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Reaction products of dichlorodiorganostannanes with sodium in liquid ammonia: *In-situ* investigations with ^{119}Sn NMR spectroscopy and usage as intermediates for the synthesis of tetraorganostannanes

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ABSTRACT

Dichlorodibutylstannane, dichlorodioctylstannane and dichlorodiphenylstannane were reacted with different amounts of sodium in liquid ammonia. At a molar ratio of R_2SnCl_2/Na of 1:2, polystannanes precipitated, in some cases accompanied by cyclic oligostannanes. The products resulting from mixtures with R_2SnCl_2/Na ratios of 1:3 to 1:10 were soluble and, hence, could be studied *in-situ* in liquid ammonia with ^{119}Sn NMR spectroscopy. The compounds obtained, tin hydrides of the type R_2SnH^- and in certain cases distannides of the composition $R_4Sn_2^{2-}$, formed essentially independent of the R_2SnCl_2/Na ratio; this, in contrast to views expressed in the literature. Our experiments showed that the chemical structure of the *in-situ* generated species did not permit to draw conclusions about the composition of the reaction products with bromoethane and *vice versa* – a practice commonly described. Furthermore, we observed migration of the butyl groups both *in-situ* during the reaction of dichlorodibutylstannane with sodium in liquid ammonia, as well as in the final reaction product. By contrast in the case of the phenyl substituent, migration was detected not during the chemical event in liquid ammonia, but only in the compounds formed. These observations imply a different mechanism for butyl and phenyl group migration.

1. Introduction

The reaction of haloorganostannanes with sodium in liquid ammonia has attracted attention since the early part of the past century [1–11]. The resulting products have been used *in-situ* as intermediates for the preparation of organotin compounds (organostannanes). In particular, conversion of such intermediates with haloalkanes and haloarenes yielded tetraorganostannanes [12–25]. In this context, also dihalodiorganostannanes, R_2SnCl_2, have been exposed to sodium, and were regarded to yield diorganotin dianions (Fig. 1, diorganostannide dianions, R_2Sn^{2-}), which can subsequently act as reaction intermediates for the synthesis of tetraorganostannanes, with the respective sodium halides as reaction byproducts [18,26–30]. However, surprisingly, recent studies performed *in-situ* with ^{119}Sn NMR spectroscopy experiments indicated that diorganostannide dianions were not formed when stoichiometric ratios of dichlorodiorganostannanes and sodium are present in liquid ammonia (i.e. 4 molar equivalents of sodium per mol stannane) [31].

Further, it has been suggested (but not spectroscopically verified) [5,26] that the composition of the reaction intermediates changes upon variation of the diorganostannane/sodium ratio. In addition, it has been claimed that treatment of dihalodiorganostannanes with less than 4 molar equivalents of sodium (preferentially two equivalents) gives rise to the formation of oligostannanes or polystannanes (Fig. 1) [1,4,5]; however the resulting products were not thoroughly characterized. Polystannanes are a unique class of polymers as their backbone consists of covalently bound metal atoms; they were first prepared by Löwig [32] and then mainly during the last two decades in various laboratories by different methods [33–52].

In order to resolve the various discrepancies alluded above, we carried out *in-situ* investigations of the species arising from reactions of dichlorodiorganostannanes and sodium at different molar ratios in liquid ammonia and explored their applicability as reaction intermediates for the synthesis of tetraorganostannanes by conversion with bromoethane.

2. Results

For the experiments, dichlorodibutylstannane and dichlorodioctylstannane were employed as representatives for alkyl

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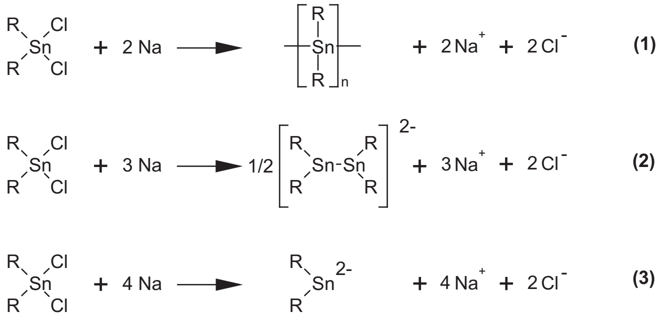

Fig. 1. Previously advanced reactions of dihalodiorganostannanes with sodium.

stannanes and dichlorodiphenylstannane as the most convenient arylstannane. All those compounds were exposed to 2, 3, 4 and 10 equivalents of sodium, respectively. A summary of the resulting products is presented in Table 1.

2.1. Dihalodiorganostannane/sodium 1:2

A general feature of reactions with a dichlorodiorganostannane/sodium ratio of 1:2 was formation of polymers (cf. Table 1). Below, the results obtained for the individual systems are described in more detail.

2.1.1. Dichlorodibutylstannane

Exposure of dichlorodibutylstannane to 2 molar equivalents of sodium in liquid ammonia caused immediate precipitation of a yellow product, which is typical for poly(dibutylstannane). The GPC diagrams revealed the presence of polymer with a molar mass of 8 kg/mol. In addition, products in a mass range of cyclic byproducts (cyclopentastannane and cyclohexastannane) were detected. ^{119}Sn NMR spectra showed a broad signal at −190 ppm characteristic for poly(dibutylstannane) and signals at −202 ppm and −203 ppm, which are typical for cyclic byproducts [50]. The elemental composition of the isolated yellow product was consistent with products of the composition $(SnBu_2)_n$, which is in agreement both with the composition of linear polymers and cyclic oligomers.

2.1.2. Dichlorodioctylstannane

Conversion of dichlorodioctylstannane with 2 molar equivalents of sodium was performed in the same manner as the above described reaction of dichlorodibutylstannane, resulting in precipitation of a yellow, pasty material. Analogously, GPC analysis indicated the generation of poly(dioctylstannane) (M_p around 6 kg/mol), together with cyclic pentamers and hexamers. The elemental composition of the isolated product was in agreement with that of $(Oct_2Sn)_n$, and ^{119}Sn NMR spectroscopy in deuterated dichloromethane revealed a broad signal at −192 ppm which corresponds to the value of poly(dioctylstannane), and signals at −203 ppm and −205 ppm for the cyclic byproducts [50].

Table 1
Overview of the detected products that emerged from reaction of dichlorodiorganostannanes, R_2SnCl_2, with different ratios of sodium in liquid ammonia.

