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Synthesis and Characterization of Novel Aryltin Trichlorides - and Trihydrides: Precursors for Polyarylstannanes

Master Thesis

Thesis Submitted to the Faculty of Chemistry, Chemical- and Process Engineering in Partial Fulfillment of Requirements for the Degree of

Master of Science

in Chemistry at the University of Technology Graz

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2012

Dedicated to my Parents

Wir konstruieren und konstruieren. Dabei ist Intuition noch immer eine gute Sache.

(Paul Klee)

Danksagung

Hiermit will ich die Chance ergreifen, all jenen Menschen Danke zu sagen, die für das erfolgreiche Zustandekommen dieser Arbeit einen essentiellen Beitrag lieferten und deren Unterstützung maßgeblich zum Gelingen beigetragen hat.

Mein primärer Dank geht an meinen Betreuer Frank Uhlig, der mir die Möglichkeit gab diese Masterarbeit in seiner Arbeitsgruppe verfassen zu können und mir hierbei mit professionellen, fachlichen Ratschlägen, aber auch durch optimistischen und motivierenden Zuspruch zur Seite stand.

Natürlich geht mein Dank auch an alle Mitglieder der AG Uhlig, die durch das angenehme Arbeitsklima, ihre Hilfsbereitschaft und den Wissensaustausch viel zum erfolgreichen Heranwachsen dieser Arbeit beigetragen haben. Hierbei soll aber ein ganz spezieller Dank meiner Arbeitskollegin und Freundin Kristina Schrempf zukommen, die durch ihre die Freundschaft, Menschlichkeit und Unterstützung die letzten Monate zu etwas ganz Besonderem für mich gemacht hat. También, me gustaría darle las gracias a Ana Torvisco por su ayuda profesional y su paciencia. Con todo esto mi trabajo ha sido más completo.

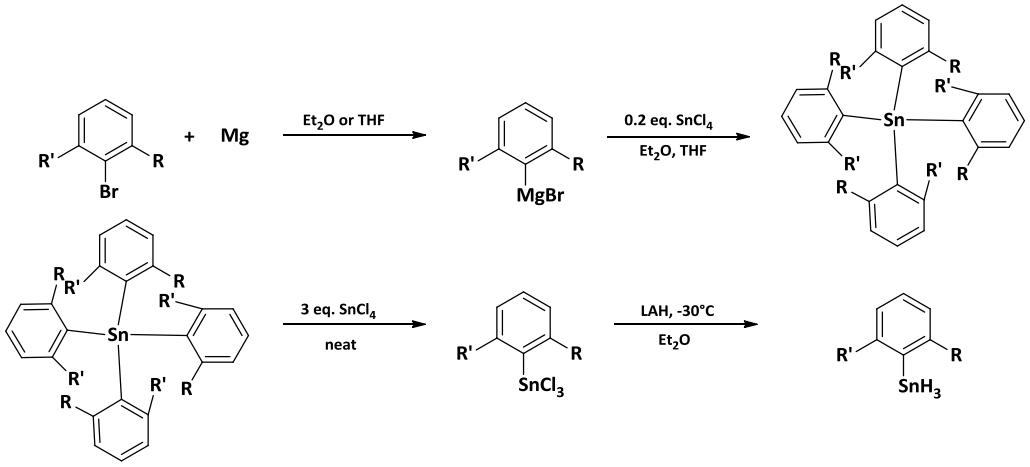
Jedoch gilt mein größter Dank meinen Eltern Carmen und Edmund Zeppek, die mir die Möglichkeit gaben dieses Studium zu beginnen und mich fortwährend nicht nur finanziell, sondern auch emotional unterstützten. Ebenso möchte ich mich bei zwei sehr besonderen Menschen in meinem Leben bedanken. Einerseits bei Bartholomäus Pieber für die immerwährende, liebevolle und aufbauende Unterstützung in den letzten Jahren und andererseits bei Eva Fischereder, für ihre Freundschaft und den Zusammenhalt, welche mein Leben bereichern. Ihr beide helft mir den Blick auf die wesentlichen Dinge nicht zu verlieren.

Weiters will ich auch all meinen Studienkollegen danken durch deren Zutun und Wissensaustausch der erfolgreiche Abschluss dieses Studiums erst möglich wurde. Sie machten die Studienzeit zu einem wunderbaren Lebensabschnitt.

Abstract

This works deals with the synthesis and characterization of novel aryl trichloro- and trihydridostannanes and initial polymerization attempts of the latter in the presence of TMEDA *via* dehydrogenative coupling.

Various *ortho*-substituted aryl trichlorostannanes were synthesized (*o*-tolyl, 2,4-xylyl, 2,6-xylyl, 1-naphthyl) by standard preparation protocols serving as starting materials for the generation of the corresponding tin trihydrides (see scheme below).



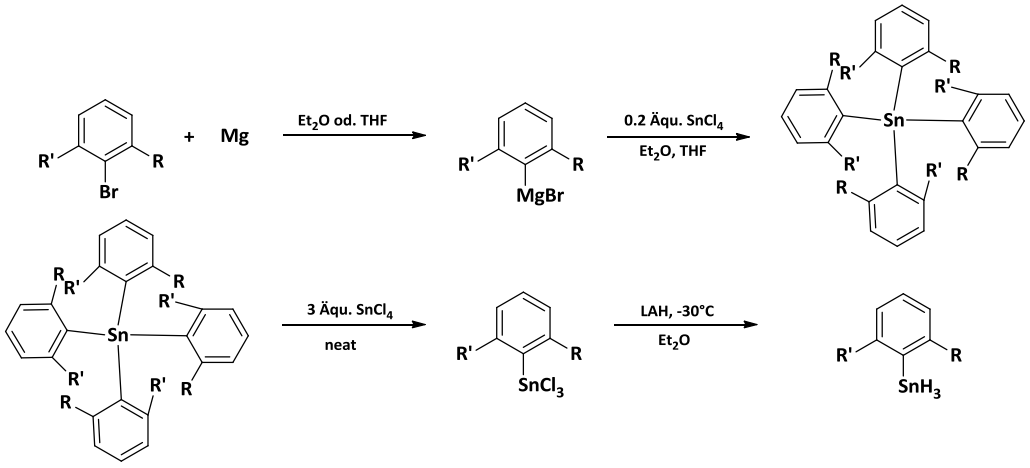
R= organic moiety
R'= H, organic moiety

The polymerization behavior of the hitherto undisclosed aryl trihydridostannanes was investigated. Dehydrogenative coupling led to a black, amorphous solid, which was insoluble in common organic solvents. Elemental analysis as well as EDX measurements displayed a carbon/ hydrogen/ tin ratio which suggested a polymer composition of $(R_{0.95}Sn)_x$. However, further investigations concerning the polymer properties have to be carried out.

