange amino-hydrochlorides are dissolved in 50 mL MeOH containing 1.0 equiv. KOH. MeOH is removed on the rotavap, the residue suspended in 20 mL CH_2Cl_2, filtered, and the solution evaporated again. The resulting colorless to slightly orange-red amines are dried in oil-vacuum at 50 °C for 2 h. They are usually pure according to ^{1}H-NMR but might be distilled under vacuum if necessary.

3-(Triphenylstannyl)propan-1-amine hydrochloride 5

Amorphous white solid. Yield: 95.4%. M.p.: 162–163 °C (dec.). ^{1}H-NMR δ: 8.60–7.85 (s, 3H, $CH_2N^+H_3$); 7.65–7.43 (m, 5H, *o*-Ph); 7.42–7.25 (m, 10H, *m*,*p*-Ph); 2.86 (t, 2H, C*H*$_2$N); 2.10 (p, 2H, $CH_2CH_2CH_2$); 1.46 (t, 2H, C*H*$_2$Sn) ^{13}C-NMR δ: 137.7 (3C, ^1J(^{119}Sn-^{13}C) = 503, ^1J(^{117}Sn-^{13}C) = 480, *i*-Ph); 136.9 (6C, ^2J(^{119}Sn-^{13}C) = 37, ^2J(^{117}Sn-^{13}C) = 35, *o*-Ph); 129.0 (3C, ^4J($^{119/117}$Sn-^{13}C) = 11, *p*-Ph); 128.6 (6C, ^3J(^{119}Sn-^{13}C) = 50, ^3J(^{117}Sn-^{13}C) = 48 , *m*-Ph); 42.9 (^3J(^{119}Sn-^{13}C) = 85, ^3J(^{117}Sn-^{13}C) = 79, N-*C*H_2); 24.8 (^2J($^{119/117}$Sn-13C) = 16, $CH_2CH_2CH_2$); 7.0 (^1J(^{119}Sn-^{13}C) = 374, ^1J(^{117}Sn-^{13}C) = 357, *C*H_2Sn) ^{119}Sn-NMR δ: –102.8. Elemental analysis (calcd.): C: 56.3% (56.7%); H: 5.5% (5.4%); N: 3.2% (3.2%).

3-(Triphenylstannyl)propan-1-amine 6

Colorless crystals out of ethyl acetate. Yield: 96.3%. M.p.: 71–73 °C. ^{1}H-NMR δ: 7.60–7.51 (m, 6H, *o*-Ph); 7.41–7.34 (m, 9H, *m*,*p*-Ph); 2.73 (t, 2H, C*H*$_2$NH$_2$); 1.86 (p, 2H, $CH_2CH_2CH_2$); 1.50 (t, 2H, C*H*$_2$Sn); 1.28 (s, 2H, CH_2NH_2). ^{13}C-NMR δ: 139.3 (3C, ^1J(^{119}Sn-^{13}C) = 489, ^1J(^{117}Sn-^{13}C) = 467 Hz, *i*-Ph); 136.7 (6C, ^2J(^{119}Sn-^{13}C) = 36, ^2J(^{117}Sn-^{13}C) = 35, *o*-Ph); 128.7 (3C, ^4J($^{119/117}$Sn-^{13}C) = 11, *p*-Ph); 128.4 (6C, ^3J(^{119}Sn-^{13}C) = 49, ^3J(^{117}Sn-^{13}C) = 47, *m*-Ph); 45.7 (^3J(^{119}Sn-^{13}C) = 68, ^3J(^{117}Sn-^{13}C) = 65, N-*C*H_2); 30.4 (^2J($^{119/117}$Sn-13C) = 22, $CH_2CH_2CH_2$); 7.9 (^1J(^{119}Sn-^{13}C) = 402, ^1J(^{117}Sn-^{13}C) = 374), *C*H_2Sn). ^{119}Sn-NMR δ: –102.7. Elemental analysis (calcd.): C: 61.6% (61.8%); H: 5.8% (5.7%); N: 3.5% (3.4%).