R_2SnCl_2: Na ratio	R = butyl	R = octyl	R = phenyl
1:2	$(SnBu_2)_n$ polymer and cyclic oligomers	$(SnOct_2)_n$ polymer and cyclic oligomers	$(SnPh_2)_n$ polymer
1:3	Bu_2SnH^-, $(Bu_4Sn_2)^{2-}$, Bu_3Sn^-, one unidentified product	Oct_2SnH^-	Ph_2SnH^-, $(Ph_4Sn_2)^{2-}$ [a]
1:4	Bu_2SnH^-, $(Bu_4Sn_2)^{2-}$, Bu_3Sn^-, one unidentified product	Oct_2SnH^-	Ph_2SnH^-, $(Ph_4Sn_2)^{2-}$
1:10	Bu_2SnH^-, $(Bu_4Sn_2)^{2-}$, Bu_3Sn^-, one unidentified product	Oct_2SnH^-	Ph_2SnH^-, $(Ph_4Sn_2)^{2-}$

[a] Additional signals are attributed to degradation products formed during transfer of the reaction solutions to the NMR tubes that could not be avoided. Thus, the signal of the distannide was not always present in the spectra.

2.1.3. Dichlorodiphenylstannane

Also treatment of dichlorodiphenylstannane with 2 molar equivalents of sodium resulted in immediate precipitation of a yellow, shiny product. The material obtained was insoluble in all tested organic solvents at room temperature and as well at elevated temperatures (close to the boiling point of the solvents). Therefore, it was not possible to determine its molar mass. The product was washed with a water/ethanol mixture (9:1) to remove sodium chloride and, thereafter, extracted with hot dichloromethane to dissolve potential byproducts, in particular cyclic oligo(diphenylstannane)s. ^{119}Sn NMR analysis of the concentrated extracts indicated that no significant amounts of cyclic byproducts were formed. Elemental analysis of the material was consistent with that of $(Ph_2Sn)_n$.

2.2. Dichlorodiorganostannane/sodium 1:3, 1:4 and 1:10

Recently, we reported [31] that in contrast to general views (Fig. 1), dichlorodibutylstannane and dichlorodiphenylstannane do not react with four equivalents of sodium to yield the respective diorganostannide dianions. Instead, the anions $HSnR_2^-$ and $(R_2Sn{-}SnR_2)^{2-}$ formed in quantities of similar order of magnitude, and in the case of dichlorodibutylstannane additionally R_3Sn^- and a fourth unidentified product (e.g. H_2RSn^- or $(HRSn{-}SnHR)^{2-}$) arose by alkyl group migration. Considering that Na in fact is present in liquid ammonia as Na^+ and solvated electrons, the latter providing the typical blue color of the corresponding solutions [53], the existence of $(R_2Sn{-}SnR_2)^{2-}$ may be somewhat surprising, as two of the highly reactive solvated electrons per dianion may remain under a dichlorodiorganostannane/sodium ratio of 1:4. In order to investigate if larger quantities of sodium would ultimately lead to cleavage of Sn–Sn bonds in the dianions and if lower amounts influence the ratio between the aforementioned stannides, dichlorodiorganostannanes were exposed to 3, 4 and 10 molar equivalents of Na. According to the literature [5,26] substantial differences in the *in-situ* formed reaction products are expected at these different ratios.

Since the solvated electrons produced upon dissolution of metallic sodium are consumed when dichlorodiorganostannanes react - due to the generation of stannides and chloride ions - the electric conductivity of the reaction mixture is expected to decrease during the reaction of dichlorodiorganostannanes with sodium because highly mobile electrons are removed from the system. Thus, we employed *in-situ* measurements of the electric conductivity in liquid ammonia to qualitatively follow the course of the reaction.

An overview of the soluble products detected by *in-situ* ^{119}Sn NMR spectroscopy in liquid ammonia obtained with the different compounds is displayed in Table 2; the results are described in more detail in the following sections.

2.2.1. Dichlorodibutylstannane

The electric conductivity of mixtures of dichlorodibutylstannane/sodium 1:4 versus reaction time is presented in Fig. 2a. The data show that the conductivity reached a constant value after 30 min, indicating that the reaction was terminated within this period (Fig. 2a). Accordingly, *in-situ* NMR measurements in liquid ammonia were performed after a reaction time of 30 min. Remarkably, regardless of the dichlorodibutylstannane/sodium molar ratio in the range of 1:3 up to 1:10, not only the same

Table 2
Overview of the soluble products which emerged after treatment of dichlorodiorganostannanes with sodium in liquid ammonia identified by *in-situ* ^{119}Sn NMR spectroscopy.

	δ ^{119}Sn (ppm)	
	200 K	220 K
Bu_2SnH^-	−228	−219
$(Bu_4Sn_2)^{2-}$	−161	−143
Bu_3Sn^-	−136	−137
Oct_2SnH^-	−223	−219
Ph_2SnH^-	−197	−192
$(Ph_4Sn_2)^{2-}$	−132	−116

intermediates emerged, but also their relative distribution did not alter strikingly (Fig. 2b). These intermediates are attributed to dibutylhydrostannide Bu_2SnH^- (−228 ppm), tetrabutyldistannide $(Bu_4Sn_2)^{2-}$ (−161 ppm), tributylstannide Bu_3Sn^- (−136 ppm) and a fourth unidentified product that arose by alkyl group migration (e.g. H_2RSn^- or $(HRSn-SnHR)^{2-}$) (−212 ppm) [31]. Thus, dichlorodibutylstannane was found to undergo alkyl group migration at molar stannane/sodium ratios between 1:3 and 1:10.

2.2.2. *Dichlorodioctylstannane*

Conversion of dichlorodioctylstannane with sodium in liquid ammonia was slower compared to dichlorodibutylstannane, as revealed by conductivity measurements. It took well over 1 h until equilibrium was established in a reaction mixture of dichlorodioctylstannane/sodium at a ratio of 1:4 (Fig. 2a).

Remarkably, the reaction mixture of dichlorodioctylstannane with three, four and ten equivalents of sodium gave rise to only one signal in *in-situ* ^{119}Sn NMR spectra within the detection limits, at −223 ppm at 200 K (−219 ppm at 220 K, $\Delta\sigma = 0.2$ ppm/K), *i.e.* in the range of the above mentioned Bu_2SnH^- anion. This signal is present as a singulet in broadband proton-decoupled ^{119}Sn NMR spectra, in contrast to the corresponding signal in proton-coupled spectra, where a doublet is visible, due to a ^{119}Sn–^{1}H coupling (Fig. 3). Therefore, we assign the signal to dioctylhydrostannide Oct_2SnH^-. The coupling constant of ^{1}J(Sn,H) = 95 Hz is in good agreement with values reported earlier for Bu_2SnH^- [31,54]. We would like to note that the transfer of the reaction products in liquid ammonia into NMR tubes was more challenging for the octyl than for the butyl compounds. Due to the lower solubility of the octyl compounds in liquid ammonia, they tended to precipitate during the transfer to the NMR test tube (yellow polymeric residue). To avoid this problem lower stannane concentrations were used - leading to a decreased sensitivity of the *in-situ* ^{119}Sn NMR spectra and therefore increased acquisition times.