Kurzzusammenfassung

Die vorliegende Arbeit beschäftigt sich mit der Synthese und Charakterisierung von neuartigen Aryltrichlor- und trihydridostannanen, wobei zweitere ersten Polymerisationsversuchen mit TMEDA in Form einer dehydrogenierenden Kupplung unterzogen wurden.

Die Synthese von in mindestens *ortho*-Position des aromatischen Rings substituierten Aryltrichlorstannanen (*o*-tolyl, 2,4-xylyl, 2,6-xylyl, 1-naphthyl) erfolgt nach Standardmethoden. Diese fungierten in weiterer Folge als Ausgangsmaterial für die Herstellung der Zinntrihydride (siehe Reaktionsschema).



R= organischer Rest
R'= H, organischer Rest

Weiters wurden Untersuchungen über das Polymerisationsverhalten der bisher literaturunbekannten Zinntrihydride angestellt. Dehydrogenierende Kupplung führte zur Bildung von schwarzen, amorphen Feststoffen, die in gängigen organischen Lösungsmitteln unlöslich waren. Elementaranalyse und EDX-Messungen zeigten ein Kohlenstoff-/ Wasserstoff-/ Zinnverhältnis, welches eine Polymerzusammensetzung von $(R_{0.95}Sn)_x$ vermuten ließ. Weitere Untersuchungen bezüglich der Polymereigenschaften sollen im Fokus zukünftiger Forschung liegen.

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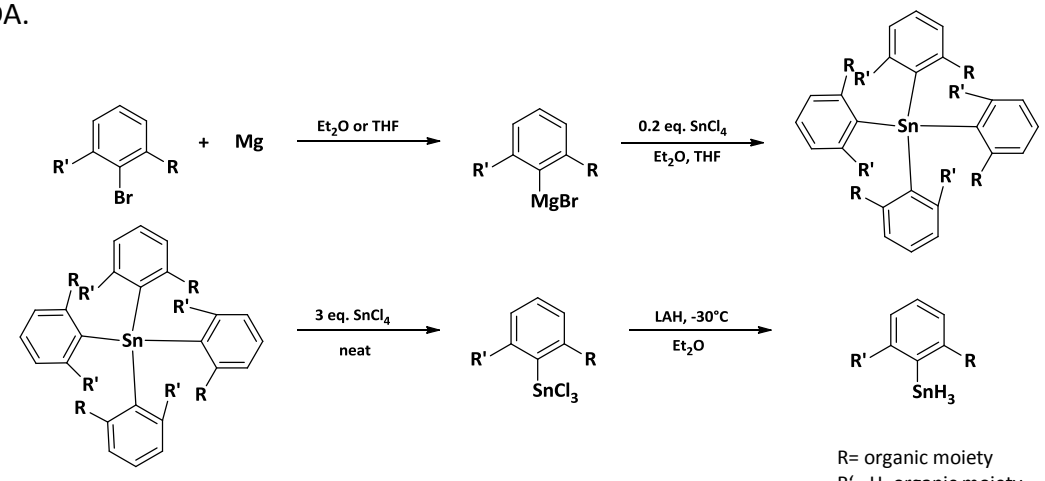
1 Introduction

Since the Bronze Age (3500 BC), which was one of the milestones in the evolution of mankind, tin has been a highly appreciated metal and raw material for further processing. But when Frankland[1,2] first described the successful synthesis of an organotin compound shortly after Cadet[3] and Zeise[4] had been established as the pioneers in metallorganic chemistry, much attention had been drawn to the organic derivatives of tin, especially to tetra coordinated ones. More advanced analytical techniques including Sn-NMR, X-ray diffraction or appropriate computational methods were implemented helping organotin chemistry to be a growing field of interest. Besides being used as fungicides, insecticides or stabilizers in PVC, organostannanes are currently widely used in chemical synthesis. They exhibit dominance in many homolytic mechanisms, where in particular, organotin hydrides are the main used agents for performing ring-closing cyclizations. Nevertheless, due to the acute toxicity of organo substituted tin compounds their use in synthetic chemistry was conotated quite negatively.

Apart from the afore mentioned use of tinhydrides, they have been investigated as monomers for polystannane synthesis in order to generate materials harboring outstanding electronic properties related to their metallic “tin-wire backbone”. Only a limited knowledge is available about the polymerization of dialkyl as well as diaryltin dihydrides. The synthesis of higher hydride functionalized derivates (tin trihydrides), as well as investigations on their polymerization behaviour has been neglected.

The focus of this work lies on the synthesis and characterization of novel organotin trihydrides (Scheme below) as well as their intial polymerization attempts in the presence of TMEDA.

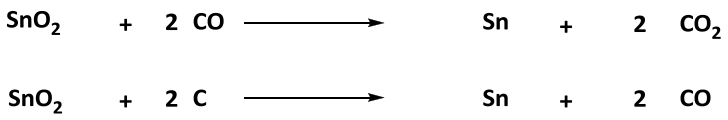


R= organic moiety
R‘= H, organic moiety

2 Literature Overview

2.1 Tin in a General Approach: Sources, Industrial Production, Application

As already mentioned before, Sn and its ubiquitous uses have been known and appreciated since its discovery in about 3500 BC. The major source of Sn can be found in the earth's crust with an abundance of 2 ppm, which in comparison to Zn, Pb or Cu is scarce. In order to gain Sn in its elementary form the, preferred extraction technique is the reduction of cassiterite (SnO_2) using carbon monoxide or carbon as a reducing agent at elevated temperatures as shown below (Scheme 1).[5,6]



Scheme 1: Preparation of metallic tin from cassiterite

Apart from being generated from natural sources, tin is also recycled from used food and drink cans. As major tin producing countries, China and Indonesia can be mentioned. Table 1 shows the tin production and reserves in the year 2009 and 2010 worldwide.