3-(Diphenyl(propyl)stannyl)propan-1-amine hydrochloride 7

Amorphous white solid. Yield: 96.1%. M.p.: 114–116 °C (dec.). ^{1}H-NMR δ: 8.28 (s, 3H, NH_3); 7.53–7.27 (m, 10H, aromatic); 2.67 (s, 2H, C*H*$_2$N); 2.08–1.90 (m, 2H, $CH_2CH_2CH_2NH_3$); 1.75–1.60 (m, 2H, aliphatic); 1.37–1.29 (m, 2H, aliphatic); 1.27–1.19 (m, 2H, $CH_2CH_2CH_2NH_3$); 0.98 (t, 3H, methyl). ^{13}C-NMR δ: 139.0 (2C, *i*-Ph); 136.7 (4C, *o*-Ph); 128.7 (2C, *p*-Ph); 128.4 (4C, *m*-Ph); 43.1 (N-*C*H_2); 24.9 $CH_2CH_2CH_2N$); 20.2 ($CH_2CH_2CH_3$); 18.9 ($CH_2CH_2CH_3$); 13.0 ($CH_2CH_2CH_3$); 6.5 $CH_2CH_2CH_2N$). ^{119}Sn-NMR δ: –72.9. Elemental analysis (calcd.): C: 52.8% (52.7%); H: 6.4% (6.4%); N: 3,4% (3.4%).

3-(Diphenyl(propyl)stannyl)propan01-amine 8

Slightly yellow oil. Yield: 95.8%. ^{1}H-NMR δ: 7.54–7.30 (m, 10H, aromatic); 2.69 (t, 2H, C*H*$_2$NH$_2$); 1.81–1.63 (m, 4H, aliphatic); 1.35–1.11 (m, 6H, aliphatic, N*H*$_2$); 1.00 (t, 3H, $SnCH_2CH_2CH_3$). ^{13}C-NMR δ: 140.3 (2C, *i*-Ph); 136.7 (4C, *o*-Ph); 128.4 (2C, *p*-Ph); 128.2 (4C, *m*-Ph); 46.0 (N-*C*H_2); 30.7 ($CH_2CH_2CH_2NH_2$); 20.2 ($CH_2CH_2CH_3$); 18.9 ($CH_2CH_2CH_3$); 13.2 ($CH_2CH_2CH_3$); 7.3 ($CH_2CH_2CH_2NH_2$). ^{119}Sn-NMR δ: –72.9. Elemental analysis (calcd.): C: 57.3% (57.8%); H: 6.6% (6.7%); N: 3.8% (3.7%).

3-(Diethyl(phenyl)stannyl)propan-1-amine hydrochloride 9

Colorless oil. Yield: 99.8%. ^{1}H-NMR δ: 8.08 (s, 3H, NH_3); 7.37–7.28 (m, 2H, *o*-Ph); 7.27–7.11 (m, 3H, *m*,*p*-Ph); 2.80 (t, 2H, $CH_2CH_2CH_2NH_3$); 1.93–1.77 (m, 2H, $CH_2CH_2CH_2NH_3$); 1.30–0.80 (m, 12H, aliphatic). ^{13}C-NMR δ: 140.0 (*i*-Ph); 136.5 (2C, *o*-Ph); 128.4 (*p*-Ph); 128.2 (2C, *m*-Ph); 43.3 (N-*C*H_2); 25.0 ($CH_2CH_2CH_2N$); 10.9 (2C, methyl); 5.0 ($CH_2CH_2CH_2N$); 1.2 (2C, CH_2CH_3). ^{119}Sn-NMR δ: –35.0. Elemental analysis (calcd.): C: 44.5% (44.8%); H: 6.7% (6.9%); N: 3.9% (4.0%).

3-(Diethyl(phenyl)stannyl)propan-1-amine 10

Slightly yellow oil. Yield: 96.8%. ^{1}H-NMR δ: 7.53–7.40 (m, 2H, *o*-Ph); 7.40–7.24 (m, 3H, *m*,*p*-Ph); 2.66 (t, 2H, $CH_2CH_2CH_2NH_2$); 1.83–1.59 (m, 2H, $CH_2CH_2CH_2NH_2$); 1.34–0.88 (m, 14H, aliphatic, N*H*$_2$). ^{13}C-NMR δ: 141.1 (*i*-Ph); 136.4 (2C, *o*-Ph); 128.0 (*p*-Ph); 127.9 (2C, *m*-Ph); 46.0 (N-*C*H_2); 30.8 ($CH_2CH_2CH_2N$); 10.9 (2C, methyl); 5.6 ($CH_2CH_2CH_2N$); 1.1 (2C, CH_2CH_3). ^{119}Sn-NMR δ: –34.7.