2.2.3. *Dichlorodiphenylstannane*

The reaction of dichlorodiphenylstannane with sodium was terminated within 30 min, as evident from conductivity measurements (Fig. 2a). After this period two strong signals were visible in ^{119}Sn NMR spectra of *in-situ* formed intermediates at dichlorodiphenylstannane/sodium ratios of 1:4 and 1:10 (Fig. 4), representing diphenylhydrostannide, Ph_2SnH^-, (−197.2 ppm) and

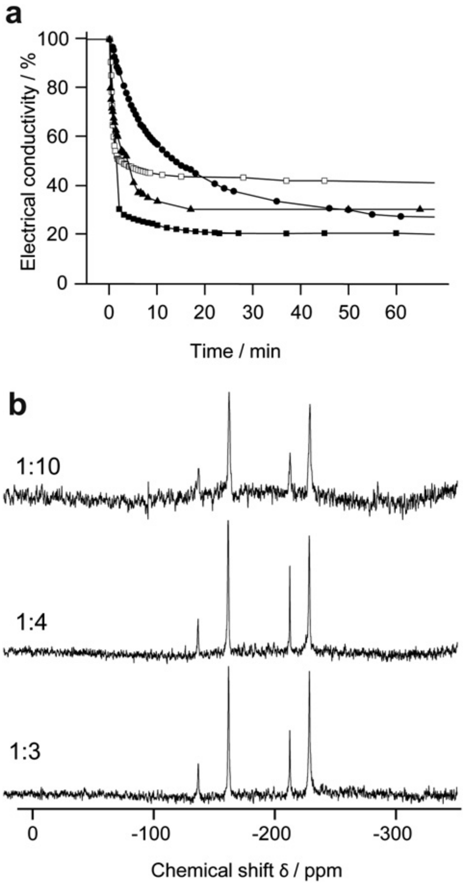

Fig. 2. a) Electrical conductivity of a mixture of dichlorodibutylstannane (■), dibromodibutylstannane (□), dichlorodioctylstannane (●) and dichlorodiphenylstannane (▲) and 4 equivalents of sodium measured *in situ* in liquid ammonia as a function of reaction time. b) ^{119}Sn NMR spectra recorded *in-situ* of dichlorodibutylstannane exposed to 10, 4 and 3 molar equivalents of sodium in liquid ammonia.

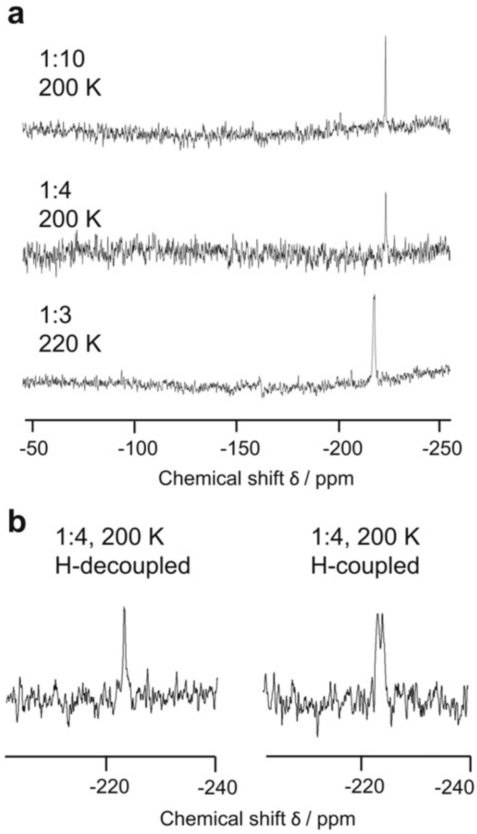

Fig. 3. a) *In-situ* ^{119}Sn NMR spectra of dichlorodioctylstannane exposed to 10, 4 and 3 molar equivalents of sodium in liquid ammonia. The spectrum of the 1:3 ratio was recorded at 220 K whereas the other measurements were performed at 200 K ($\Delta\sigma = 0.2$ ppm/K). b) ^{1}H decoupled and ^{1}H coupled ^{119}Sn NMR spectra of the signal at −223.3 ppm (^{1}J(Sn,H) = 95 Hz).

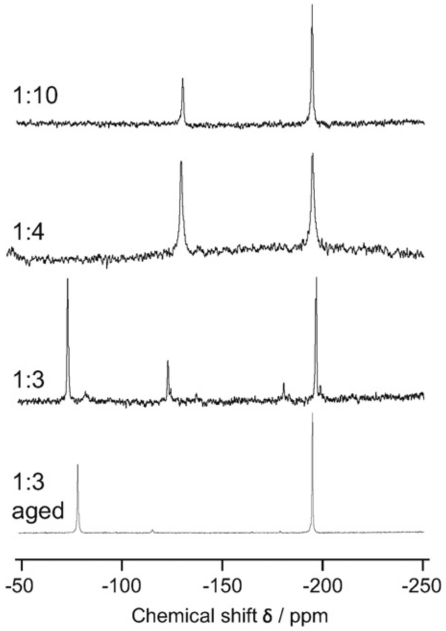

Fig. 4. *In-situ* ^{119}Sn NMR spectra of dichlorodiphenylstannane exposed to 10, 4 and 3 molar equivalents sodium in liquid ammonia including a sample of 1:3 ratio that was aged for 2 h.

tetraphenyldistannide, $(Ph_4Sn_2)^{2-}$ (−131.7 ppm), respectively [31]. Reliable *in-situ* measurements of 1:3 mixtures were somewhat more difficult to perform with reaction mixtures based on dichlorodiphenylstannane than on dichlorodibutylstannane, because in the former a higher tendency to form precipitates (polymers or other products) was observed. When such solutions (still dark red) were investigated by ^{119}Sn NMR spectroscopy, several signals emerged. In addition to the peak of diphenylhydrostannide at −197.2 ppm, two other strong signals at −65 ppm and −125 ppm arose (Fig. 4). Unfortunately, the species causing the latter signals could not be identified. The solutions lost their characteristic dark red color after about 2 h at 200 K; a yellow precipitate was formed, but the NMR spectra still featured the diphenylhydrostannide signal at −197.2 ppm together with the strong signal at −75 ppm, which could not be attributed to a specific compound.