Table 1: Worldwide production of tin[7]

	mine production [t]		**reserves [t]**
	2009	2010	
United States	0	0	0
Australia	1400	2000	180000
Bolivia	19000	16000	400000
Brazil	13000	12000	590000
China	115000	115000	1500000
Congo (Kinshasa)	9400	9000	NA
Indonesia	55000	60000	800000
Malaysia	2380	2000	250000
Peru	37500	38000	710000
Portugal	30	100	70000
Russia	1200	1000	350000
Thailand	120	100	170000
Vietnam	3599	3500	NA
other countries	2000	200	180000
world total	260000	261000	5200000

Approximately 50% of the produced tin is used as solderin material, which can be explained by the high demand in the production of the growing field of telecommunication devices. Herein, tin exchanges the heavy use of its toxic homologue, lead. About 20% of the production belongs to the generation of tinplates, which before were used intensively for the fabrication of cans. Only about 14% of the tin occurrence is used for the elaboration of basic chemicals subjected to further chemical conversion. In addition, occurrence of tin in glass and brass and bronze makes up 2 and 6% respectively.

Table 2 illustrates the use of organotin compounds in industrial applications.[8]

Table 2: Industrial applications of organotin compounds

industrial application	**function**	**OTC**
PVC stabilizer	stabilization against decomposition by heat and light	R_2SnX_2 and $RSnX_3$
antifouling paints	biocide	R=Me, Bu, Oct R_3SnX
Agrochemicals	fungicide, instecticide, miticide, antifeedant	R=Bu, Ph R_3SnX, , $RSnX_3$ R=Me,Bu
wood preservation, glass treatment	precursors for tin (IV) oxide films on glass	Me_2SnX_2
materials protection (stone leather, paper)	fungicide, algicide, bactericide,	Bu_3SnX
impregnation of textile	insecticide, antifeedent	Ph_3SnX
poultry farming	dewormer	Bu_2SnX_2

Interestingly, tin in its metal form and its metallorganic derivatives exhibit a wide range of different and important applications including as stabilizers, industrial catalysts, industrial and agricultural biocides, fungicides, wood-preserving and anti-fouling agents, surface disinfectants, slimicides, laundry sanitizers or hospital and veterinary disinfectants.[9,10]

2.2 Toxicity of Organotin Compounds

Due to the increased production of tin organometallic derivatives for commercial uses during the last 50 years, concerns regarding their toxicity have become prevalent specifically regarding the penetration of worldwide ecosystems and their persistence in the latter. Currently, a wide span of different organotin compounds is known and aside from methyltins, which are generated during biomethylation, these do not stem from anthropogenic origin.[11] While tin in its metal form is not considered to exhibit harmful effects on the environment the toxicological aspect of their organic derivatives is quite complex.[8] Since the biocidal properties of the latter were described in detail by van der Kerk and Luijten[12,13] in the late 1950s it is known that derivatives of R_3SnX, the trialkyl, -triaryl tin hydroxides and tin salts harbor the highest fungitoxicity. The toxicity only depends on R (hydrocarbon radical residue) and not on X, as long as X itself is not a toxic compound.

Hence, the biological effects strongly depend on both, the nature and the size of the organic moiety, resulting in a more or less cationic tin species, which is indeed highly toxic. Therefore, the maximum toxicity level is reached regarding trisubstituted compounds $R_nSnX_{4-n.}$[8] So the toxicity towards organisms decreases as followes: $R_3SnX > R_2SnX_2 > RSnX_3$.[14] However, according to Smith, triethyltin acetate can be seen as the most toxic organostannane for mammals, with an LD_{50} value of 4mg/kg in rats.[15]

Much attention has been drawn to the extended toxicity of TBT (tributyltin hydride) as a water pollutant, as well as contaminating sediments, because of its harmful effect on the aquatic life and terrestrial ecosystems.[16] But also bioaccumulation and persistence in the environment is one major criterion regarding the toxicity of organstannanes due to their lipophility.[17] Apart from bioaccumulation, the persistence of organotin compounds, especially regarding butyltins is an environmental issue.[18]

Figure 1 illustrates the distribution and fate of those environmental contaminants.

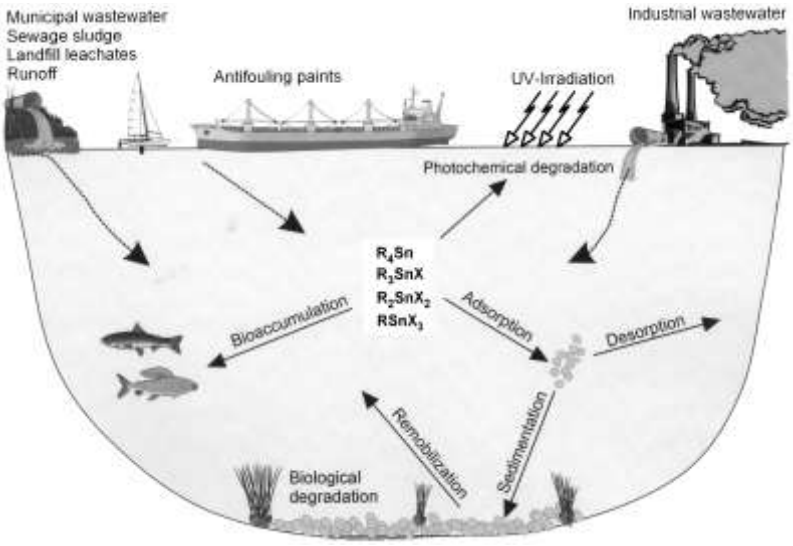
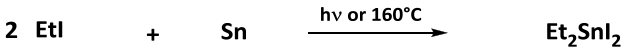


Figure 1: Distribution and fate of OTC as pollutants in the aquatic environment [8]

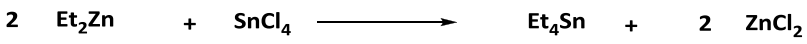
2.3 The History of Organotin Compounds

Organotin compounds or organostannanes are chemical compounds containing at least one Sn-C bond. The first organotin compound described in literature was published by Frankland more than 160 years ago synthesized by heating up ethyl iodide in the presence of metallic tin leading to a yellow oily fluid (Scheme 2).[1,2]



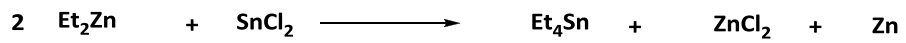
Scheme 2: Synthesis of the first organo stannane (direct method)

Subsequently, Buckton[19] generated tetraethyltin on the so-called indirect route, in comparison to Scheme 2, by treating tin(IV) chloride with diethylzinc (Scheme 3).