General procedure for aminopropyl tinhalogenides

10 mmol/L of the desired aminopropyltin hydrohalide (chloride, bromide, iodide) is placed in a Schlenk tube equipped with a reflux condenser and a vacuum supply on the top of the reflux condenser. Vacuum is applied to the apparatus and the tube placed in an oil bath under siring. The oil bath is then heated until evolution of benzene is visible and held at this temperature. After gas evolution has stopped, the flask is heated up until the product starts to distill into the reflux condenser (usually around 200 °C). The whole apparatus is then allowed to cool down to RT. Afterwards the product is washed into a second flask with CH_2Cl_2. The solvent is then removed in vacuum and the product recrystallized.

3-(Chlorodiethylstannyl)propan-1-amine 11

Colorless crystals out of benzene. Yield: 92.1%. M.p.: 140–141 °C. ^{1}H-NMR δ: 2.64 (s, 2H, CH_2NH_2); 1.70 (p, 2H, $CH_2CH_2CH_2$); 1.60 (s, 2H, CH_2NH_2); 1.27–0.93 (m, 12H, $CH_2CH_2CH_2Sn$, CH_3CH_2Sn, CH_3CH_2Sn). ^{13}C-NMR δ: 42.9 ($^3J(^{119}Sn\text{-}^{13}C)$ = 37, $^3J(^{117}Sn\text{-}13C)$ = 35, N-CH_2); 29.7 ($^2J(^{119/117}Sn\text{-}^{13}C)$ = 30, $CH_2CH_2CH_2$); 13.3 ($^1J(^{119}Sn\text{-}^{13}C)$ = 490, $^1J(^{117}Sn\text{-}^{13}C)$ = 468, CH_2CH_2Sn); 12.0 (2C, $^1J(^{119}Sn\text{-}^{13}C)$ = 495, $^1J(^{117}Sn\text{-}^{13}C)$ = 473, CH_3CH_2Sn); 10.7 (2C, $^2J(^{119}Sn\text{-}13C)$ = 33, $^2J(^{117}Sn\text{-}^{13}C)$ = 32), CH_3). ^{119}Sn-NMR δ: –25.5. Elemental analysis (calcd.): C: 31.0% (31.1%); H: 6.6% (6.7%); N: 5.2% (5.2%).

3-(Bromodiethylstannyl)propan-1-amine 12

Colorless crystals out of benzene. Yield: 94.3%. M.p.: 99–100 °C. ^{1}H-NMR δ: 2.70 (s, 2H, CH_2NH_2); 2.00–1.50 (m, 4H, $CH_2CH_2CH_2$, CH_2NH_2); 1.50–1.00 (m, 12H, $CH_2CH_2CH_2Sn$, CH_3CH_2Sn, CH_3CH_2Sn). ^{13}C-NMR δ: 43.0 ($^3J(^{119/117}Sn\text{-}13C)$ = 38, N-CH_2); 26.9 ($^2J(^{119/117}Sn\text{-}^{13}C)$ = 30, $CH_2CH_2CH_2$); 14.7 ($^1J(^{119}Sn\text{-}^{13}C)$ = 471, $^1J(^{117}Sn\text{-}^{13}C)$ = 451, CH_2CH_2Sn); 12.7 (2C, $^1J(^{119}Sn\text{-}^{13}C)$ = 475, $^1J(^{117}Sn\text{-}^{13}C)$ = 455, CH_3CH_2Sn); 10.9 (2C, $^2J(^{119/117}Sn\text{-}^{13}C)$ = 33), CH_3). ^{119}Sn-NMR δ: –25.9. Elemental analysis (calcd.): C: 26.1% (26.7%); H: 5.5% (5.8%); N: 4.5% (4.5%).