Table 3

Summary of the compounds that resulted from reaction of *in-situ* prepared dichlorodiorganostannane-sodium mixtures in liquid ammonia with bromoethane (30 min equilibration time for butyl and phenyl; 90 min for octyl).

R_2SnCl_2:Na ratio	R = butyl	R = octyl	R = phenyl
1:10	$BuSnEt_3$ Bu_2SnEt_2 Bu_3SnEt	Oct_2SnEt_2[a] $Oct_xSn_2Et_{6-x}$ unident. prod. (−125 ppm)	Ph_2SnEt_2 $Ph_4Sn_2Et_2$ unident. prod. (−28 ppm)
1:4	$BuSnEt_3$ Bu_2SnEt_2 Bu_3SnEt	$OctSnEt_3$ Oct_2SnEt_2 Oct_3SnEt $Oct_xSn_2Et_{6-x}$ Oct_6Sn_2O	Ph_2SnEt_2
1:3	Bu_3SnOH Bu_2SnEt_2 Bu_3SnEt $Bu_4Sn_2Et_2$ $Bu_3Sn_2Et_3$	Oct_2SnEt_2 $Oct_xSn_2Et_{6-x}$ Oct_6Sn_2O	$PhSnEt_3$ Ph_2SnEt_2 Ph_3SnEt

[a] Minor quantities of Oct_3SnEt and $OctSnEt_3$ might be present but were not observed due to a relatively low signal/noise ratio in the spectra.

2.3. *In-situ prepared alkylstannides as intermediates: reactions with bromoethane*

The above described invariability of detected products arising at dichlorodialkylstannane/sodium ratios between 1:3 and 1:10, as well as in dichlorodiphenylstannane/sodium 1:4 and 1:10 mixtures are not in agreement with previous suggestions in the literature [5,26]. In fact, it has been concluded after reactions of *in-situ* formed products with haloalkanes that the composition of the formed products should change upon variation of the dihalodiorganostannane/sodium ratio (note that these conclusions were not based on direct spectroscopic data). Hence, in the following we investigated if related products with haloalkanes can indeed provide information on *in-situ* formed products and *vice versa*, as an example of reactions with bromoethane. An overview on the results, which will be detailed below, is presented in Table 3.

2.3.1. *Conversion of butylstannides*

Butylstannides were exposed to an excess of bromoethane and products studied with ^{119}Sn NMR spectroscopy. At dichlorodibutylstannanes/sodium ratios of 1:4 and 1:10, the spectra did not differ considerably (Fig. 5a). A main product accompanied by two side products emerged in a region of 0 to −10 ppm (Table 4), *i.e.* in the typical range of tetraalkylstannanes, which is consistent with the

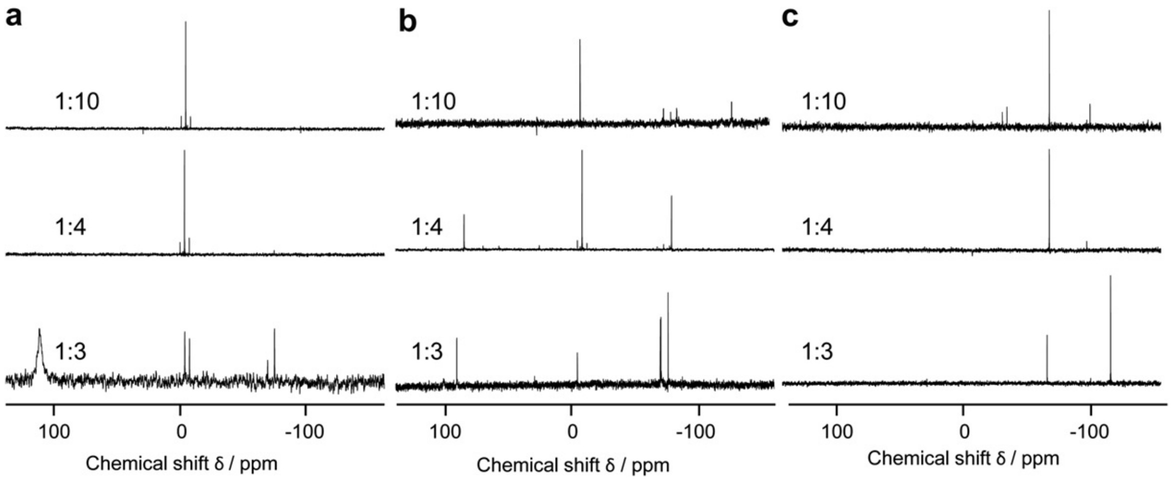

Fig. 5. ^{119}Sn NMR spectra of the reaction products of a) dichlorodibutylstannane, b) dichlorodioctylstannane and c) dichlorodiphenylstannane exposed first to 10, 4 or 3 molar equivalents of sodium and then converted with bromoethane.

chemical shifts of the $Sn{-}CH_2$ signals in ^{13}C NMR spectra (around 0 ppm, Table 5). Experiments with ^{13}C labeled bromoethane, $Br^{13}CH_2CH_3$, allowed identification of the reaction products *via* the signal splitting pattern caused by $^{119}Sn{-}^{13}C$ couplings (Fig. 6 and Tables 4 and 5). Thus, it was concluded that the primary product of the mixtures with 1:4 and 1:10 ratios was dibutyldiethylstannane, Bu_2SnEt_2, and the side products were butyltriethylstannane, Bu-$SnEt_3$, and tributylethylstannane, Bu_3SnEt, which had been established by alkyl group exchange reactions [31]. The very weak signal at −75 ppm in the spectra representing the 1:4 ratio is probably due to tetrabutyldiethyldistananne. Tributylethylstannane and dibutyldiethylstannane were found in similar quantities at a dichlorodibutylstannane/sodium ratio of 1:3, but in addition distannanes formed (Fig. 5a). The latter were identified not only by the chemical shifts (about −70 ppm, typical for distannanes [55]), but also by the signal splitting patterns in ^{119}Sn NMR spectra (Tables 4 and 5). The broad signal at 105 ppm was attributed to Bu_3SnOH [31].

Table 5
^{13}C NMR data of the reaction products of a mixture Bu_2SnCl_2: Na, 1:4, with ^{13}C labeled bromoethane $Br^{13}CH_2CH_3$.