Scheme 3: First indirect method synthesizing tetraalkyl stannanes

Replacement of tin(IV) chloride tin(II) chloride improved the indirect route due to easier handling of the starting material and reaction ongoing in a more controllable fashion (Scheme 4).

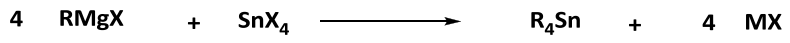


Scheme 4: Improvement of the indirect route by Frankland

With the discovery of organomagnesium halides in ether solution, by Grignard in 1900 the synthetic scope for organostannanes was widely broadened. Pope and Peachey[20] showed an improved application for Grignard reagents realizing the formation of several simple and mixed tetraalkyl tin derivatives and Pfeiffer *et al.* generated arylstannanes.[21,22]

2.3.1 Tetra Organostannanes R_4Sn

The most known and used protocol for generating tetra organostannanes is the reaction of the appropriate Grignard reagent RMgX or the organolithium compound with a tin halide, in most cases tin(IV) chloride (Scheme 5).[23-34] Usually the used solvent is ether, dibutyl ether or tetrahydrofuran.

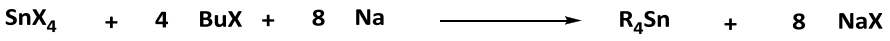


Scheme 5: Grignard Reaction generating tetra organostannanes

By using an excess of the Grignard reagent the reaction is driven to full conversion but might contain R_3SnX as a side product. Hence, using the Grignard route, tetravinyl[35], tetrallyl[36-38], tetraalkyl[27-33] and tetraaryl stannanes[22,39-42] are easily prepared up to 90% yield and higher. An interesting procedure was described by Kipping and Smith generating tetra organostannanes without preparation of the Grignard reagent, adding the organic halide to magnesium powder and tin(IV) chloride in ether.[43] This reaction procedure was further discussed in the literature, whereby ether frequently was replaced by hydrocarbon solvents.[44-47]

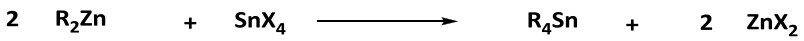
For tetraalkyl organostannanes with alkyl moieties longer than C_4, the Grignard way might not be the reaction pathway of choice concerning the yields. In that case, a Wurtz-type

coupling reaction of $SnCl_4$ with a sodium-tin alloy in a hydrocarbon solvent is more successful as shown by van der Kerk and Luijten, generating the butyl derivative in relatively high yields, but with difficult to control reaction conditions and distannanes as side products (Scheme 6).[48,49]



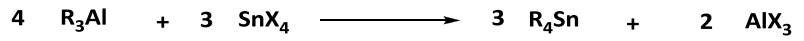
Scheme 6: Wurtz-type coupling generating tetraalkyl organostannanes

Lithiation of the organohalide and treatment with SnX_4 turned out to be a suitable route for tetraarylstannanes[23] and Me_4Sn[50]. However, product yields for this approach can be declared as rather low due to distannane formation as a side reaction. Concerning the preparation of tetraaryltins, diarylzinc reagents have proven to be more successful, since in this transarylation reaction no formation of distannanes can be detected and therefore diphenylzinc results in Ph_4Sn in higher than 90% yield (Scheme 7).[51]



Scheme 7: Preparation of tetraorgano stannanes using diorgano zinc reagents

Also, by employing triorganoaluminium reagents, distannane formation can be avoided (Scheme 8).[52,53] Today R_3Al in generally is used in the industrial preparation of tetraalkyltins.



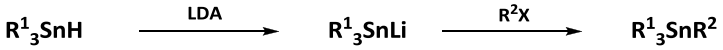
Scheme 8: Preparation of tetraorgano stannanes using triorgano aluminium reagents

Carrying out the reaction using stoichometric amounts of $SnCl_4$ and R_3Al the tetraaryl compound is only obtained with about 10% yield, while the remaining product can be assigned as stable complexes $R_2SnCl_2(AlCl_3)$, $R_3SnCl(AlCl_3)$. Hence, an excess of R_3Al is necessary to gain complete alkylation. To overcome this disadvantage, Sundermeyer and Verbeek introduced a modified method of preparing the alkylating agent $Na[AlMeCl_3]$ in one step, which then reacts in a quantitative way with $SnCl_4$ to afford $SnMe_4$ with 95% yield.[54]

All so far mentioned techniques can be performed with the use of $SnCl_4$, whereas organotin halides can be applied as described by Sisido and Kozima (Scheme 9).[55]

Scheme 9: Generating R_4Sn by reduction of the dichloride with a metal

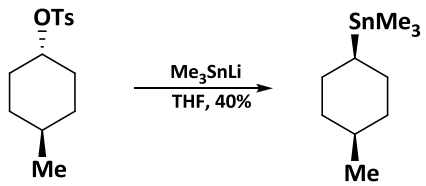
Alternatively, a trialkyl or triaryltin hydride can be transformed into a nucleophile by deprotonation with a strong base, e.g. LDA generating an anionic tin species which further displaces halides to afford tetraalkyl tins (scheme 11).[56-58]



Scheme 11: Nucleophilic attack of a deprotonated tin species generating tetraorgano stannanes