3-(Diethyiodolstannyl)propan-1-amine 13

Colorless crystals out of benzene. Yield: 95.1%. M.p.: 113–114 °C. ^{1}H-NMR δ: 2.84 (t, 2H, CH_2NH_2); 2.06 (s, 2H, CH_2NH_2); 1.83 (p, 2H, $CH_2CH_2CH_2$); 1.47 (t, 2H, $CH_2CH_2CH_2Sn$); 1.42–1.25 (m, 10H, CH_3CH_2Sn, CH_3CH_2Sn). ^{13}C-NMR δ: 43.2 ($^3J(^{119/117}Sn\text{-}^{13}C)$ = 37, N-CH_2); 27.2 ($^2J(^{119/117}Sn\text{-}^{13}C)$ = 32, $CH_2CH_2CH_2$); 16.6 (CH_2CH_2Sn); 13.7 (2C, CH_3CH_2Sn); 11.4 (2C, $^2J(^{119/117}Sn\text{-}^{13}C)$ = 33; CH_3). ^{119}Sn-NMR δ: –30.7. Elemental analysis (calcd.): C: 23.0% (23.2%); H: 5.0% (5.0%); N: 3.9% (3.9%).

3-(Diethylfluorostannyl)propan-1-amine 14

In a Schlenk tube 1.5 g (5.5 mmol/L, 1.0 equiv.) 3-(chlorodiethylstannyl) propan-1-amine (**5**) are dissolved in 20 mL acetone/THF 1:1 and 0.32 g (1.0 equiv.) potassium fluoride are added under stirring at RT. After 2 h the solvent is removed in vacuum. The residue is suspended in CH_2Cl_2, filtered and the solvent removed again. The product is recrystallized out of benzene to yield 3-(diethylfluorostannyl)propan-1-amine as colorless, clear crystals (0.72 g, 51.2%). M.p.: 125–126 °C. ^{1}H-NMR δ: 2.60 (t, 2H, CH_2NH_2); 1.70 (p, 2H, $CH_2CH_2CH_2$); 1.55 (s, 2H, CH_2NH_2); 1.19 (t, 6H, CH_3CH_2Sn); 1.09–0.95 (m, 6H, $CH_2CH_2CH_2Sn$, CH_3CH_2Sn). ^{13}C-NMR δ: 42.5 ($^3J(^{119/117}Sn\text{-}^{13}C)$ = 36 Hz, N-CH_2); 26.8 ($^2J(^{119/117}Sn\text{-}^{13}C)$ = 28 Hz, $CH_2CH_2CH_2$); 10.4 (2C, $^2J(^{119/117}Sn\text{-}^{13}C)$ = 31 Hz), CH_3); 9.7–9.1 (3C $^1J(^{119/117}Sn\text{-}^{13}C)$ = 509 Hz, CH_3CH_2Sn, CH_2CH_2Sn). ^{19}F-NMR δ: –175.0 ($^1J(^{119}Sn\text{-}^{19}F)$ = 2069, $^1J(^{117}Sn\text{-}^{19}F)$ = 1979). ^{19}F-NMR (s-st) δ: 21,2. ^{119}Sn-NMR δ: –34.8 (d). ^{119}Sn-NMR (s-st) δ: –74.2 ($^1J(^{119}Sn\text{-}^{19}F)$ = 1920).

(3-Aminopropyl)diethylstannyl acetate 15

In a Schlenk tube 1.5 g (5.5 mmol/L, 1.0 equiv.) 3-(chlorodiethylstannyl) propan-1-amine (**5**) are dissolved in 20 mL MeOH and 0.46 g (1.0 equiv.) sodium acetate are added under stirring at RT. After 5 min the solvent is removed in vacuum. The residue is suspended in CH_2Cl_2, filtered, and the solvent removed again. The product is recrystallized out of benzene to yield (3-aminopropyl)diethylstannyl acetate as colorless, clear crystals (1.48 g, 90.9%). M.p.: 107–108 °C. ^{1}H-NMR δ: 2.73 (t, 2H, CH_2NH_2); 1.95 (s, 3H, C=OCH_3); 1.88 (s, 2H, CH_2NH_2); 1.78 (p, 2H, $CH_2CH_2CH_2$); 1.36–0.95 (m, 12H, $CH_2CH_2CH_2Sn$, CH_3CH_2Sn, CH_3CH_2Sn). ^{13}C-NMR δ: 176.8 (*C*=O); 42.7 ($^3J(^{119/117}Sn\text{-}13C)$ = 34, N-CH_2); 26.9 ($^2J(^{119/117}Sn\text{-}^{13}C)$ = 29, $CH_2CH_2CH_2$); 23.0 (O=*C*CH_3); 10.6 (2C, $^2J(^{119/117}Sn\text{-}^{13}C)$ = 40, CH_3); 10.3 ($^2J(^{119/117}Sn\text{-}^{13}C)$ = 495, CH_2CH_2Sn); 9.7 (2C, CH_3CH_2Sn, $^2J(^{119/117}Sn\text{-}^{13}C)$ = 506). ^{119}Sn-NMR δ: –53.0. Elemental analysis (calcd.): C: 36.8% (36.8%); H: 7.2% (7.2%); N: 4.8% (4.8%).