	δ	$^1J(^{119}Sn,C)$	$^1J(^{117}Sn,C)$
	ppm	Hz	Hz
Bu_3Sn ($^{\mathbf{13}}\mathbf{C}H_2CH_3$)	0.11	321.4	309.0
Bu_2 Sn ($^{\mathbf{13}}\mathbf{C}H_2CH_3)_2$	0.28	319.1	305.0
Bu Sn ($^{\mathbf{13}}\mathbf{C}H_2CH_3)_3$	0.67	318.8	304.6
Bu_2 Sn ($^{\mathbf{13}}\mathbf{C}H_2CH_3$)–$Bu_2$ Sn ($^{\mathbf{13}}\mathbf{C}H_2CH_3$)	1.53	245.5	234.2
Bu Sn ($^{\mathbf{13}}\mathbf{C}H_2CH_3)_2$–$Bu_2$ Sn ($^{\mathbf{13}}\mathbf{C}H_2CH_3$)	1.88	245.4	234.5
Bu_2 Sn ($^{\mathbf{13}}\mathbf{C}H_2CH_3$)–O–$Bu_2$ Sn ($^{\mathbf{13}}\mathbf{C}H_2CH_3$)	7.73	373.8	358.8
Bu Sn ($^{\mathbf{13}}\mathbf{C}H_2CH_3)_2$–O–$Bu_2$ Sn ($^{\mathbf{13}}\mathbf{C}H_2CH_3$)	8.23	376.3	358.8

2.3.2. *Conversion of octylstannides*

The product composition resulting from the reaction of bromoethane with dichlorodioctylstannane/sodium mixtures at molar ratios between 1:3 and 1:10 strongly depended on that ratio (Fig. 5b). The corresponding products were designated by ^{119}Sn NMR spectroscopy on the basis of the above discussed values of the butylstannanes (Table 6). Mono- and distannanes were found in all cases, yet the ratio between these species shifted to the distannanes with decreasing dichlorodioctylstannane/sodium ratio. Distannanes dominated at a ratio of 1:3, while dioctyldiethylstannane, Oct_2SnEt_2, was the main product at 1:4 and 1:10. Alkyl group exchange was little pronounced at 1:4 ratio, while at 1:3 ratio strong NMR signals at −69.7 ppm and −70.1 ppm indicated alkyl group exchange in distannanes, resulting in derivatives of the general composition $Et_xOct_{6-x}Sn_2$ (Fig. 5b). The compound causing the signal at about −125 ppm observed in the case of a 1:10 ratio could not be identified. NB oxidation products, $Oct_3Sn{-}OH$ (99 ppm) and $Oct_3Sn{-}O{-}SnOct_3$ (96 ppm), were observed in some cases.

2.3.3. *Evolution of the octylstannides*

The low reaction rate of dichlorodioctylstannane with sodium (Fig. 7a) was beneficially employed to convert portions of dioctylstannane/sodium 1:4 mixtures with bromoethane already before the equilibrium of the intermediate products was established *in situ*. The ^{119}Sn NMR spectra of the reaction products (Fig. 7b) imply that during the decrease of the conductivity in the reaction mixtures various intermediates formed, which, however, could not be detected *in-situ* by ^{119}Sn NMR during the formation and after the equilibrium was reached (see above). For example, besides the signals of diethyldioctylstannane (−4.4 ppm), tetraoctyldiethyldistannane and derivatives of the composition $Et_xOct_{6-x}Sn_2$ at about −70 ppm were detected, and the spectra of the reaction products after 7 and 14 min equilibration time (Fig. 7b) showed the signals of chloroethyldioctylstannane (148 ppm [55]), together with numerous signals between −150 ppm and −250 ppm. After 21 min a group of signals around −210 ppm was present. These signals might represent oligostannanes (For comparison: dimers −70 ppm, polystannanes −192 ppm and cyclic oligostannanes −203 ppm [55]). Finally, after 100 min equilibration time the number of significant species was reduced.

2.3.4. *Conversion of diphenylstannides*

In the case of conversion of *in-situ* prepared diphenylstannides, the ratio of dichlorodiphenylstannane/sodium in the initial solution had a significant influence on the products formed after subsequent reaction with bromoethane. The simplest situation occurred at a dichlorodiphenylstannane/sodium ratio of 1:4 where only one product was observed after conversion with bromoethane in ^{119}Sn NMR spectra, namely at −65.4 ppm – diethyldiphenylstannane [56] (Fig. 5c) (sometimes a small signal around −90 ppm was detected, which was not due to either Ph_3SnEt, $\delta\ ^{119}Sn = -98$ ppm or to dimeric species $Ph_4Et_2Sn_2$, $\delta\ ^{119}Sn = -116$ ppm). A stannane/sodium ratio of 1:3 might result in favored formation of distannanes due to stoichiometric considerations (equation (2) in Fig. 1), and indeed a dominating additional signal at −116 ppm was observed in ^{119}Sn NMR spectra (Fig. 5c, identified by the accompanied tin satellites $^1J(Sn,Sn) = 3472$ Hz in other experiments), attributed to diethyltetraphenyldistannane (Table 6).

When dichlorodiphenylstannane was exposed to ten equivalents of sodium and subsequently converted with bromoethane, the main product was again diethyldiphenylstannane. But the additional sodium seemed to trigger the breakage of the tin–carbon bond, as the signals at −34 ppm and −98 ppm in the ^{119}Sn NMR spectra can be attributed to triethylphenylstannane (−34 ppm) and ethyltriphenylstannane (−98 ppm) [56,57]. A signal at −28 ppm could not be identified.

Table 4
^{119}Sn NMR data of the products resulting from conversion of a mixture of Bu_2SnCl_2/Na 1:4 with ^{13}C labeled bromoethane, $Br^{13}CH_2CH_3$.

			δ	$^1J(Sn,C)$	$^2J(Sn,C)$	$^1J(Sn,Sn)$
			ppm	Hz	Hz	Hz
Bu_3 **Sn** ($^{13}CH_2CH_3$)		d	−7.9	318.8		
Bu_2 **Sn** ($^{13}CH_2CH_3)_2$		t	−4.1	319.2		
Bu **Sn** ($^{13}CH_2CH_3)_3$		q	−0.6	319.3		
Bu_2 **Sn** ($^{13}CH_2CH_3$)–Bu_2 **Sn** ($^{13}CH_2CH_3$)		dd	−75.3	245.3	41.7	2580
Bu_2 **Sn** (a) ($^{13}CH_2CH_3$)–Bu **Sn** (b) ($^{13}CH_2CH_3)_2$	a	dt	−73.8	246.0	42.1	
	b	td	−69.1	245.3	41.4	
Bu_2 **Sn** ($^{13}CH_2CH_3$) OH		d	99.9	374.0		
Bu_2 **Sn** ($^{13}CH_2CH_3$)–O–Bu_2 **Sn** ($^{13}CH_2CH_3$)		d	90.1	374.9		
Bu **Sn** (a) ($^{13}CH_2CH_3)_2$–O–Bu_2 **Sn**(b) ($^{13}CH_2CH_3$)	a	t	90.4	375.4		
	b	d	90.6	374.6		