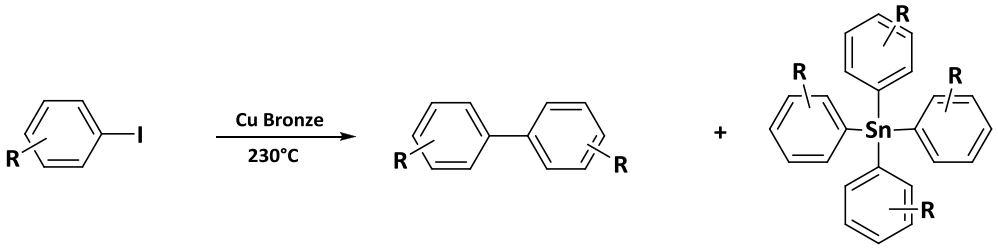
Competition between an S_N2 mechanism and radical processes are considered to be responsible for complete inversion of the configuration using Ph_3SnM as an educt as illustrated in scheme 12. Not limited to halides, also the well known leaving group tosylate is displaced under full inversion (Scheme 13). However, leaving groups other than Tos and halides have found limited use.

Scheme 12: Displacement of a halide with Me_3SnLi under full inversion



Scheme 13: Displacement of a tosylate with Me_3SnLi under full inversion

More recently, in 2006 Shaikh *et al.* discovered that the traditional known Ulmann coupling reaction conditions can be modified by not just using copper but an activated copper bronze (9:1 mixture of copper and tin) in order to obtain tetraaryl stannanes along the production of substituted biaryls.[59]

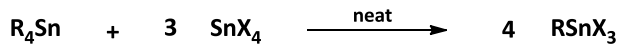


Scheme 16: Ulmann coupling using copper bronze generating tetraaryl stannanes

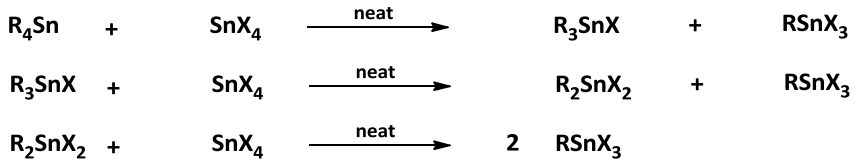
Regarding this work, tetraorgano stannanes are important precursor for the synthesis of $RSnX_3$ compounds (see chapter 2.3.2).

2.3.2 Monoorganotin trihalides $RSnX_3$

Among the organotin halides, the compounds $RSnX_3$ tend to undergo a second substitution, so methods using $SnCl_4$ with an organometallic reagent like RMgX or RLi are not ideal.
However, Kozeschkow described one of the first methods for successful preparation of $RSnX_3$ compounds in the 1930s starting from the corresponding tetraaryl stannane subjecting it to a redistribution reaction with a tin tetrahalide at elevated temperatures without the use of solvents.[60-63] Scheme 17 shows the overall reaction, which in fact consists of three consecutive redistribution reactions including R_2SnX_2 as an intermediate (Scheme 18).

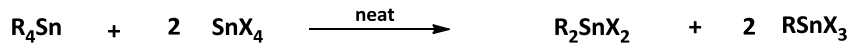


Scheme 17: Overall reaction sequence for the Kozeschkow redistribution reaction generating $RSnX_3$



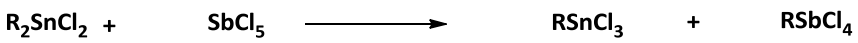
Scheme 18: Kozeschkow redistribution reaction proceeding in three steps

However, this reaction sequence is limited to the R-moieties like vinyl[64,35], phenyl[65,66], mesityl[67], allyl[36-38] and acryl[68] esters, because the third redistribution reaction fails using alkyl substituents. For that reason monoalkyltin halides are generated using a modification of the latter, affording R_2SnX_2 and the desired product $RSnX_3$ in an one to two ratio (Scheme 19).



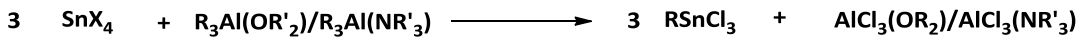
Scheme 19: Preparation of monoalkyl tinhalides *via* Kozeschkow redistribution reaction

Applying a related distribution reaction where Me_2SnCl_2 is treated with $SbCl_5$, $MeSnCl_3$ can be generated. However, it was found out that for R=Ph $SbCl_5$ is too strong Lewis acid, so that the phenyl group is more likely to be transferred from the tin to the antimony to resulting in Ph_2SbCl_3. This disadvantage can be avoided by using a less strong acid like BCl_3 (Scheme 20).[69]



Scheme 20: Preparation of $MeSnCl_3$ using $SbCl_5$

As already reported in chapter 2.3.1, the synthesis of R_4Sn compounds can be achieved by using aluminium trialkyls to substitute the $SnCl_4$. Müller and Buschhoff[70] described that R_3Al also displays a convenient agent for the monoalkylation of $SnCl_4$. In order to minimize the alkylating effect of the aluminum reagent, an ether or tertiary amine complex is build up which subsequently reacts with $SnCl_4$ yielding in $RSnCl_3$ (R=*n*-butyl or octyl) up to 90% (Scheme 21).

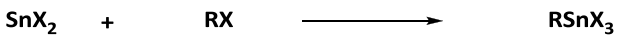


Scheme 21: Monoalkylation of tin(IV) chloride using R_3Al complexes

In this manner alkyltrichloro stananes like R= *n*-butyl or octyl can be synthesized in yields up to 90%.

In comparison to the less selective organolithium and Grignard reagents, mesitylcopper $[CuMes]_5$(toluene), described by Jäkle and Manners, easily and selectively reacts with $SnCl_4$ resulting in $MesSnCl_3$ with 92% yield.[71]

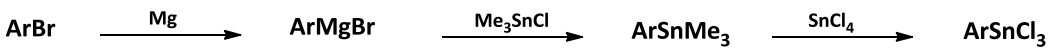
Furthermore, an oxidative addition of a tin(II) halide provides a convenient and selective one-step method preparing monoorganotin trihalides (Scheme 22).