Triphenylstannane 16

Colorless crystals out of pentane. M.p.: 27–28 °C. Yield: 91.2%. ^{1}H-NMR δ: 7.54–7.48 (m, 6H, *o*-Ph), 7.15–7.11 (m, 9H, *m*,*p*-Ph), 6.91 (s, 1H, $^1J(^1H\text{-}^{119}Sn)$ = 1934, $^1J(^1H\text{-}^{117}Sn)$ = 1848, Sn-*H*). ^{13}C-NMR δ: 137.7 (6C, $^2J(^{13}C\text{-}^{119}Sn)$ = 41, $^2J(^{13}C\text{-}^{117}Sn)$ = 39, *o*-Ph), 137.3 (3C, $^1J(^{13}C\text{-}^{119}Sn)$ = 534, $^1J(^{13}C\text{-}^{117}Sn)$ = 511, *i*-Ph), 129.3 (3C, $^4J(^{13}C\text{-}^{119/117}Sn)$ = 11, *p*-Ph), 129.0 (6C, $^3J(^{13}C\text{-}^{119}Sn)$ = 53, $^3J(^{13}C\text{-}^{117}Sn)$ = 50, *m*-Ph). ^{119}Sn-NMR δ: –162.8. Elemental analysis (calcd.): C: 61.4% (61.6%); H: 4.5% (4.6%).

Diphenyl(propyl)stannane 17

^{1}H-NMR δ: 7.51–7.41 (m, 4H, *o*-Ph); 7.21–7.06 (m, 6H, *m*,*p*-Ph); 6.28 (s, 1H, $^1J(^{119}Sn\text{-}^1H)$ = 1804, $^1J(^{117}Sn\text{-}^1H)$ = 1723, Sn-*H*); 1.65–1.49 (m, 2H, $SnCH_2CH_2CH_3$); 1.19 (t, 2H, $SnCH_2CH_2CH_3$); 0.88 (t, 3H, $SnCH_2CH_2CH_3$). ^{13}C-NMR δ: 138.3 (4C, *o*-Ph); 137.5 (2C, *i*-Ph); 129.0 (2C, *p*-Ph); 128.8 (4C, *m*-Ph); 20.9 ($SnCH_2CH_2CH_3$); 18.8 ($SnCH_2CH_2CH_3$); 13.1 ($SnCH_2CH_2CH_3$). ^{119}Sn-NMR δ: –139.8.

Diethyl(phenyl)stannane 18

^{1}H-NMR δ: 7.48–7.38 (m, 2H); 7.20–7.01 (m, 3H); 6.05 (s, 1H, $^1J(^{119}Sn\text{-}^1H)$ = 1813, $^1J(^{117}Sn\text{-}^1H)$ = 1734); 1.34–0.88 (m, 10H). ^{13}C-NMR δ: 138.9 (*i*-Ph); 137.4 (2C, *o*-Ph); 128.7 (*p*-Ph); 128.6 (2C, *m*-Ph); 11.8 (2C, methyl); 1.1 (2C, $SnCH_2CH_3$). ^{119}Sn-NMR δ: –98.5.

Supplementary data

Supplementary data are available with the article through the journal Web site at http://nrcresearchpress.com/doi/suppl/10.1139/cjc-2013-0504. CCDC Nos. 969138–969144 contain the supplementary crystallographic data for compounds **6** and **11–16,** respectively. These data can be obtained, free of charge, via http://www.ccdc.cam.ac.uk/products/csd/request (Or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1E2, UK; fax: +44 1223 33603; or e-mail: deposit@ccdc.cam.ac.uk).

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