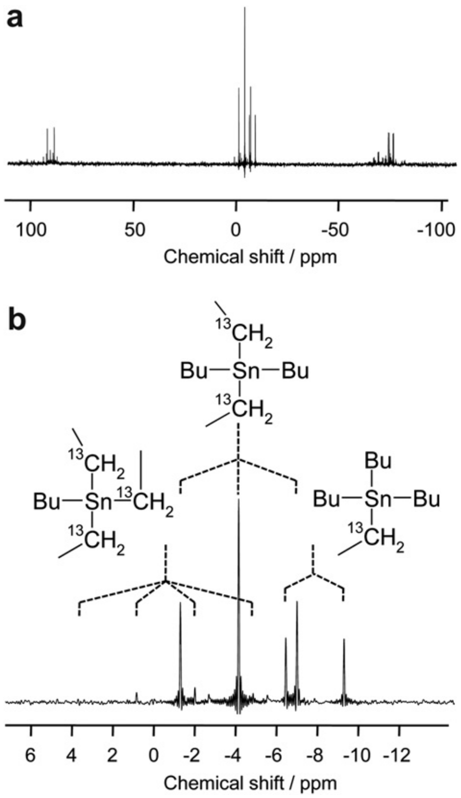

Fig. 6. a) ^{119}Sn NMR spectrum of the reaction products of dichlorodibutylstannane exposed first to 4 equivalents of sodium and then converted with Br^{13}CH$_2$CH$_3$, b) magnification of the region of the monostannanes.

3. Discussion

In the range of dichlorodiorganostannane/sodium ratios of 1:2 to 1:10 in liquid ammonia, polymers formed only at a ratio of 1:2, with all three stannanes investigated. The polystannanes with aliphatic side groups were accompanied by cyclic oligo(dialkylstannane)s, while no evidence for cyclic oligo(diphenylstannane)s was found. Indeed, polymer as well as cyclic oligomer formation agrees with a 1:2 ratio of dichlorodiorganostannane and sodium (cf. reaction scheme in Fig. 1). Already at a ratio of 1:3 formation of polymeric material was completely suppressed. Yet this does not necessarily imply that polymers never formed at this ratio, as macromolecules might have been generated in an early stage of the reaction and decomposed later.

Surprisingly, and in contrast to concepts advanced in the literature (see Introduction), the differences in the distribution of the *in-situ* formed products at dichlorodiorganostannane/sodium ratios of 1:3 to 1:10 were not significant. Stannides of the composition R$_2$SnH$^-$ were detected in all cases and dinuclear compounds of the type R$_4$Sn$_2$$^{2-}$ with R = butyl and R = phenyl. In any solution, there was no evidence for the presence of the frequently proposed SnR$_2$$^{2-}$ dianion. In fact, SnR$_2$$^{2-}$ is expected to act as a very strong base, which may readily be able to undergo an acid–base reaction with ammonia, thus forming NH$_2$$^-$ and R$_2$SnH$^-$. Therefore, it cannot be excluded that the detected R$_2$SnH$^-$ developed from very short-living SnR$_2$$^{2-}$.

Table 6
^{119}Sn NMR data of the products resulting from conversion of Oct$_2$SnCl$_2$/Na and Ph$_2$SnCl$_2$/Na mixtures with bromoethane.

	δ ^{119}Sn (ppm)		
Oct$_3$SnEt	−8.3	Ph$_3$SnEt	−34
Oct$_2$SnEt$_2$	−4.4	Ph$_2$SnEt$_2$	−65
OctSnEt$_3$	−0.7	PhSnEt$_3$	−98
Oct$_4$Et$_2$Sn$_2$	−75.7	Ph$_4$Et$_2$Sn$_2$	−116
Oct$_3$Et$_3$Sn$_2$	−70.1/70.2		
Oct$_2$Et$_4$Sn$_2$	−69.7		

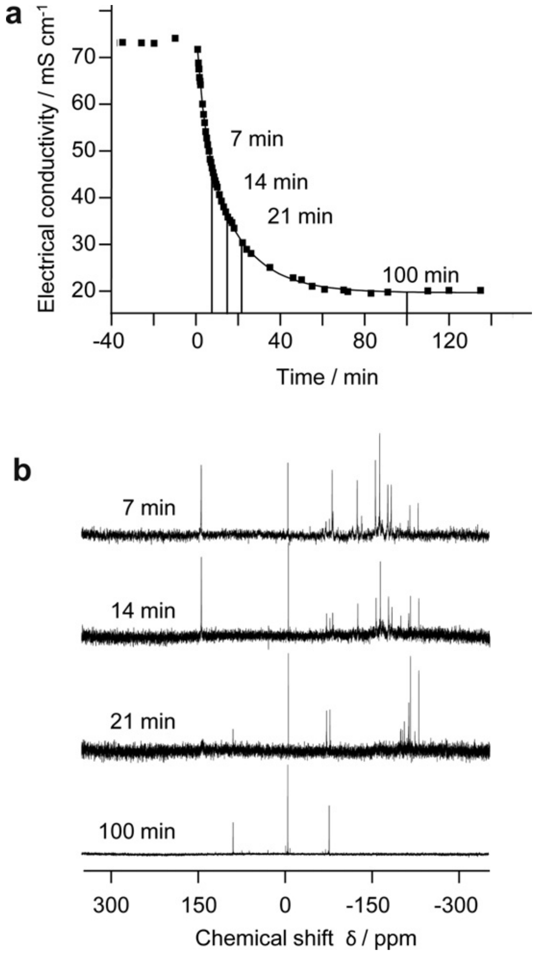

Fig. 7. a) Time-dependent conductivity of a mixture of dichlorodioctylstannane and four equivalents of sodium in liquid ammonia including marks at the times selected for addition of bromoethane. b) ^{119}Sn NMR spectra of the reaction products with bromoethane after the times indicated in Fig. 3a.

Migration of alkyl groups in the *in-situ* formed species was found to occur with butyl but not with octyl moieties. Also, formation of tetraalkyldistannides was observed with butyl but not with octyl groups. Obviously, octyl moieties impede both formation of dimers and alkyl group migration in liquid ammonia, which might be due to steric reasons.