Scheme 22: Preparation of $RSnX_3$ *via* oxidative addition

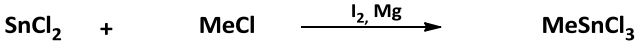
Janiak and Schwichtenberger[72] described the selective addition using pentaphenylcyclopentadienyl as an organic substituent, but in other cases the reaction does not proceed selectively. For that reason, catalysts like primary amines, organic disulfides, quarternary ammonium halides, and trialkylantimony have to be applied to obtain reasonable yields of $RSnCl_3$.[73]

The Grignard route was used by Elhamzaoui to prepare an arylmagnesium bromide which was then treated with trimethyl tinchloride to obtain a mixed tetraorgano stannane. Since alkyl groups are more likely to be exchanged, further conversion with $SnCl_4$ leads to the corresponding aryltrichloro stannane (Scheme 23).[74]



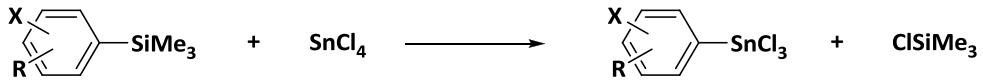
Scheme 23: Synthesis of $ArSnCl_3$ on the Grignard route *via* $ArSnMe_3$ as an intermediate

Moreover, Matsuda and co-workers published a protocol generating Me_3SnCl by reacting MeCl and $SnCl_2$ in the presence of a small amount of I_2 and magnesium in 95% yield (Scheme 24).[75]



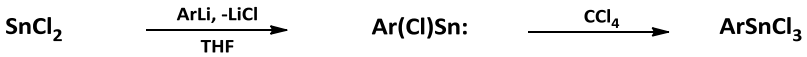
Scheme 24: Oxidative addition of tin(II) chloride in the presence of iodide and magnesium

Lazarev reported the selective cleavage of a Si-C induced by $SnCl_4$ affording the corresponding $ArSnCl_3$ compound (Scheme 25).[76]



Scheme 25: Selective cleavage of a Si-C bond with $SnCl_4$

An additional interesting route for the preparation of aryltrichloro stannanes is the *in-situ* generation of a chlorostannylene by treating the lithiated arylcompound with tin(II) chloride and subsequent reduction with CCl_4 as illustrated in Scheme 26. Saito described the reaction for R= terphenyl with a yield of 45%.[77]

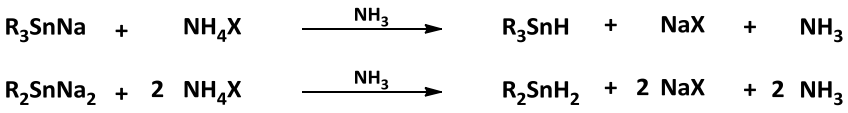


Scheme 26: Generating $ArSnCl_3$ *via* a tin(II) intermediate

2.3.3 Organotin Hydrides R_nSnH_x

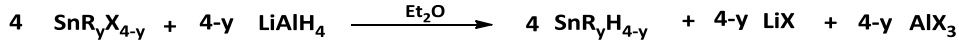
Hydrides of the elements in the group 14 become increasingly unstable the heavier the homologue becomes. Organotin hydrides are organic derivatives of stannane, in which at least one hydrogen is replaced by an organic group. By increasing substitution of a hydrogen by an organic moiety, stability is greatly improved.

Although Paneth[78] was first in describing stannane SnH_4, as well as taking into account the investigation on elements of group 14 generating hydrides in 1920, the preparation of organic derivatives received little attention. Subsequently, Kraus and Greer[79] published in 1922 the first synthesis of trimethyl stannane and described its properties. They isolated the tinhydride by treating organotin sodium with ammonium chloride or bromide in liquid ammonia as shown in Scheme 27.



Scheme 27: First synthesis of organotin hydrides by Kraus and Greer

In this manner the afore mentioned trimethyltin hydride as well as triphenyltin hydride[51,80] and dimetyhlethyltin hydride[81] were generated. Afterwards, the investigation on tin hydrides was quite neglected due to the difficult preparation method leading to less accessible compounds because of their instability, until 1947, when Finholt, Bond and Schlesinger[82] developed a novel and more convenient route generating tinhydrides. This method involves the reduction of the corresponding tin halide with lithium aluminium hydride in solvents like ether, dioxane or THF. Furthermore, the reaction proceeds smoothly, usually at room temperature producing products of high purity (Scheme 28).

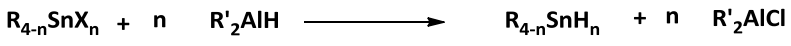


Scheme 28: General route synthesizing organotin hydrides with LAH

Subsequently, Gilman and Eisch employed this procedure to synthesize triphenyltin hydride.[83] Various other novel tinhydrides were first mentioned by van der Kerk, Noltes and Luijten by slight modifications to the isolation procedure.[64] Until 1963, triphenyltin hydride

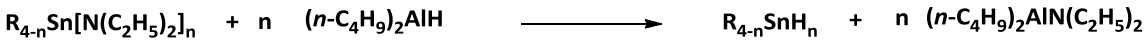
was the only known tin hydride harbouring an aryl group. Afterwards also following aryltin hydrides also were generated using the $LiAlH_4$ method: tris(*p*-tolyl), tris(*p*-fluorophenyl), trismesityl tin hydrides [84] and tris(*m*-tolyl), tris(*o*-tolyl) and tris(*o*-biphenylyl)tin hydrides.[85] Lithium aluminium hydride also reduces bis(tri-*n*-butyl)oxide to yield in tri-*n*-butyltin hydride in 88% yield.[86]

In 1955, Ziegler and Gellert reported the synthesis of organotin hydrides at -20 to 0°C in good yields utilizing dialkylaluminium hydrides like DIBAL. Hereby, solvents can be neglected (Scheme 29).[87,88]



Scheme 29: Preparation of organotin hydrides using dialkylaluminium hydrides

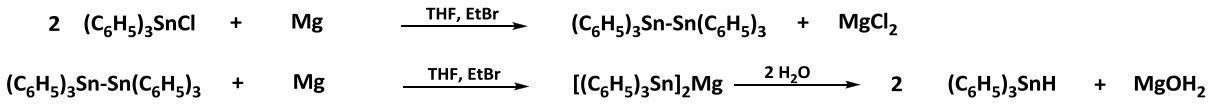
Furthermore, di-*n*-butylaluminium hydride transforms diethylamino stannanes into the corresponding hydrides as shown in Scheme 30.[89]



Scheme 30: Synthesis of organotin hydrides *via* reduction of diethylamino stannanes

Van der Kerk, Noltes and Luijten also reported that organotin halides can be reduced in good yields with amalgamated aluminium and water, but yields were not satisfactory.[90]

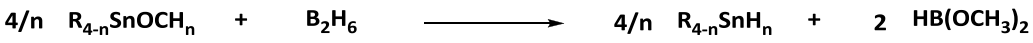
As another route the hydrolysis of for instance (triphenyltin)magnesium in a THF solution, itself generated by reaction of triphenyltin chloride with magnesium using ethyl bromide as initiator, with aqueous ammonium chloride yielding in 82% triphenyltin hydride can be mentioned (Scheme 31).[91]



Scheme 31: Hydrolysis of triphenylmagnesium resulting in Ph_3SnH

In comparison to the latter method, the hydrolysis of triphenyltinlithium with 1 *M* hydrochloric acid affords 69% of the corresponding hydride[92] and hydrolysis of tri-*n*-butyllithium using water results in 54% yield of the hydride[93].

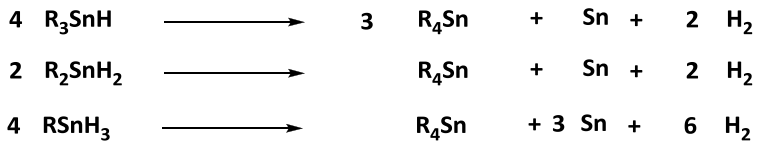
Finally, organotin hydrides in excellent yields can be obtained by the reaction of organotin methoxides with diborane (Scheme 32).[94]



Scheme 32: Generating organotin hydrides by reduction of organotin methoxides with diborane

2.3.4 Properties of Organotin Hydrides

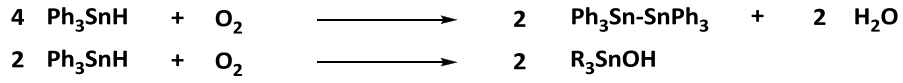
With the exception of diphenyltin dihydride, tribenzyltin hydride and methyltin trihydride, all currently known tin hydrides are colourless, distillable liquids, which in function of the number of organic substituents, decompose very easily at room temperature under disproportion and formation of metallic tin as shown in the Scheme 33.[23] For alkyl compounds stability increases with the size of the substituent.[95]



Scheme 33: Decomposition of organotin hydrides

Especially when exposed to atmospheric oxygen, organotin hydrides decompose resulting in a white to yellow or grey precipitate.[83,96-98]

For example, triphenyltin hydride in the presence of oxygen gives hexaphenylditin,[51] while ethyldimethyltin hydride and triethyltin hydride lead to the corresponding hydroxide shown in Scheme 34.[82,97]



Scheme 34: Reaction of organotin hydrides with oxygen

2.3.5 Polystannanes

2.3.5.1 Polystannanes in General

Linear polystannes are compounds with the general formula $(R_2Sn)_n$, harboring a covalently linked metal (tin) backbone, which can be seen as a molecular metal wire embedded in an organic jacket.[99] At the same time, being the formally structural analogues of saturated polymeric hydrocarbons, the polymers of group 14 elements have the capacity to catenate.[100] Induced by a very low band gap as well as σ-conjugation between the Sn sp^3 orbitals in the metallic backbone, these polymers exhibit an increased degree of electron delocalization with catenation.[101,102] These compounds bear strong σ→σ* transitions at about 390-340 nm. Even lower band gaps should be achieved if π-electrons in terms of covalently bond aromatic groups, can be found on the "tin-wire" leading as well to σ→π delocalization.[103] The mentioned outstanding property of a potentially highly conductive metallic material could be promising for applications in charge-transport, photoresists in microlithiography, non-linear optical materials, semiconductors in doping, and electronic devices.[104-106] Furthermore, those electronic properties make them thinkable as one dimensional quantum wires in printed electronic applications.[107] Those features are highly dependent on the already mentioned σ-delocalization which is not only a function of the substituents attached to the main chain, but also depend upon the changes in solid-state structures, backbone conformation and chain length.

However, since 1992, only a few working groups have dedicated themselves successfully to the synthesis and characterization of polystannanes.

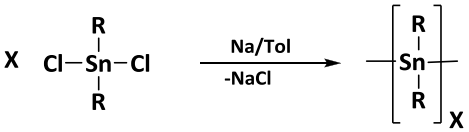
2.3.5.2 Synthesis of Polystannanes

Over the years different polymerization methods have been established in order to synthesize polystannanes, however, these are often accompanied with the formation of side products.

2.3.5.2.1 Wurtz-Type Coupling

The first described oligo- or polystannanes were published by Löwig in 1852. Shortly after, the first organotin compound was synthesized by Frankland[1,2] generated *via* the reaction of Sn/K or Sn/Na alloys with iodoethane in the presence of quartz sand in order to improve the reaction control. However, it was found out that Sn/Na is more convenient for that preparation. The elemental composition of the afforded compounds were very similar to oligo(diethylstannane) or poly(diethylstannane).[108] Subsequently, Cahours isolated a compound with elemental composition corresponding to the formula $(SnEt_2)_x$ generated by heating iodoethane in the presence of metallic tin and sodium. With those findings, Cahours was the pioneer in applying a Wurtz-type reaction for the preparation of polystannanes. He also tried to afford poly(dimethylstannane) by a Wurtz reaction, but was not able to prove his results[109,110] until Price *et al.* confirmed that poly(dibutylstannane) synthesized *via* Wurtz coupling leads to a bimodal molar mass distribution.[111]

Currently, Wurtz-type coupling with sodium in organic solvents like toluene is widely used to gain poly(dialkylstannanes)s of high molar mass. However, the reaction conditions lead to oligomeric stannanes or cyclic oligomers in poor yields.[108,112-117] Scheme 35 displays the Wurtz-type coupling for the preparation of polystannanes.