Further, it is evident that, again in contrast to previous concepts proposed in the literature, the use of the reaction products of dichlorodiorganostannane with sodium as soluble intermediates for subsequent reactions with haloalkanes only allows limited conclusions about the nature of the intermediates. In particular the existence of the intermediate hydrodiorganostannides, R$_2$SnH$^-$ (which were present in all reaction solutions of dichlorodiorganostannanes with sodium) as well as the appearance of the dinuclear species R$_4$Sn$_2$$^{2-}$ in the *in-situ* reactions of dichlorodibutylstannane and dichlorodiphenylstannane with sodium were not reflected in the products arising after subsequent reaction with bromoethane. On the other hand, the chemical structure of the intermediates does not allow definite conclusions for the

Table 7
Quantities applied for the conversion of dichlorodiorganostannanes with 2 molar equivalents of sodium.

	sodium		R_2SnCl_2	
	mg	mmol	mg	mmol
Bu_2SnCl_2	151.5	6.59	1000.7	3.29
Ph_2SnCl_2	181.9	7.91	1360.5	3.96
Oct_2SnCl_2	227.0	9.87	2053.6	4.94

composition of the products emerging after subsequent reaction with bromoethane. For example, the presence of *in-situ* generated R_2SnH^- does not result in formation of tin hydrides after conversion with bromoethane. Also, solutions with virtually the same *in-situ* prepared products can lead to different reaction products after conversion with bromoethane if different ratios between dichlorodiorganostannane and sodium were initially present. Note that the formation of the detected *in-situ* formed products requires less than four equivalents sodium per dihalodiorganostannane, i.e. unreacted sodium was present at least in the case of four or ten equivalents. This leads to the conclusion that unreacted sodium is involved in the conversion of intermediate stannides with bromoethane.

Remarkably, even an excess of sodium is not able to cleave Sn–Sn bonds in $R_4Sn_2^{2-}$ (detected with R = butyl and R = phenyl), while subsequent cleavage of those Sn–Sn bonds after addition of bromoethane was observed - in particular when four equivalents of sodium per tin atom were present. This implies that bromoethane or reaction products of bromoethane, respectively, were involved in Sn–Sn cleavage. On the other hand, the occurrence of binuclear species in reaction products with bromoethane does not allow to conclude that the *in-situ* generated intermediate products also contained binuclear stannanes, as especially evident from the solutions with dichlorodioctylstannane/sodium 1:3, where Oct_2SnH^- dominated in the *in-situ* generated reaction solution, while binuclear species dominated after conversion with bromoethane.

However, an exchange of organic side groups in *in-situ* generated species was also reflected in the reaction products with bromoethane. Yet the reverse conclusion about side group exchange in *in-situ* generated species derived from the presence of side group exchange after exposure to bromoethane, is not valid. While considerable breakup of tin-carbon bonds happened during the reaction of dichlorodibutylstannane with sodium, exchange of phenyl groups was observed only after the reaction of bromoethane with the 1:10 mixture of dichlorodiphenylstannane/sodium; phenyl group exchange was not visible in the *in-situ* ^{119}Sn NMR measurements. This implies that exchange of phenyl groups took place simultaneously with the reaction of the *in-situ* generated intermediates with bromoethane.

As a consequence of the above considerations, conclusions regarding the composition of solutions of dichlorodioctylstannane and sodium at different reaction times by analysis of the reaction products observed after addition of bromoethane should be taken with care. These experiments may only indicate that numerous intermediates are formed initially which ultimately converge to few products.

Finally, it appears that the halogen atoms present in the system do not exert a pronounced influence on the product distributions. Substitution of dichlorodibutylstannane by dibromodibutylstannane did not change, considerably, the course of the conductivity of reaction solutions with four equivalents sodium (Fig. 2a), and there was no fundamental alteration in the reaction products after subsequent conversion with bromoethane. Moreover, when bromoethane was substituted by iodoethane added to reaction solutions of dichlorodibutylstannane and four equivalents of sodium, product formation essentially did not differ.

4. Conclusions

Reaction of dichlorodiorganostannanes with two equivalents of sodium in liquid ammonia resulted in the formation of polystannanes, which were accompanied by cyclic byproducts in the case of the alkylstannanes. However, conversion of dichlorodiorganostannanes with three to 10 molar equivalents of sodium yielded soluble intermediates. Instead of the frequently proposed R_2Sn^{2-} dianions [4,5,12,17,26,29,30], R_2SnH^- and in the case of R = butyl and R = phenyl also dinuclear species of the type $R_4Sn_2^{2-}$ emerged. These species did not allow reliable conclusions about the reaction products resulting from exposure to bromoethane and *vice versa*. Migration of organic groups in *in-situ* formed reaction products was reflected also in products resulting after conversion with bromoethane, while the reverse conclusion was not true. Finally, when *in-situ* formed reaction products are employed as intermediates for the preparation of tetraorganostannanes by conversion with haloalkanes, a large number of products can arise when the haloalkanes are added before that equilibrium is reached.

5. Experimental

5.1. Materials

Ammonia was purchased from PanGas (Dagmarsellen, Switzerland, 99.999%), dichlorodibutylstannane, dichlorodioctylstannane from ABCR GmbH (Karlsruhe, Germany) and dichlorodiphenylstannane from Sigma Aldrich (Buchs, Switzerland). All substances were recrystallized twice by dissolving in boiling pentane and subsequent precipitation of the products at 200 K. Bromoethane was purchased from Acros Organics (Basel, Switzerland), $Br^{13}CH_2CH_3$ and deuterated dichloromethane (99.9% D) from Cambridge Isotope Laboratories (ReseaChem GmbH, Burgdorf, Switzerland), and organic solvents from Fluka (Buchs, Switzerland).

5.2. Methods

^{119}Sn NMR spectra were recorded with a Bruker UltraShield 300 MHz/54 mm Fourier-transform spectrometer at a frequency of 112 MHz with either inverse-gated decoupling or without decoupling, as indicated in the text. In both cases a delay time of 0.5 s, an acquisition time of 0.1 s and a pulse angle of 3 μs (90°) were applied. The sweep width was 700 ppm with a 16 k data point acquisition range resulting in a digital resolution of 4.78 Hz. Chemical shifts (δ) are reported in ppm referred to tetramethylstannane ($\delta(Me_4Sn) = 0$ ppm).

Electrical conductivity measurements in liquid ammonia solutions were performed with a TetraCon 325/Pt electrode from WTW (Weilheim, Germany) in combination with a WTW MultiLab 540 instrument. A 100 mL three-neck flask was filled to the top with ammonia (about 150 mL) to ensure complete coverage of the electrodes. After ~200 mg of sodium were dissolved in the ammonia the conductivity cell was immersed under nitrogen counter flow. The dichlorodiorganostannanes were introduced through the side necks of the flask and the conductivity monitored as a function of time. Conductivity was recorded during the reaction of dichlorodiorganostannanes with 4 molar equivalents of sodium until a plateau value was reached. At this stage of the reaction only soluble products were present.

Elemental analysis was performed by the Microelemental Analysis Laboratory of the Department of Chemistry at ETH Zürich.

Gel permeation chromatography was performed with a Viscotek VE7510 equipped with degasser, VE1121 solvent pump, VE520 autosampler and Model 301 triple detector array. A PL gel 5 μm Mixed-D column from Polymer Laboratories Ltd. (Shropshire, United Kingdom) was used, calibrated with poly(styrene) standards.

Liquid ammonia was condensed in a three-neck flask with flat bottom equipped with a magnetic glass-coated stirring bar (Teflon-coated stirring bars were attacked by the sodium) that was evacuated, flame-dried and flushed with nitrogen three times. A cold finger condenser equipped with a calcium chloride drying tube was mounted under nitrogen counter flow and was flushed with nitrogen for another 10 min. Subsequently the ammonia gas bottle was connected via a plastic tube, which was flushed with ammonia for 30 s. The nitrogen flow was arrested and the equipment was flushed with ammonia for 5 min. The drying tube outlet was closed with a balloon before the cold finger condenser was filled with a dry ice/isopropanol mixture. Also, the reaction vessel was surrounded by a dry ice/isopropanol bath to cool the condensed ammonia to 200 K. When the desired amount of ammonia was condensed (90 mL for NMR experiments and 150 mL for conductivity measurements), the ammonia flow was stopped, a smooth nitrogen flow restarted and the apparatus was opened by removing the balloon.

5.3. Reactions

5.3.1. Preparation of reaction mixtures for in-situ NMR investigations

For reactions of dichlorodibutylstannane and dichlorodiphenylstannane typically 8 mmol of sodium were introduced in a nitrogen counter flow into 90 mL condensed ammonia and dissolved by stirring for 15 min to result in a homogeneous blue solution. Thereafter 2.67 mmol, 2 mmol and 0.8 mmol respectively of dichlorodiorganostannane dissolved in 1 mL THF were slowly added. The color changed from blue to dark red. The mixtures were stirred for 30 min in order to complete the reactions and subsequently transferred via a bended glass tube directly into precooled (200 K) and dried NMR tubes (Type 5UP 5 × 178 mm; ARMAR AG, Döttingen Switzerland) equipped with a sealed capillary with deuterated dichloromethane. The transfer was performed with nitrogen overpressure and argon counter flow by carefully excluding oxygen. The filled NMR tubes were flushed with argon and stored at 200 K before they were inserted into the precooled NMR spectrometer.

To avoid precipitation during the transfer to the NMR tube, the applied concentration of dichlorodioctylstannane was significantly lower than in the cases of the other two dichlorodiorganostannanes. 2 mmol sodium were dissolved in liquid ammonia by stirring for 15 min and subsequent addition of 0.67 mmol (1:3 ratio) or 0.5 mmol (1:4 ratio) dichlorodioctylstannane. The mixtures with the 1:10 ratio were prepared by dissolving 4 mmol sodium together with 0.4 mmol dichlorodioctylstannane. Besides the differences in concentration, the reaction was performed as described above for the other stannanes.

5.3.2. Reactions with 2 molar equivalents of sodium

About 8 mmol sodium (detailed quantities see Table 7) were stirred in 90 mL liquid ammonia at 200 K for 15 min to obtain a homogeneous solution. The flask was wrapped with white soft tissue and aluminum foil to exclude light and 4 mmol of the respective dichlorodiorganostannane dissolved in 10 mL THF were added dropwise to the sodium solution under continuous stirring, whereupon the deep blue color disappeared and a yellow precipitate formed. After about 2 min, the ammonia was removed under a constant nitrogen flow by warming the flask to room temperature, and THF was evaporated at room temperature *in vacuo* (0.1 mbar, 12 h). For gel permeation chromatography (GPC) analysis the obtained material was dissolved in tetrahydrofuran (THF); this solution was directly used after filtration with syringe filters (0.45 μm PTFE filters). The residues stemming from the reactions of the different stannanes were further processed as follows:

5.3.2.1. Dichlorodibutylstannane. The residue was dissolved in 50 mL dichloromethane and the insoluble parts (sodium chloride) were filtered off. Subsequently the solvent was removed in a rotary evaporator and the product dried *in vacuo* (0.1 mbar, 24 h). Elemental analysis (in % w/w, in brackets values calculated for $(SnBu_2)_n$): C 40.75 (41.25), H 7.56 (7.79).

5.3.2.2. Dichlorodioctylstannane. The remaining product was dissolved in 50 mL dichloromethane, filtered off to remove insoluble NaCl, the solvent was thereafter removed in a rotary evaporator and the product dried *in vacuo* (0.1 mbar, 24 h). Elemental analysis (in % w/w, in brackets values calculated for $(SnOct_2)_n$): C 55.15 (55.68), H 9.17 (9.93).

5.3.2.3. Dichlorodiphenylstannane. The resulting product was washed with 50 mL of a water/ethanol (9:1) mixture until no chloride could be detected in the washing solution (usually 3–4 times, until the addition of 5 mL saturated $AgNO_3$ solution did not lead to the visible formation of AgCl precipitates). Then, the material was washed three times with 50 mL dichloromethane, and finally the product was dried *in vacuo* (0.1 mbar, 24 h). Elemental analysis (in % w/w, in brackets values calculated for $(SnPh_2)_n$): C 51.79 (52.81), H 3.76 (3.69).

5.3.3. Reactions of organostannide intermediates with bromoethane

In a typical reaction, 218 mg of sodium (9.45 mmol) were dissolved in 90 mL liquid ammonia and stirred for 15 min. Thereafter 720.9 mg of dichlorodibutylstannane (2.37 mmol, or other dichlorodiorganostannanes, respectively) dissolved in 5 mL tetrahydrofuran (THF) were added. The deep red mixture of dichlorodiorganostannanes and sodium was transferred after establishment of the equilibrium (30 min for dichlorodibutylstannane and dichlorodiphenylstannane, 90 min for dichlorodioctylstannane) via bended glass tubes by nitrogen overpressure directly into a 100 mL 2-neck round bottom flask containing a stirred solution of 5 mL bromoethane diluted with 20 mL THF kept at 200 K. The solution instantaneously turned colorless and a white precipitate formed. The ammonia was evaporated by warming the reaction mixture to room temperature in a nitrogen flow, and THF was removed at room temperature *in vacuo* (about 0.1 mbar). The reaction products were dissolved in deuterated dichloromethane and analyzed by means of ^{119}Sn NMR spectroscopy.

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