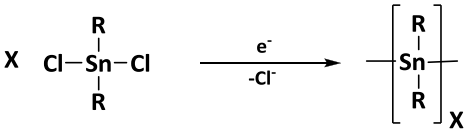
Scheme 35: Wurtz-type coupling for the preparation of polystannanes

Mechanistic suggestions consider that polymerization (chain growth) occurs at the surface of metallic sodium followed by a second slower step of chain prolongation by condensation reactions.[118,119]

Very recently, Caseri *et al.* proposed a modification of the traditional Wurtz-type polymerization method converting R_2SnCl_2 compounds with sodium in liquid ammonia, whereby polymers are generated either in an one-step polymerization using two equivalents of sodium or *via* a two-step proceeding with four equivalents. The reaction is very likely to proceed *via* stannide ions including a radical mechanism.[120]

2.3.5.2.2 Electrochemical Synthesis

The electrochemical pathway for the reduction of diorganotin dihalides can be seen as a promising route for the synthesis of moderate molecular weight polymers in good as well as reproducible yields (Scheme 36).[121,122]



Scheme 36: Electrochemical synthesis for polystannanes

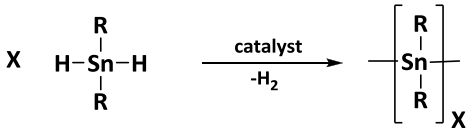
Electrochemical conversions were performed in an one-compartement cell furnished with a platinum cathode and a silver anode using 1,2-dimethoxyethane as solvent and tetrabutylammonium chloride as supporting electrolyte. The reaction was carried out for Bu_2SnCl_2 as well as for Oct_2SnCl_2 yielding up to 56% of the corresponding polymer.[122] Using R_3SnCl compounds as starting material, crosslinked polystannanes with a network-σ-conjugated systems were produced. However, the product still exhibited Sn-Cl groups after reaction completion, in addition the conversion proceeds under the formation of unknown fractions of cyclic oligomers.[123]

2.3.5.2.3 Solvent- and Catalyst Free Dehydrogenation

Recently, Foucher *et al*. reported the successful preparation of oligo- and polystannanes *via* thermal hydrocoupling under inert conditions. *n*-Bu_2SnH_2 was heated for 6 h yielding in a hydride terminated distannane, cyclic species and a polymer. Generated polystannanes showed modest molecular weight and broad polydispersity.[124]

2.3.5.2.4 Catalytic Dehydropolymerization

So far, the most common and widely applied method of generating organo polystannanes is the catalytic dehydrocoupling of tin hydrides with early transition metal complexes based on palladium, zirconium, rhodium, platinum or lanthanides (Scheme 37).[104,115,125-132]

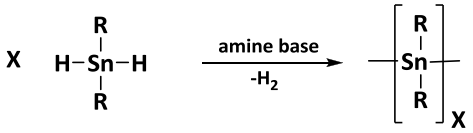


Scheme 37: Catalytic dehydropolymerization generating polystannanes

Initial polymerization attempts on this field in most cases led to a significant number of side products including cyclic oligomers or other impurities. More recently, investigations on using a Wilkison's catalyst [$RhCl(PPh_3)_3$] turned out to be very successful affording polyalkylstannanes in high yields (65-90%) without significant byproducts.[100,126,133] This method allowed the systematic investigation on material properties without the disturbing influence of the side products. However, usage of the Wilkinson catalyst is not suitable for the two aromatic substituents on the tin educt. Recently a synthetic route applying lanthanide diamide based catalysts for the generation of polystannanes and distannanes was established.[133]

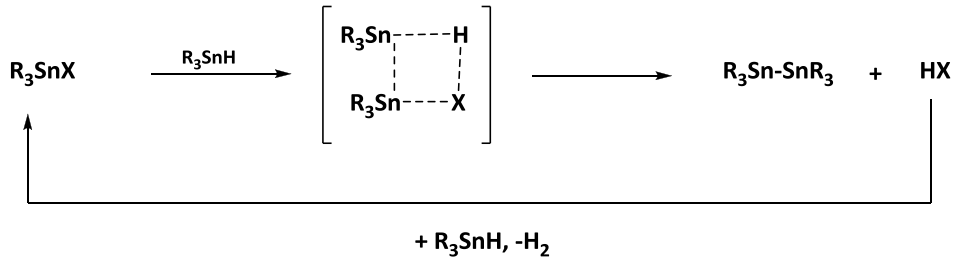
2.3.5.2.5 Dehydrogenative Coupling Using an Amine Base

Adding a nitrogen base like pyridine to a tin hydride solution in order to afford the formation of a Sn-Sn bond was first described by Neumann[134] and successfully further applied by Davies and Mathiasch (Scheme 38).[135,136]



Scheme 38: Dehydrogenative coupling using an amine base

Although further investigations on the reaction mechanisms have been neglected thus far, the reaction progress is considered to occur *via* either a polar process or a radical chain mechanism. It is indeed possible that the polar mechanism proceeds *via* the formation of a four-membered transition state as involving a R_3SnX species as shown in Scheme 39.[137,138]



Scheme 39: Polar transitions state in dehydrogenative coupling

Regarding the radical formation pathway a $R_3Sn\cdot$ radical would displace a hydrogen atom from another tin hydride resulting in a H· species which subsequently leads to the production of H_2 through abstracting a hydrogen from another tin centre.[136] Recently, Uhlig *et al*. described the application of TMEDA (tetramethylene diamine) as a convenient amine base generating poly(dialkylstannane)s as well as poly(diarylstannane)s. Also for this synthetical route a radical mechanism is considered but not proven by any experimental means yet.[139]

2.3.5.3 Characteristics of Polystannanes

Much attention concerning the properties of polystannanes had been drawn to the visible spectroscopic properties, whereas the stability investigations had been quite neglected until Caseri *et al.* dedicated themselves to the topic.[140]

2.3.5.3.1 Visible Properties of Polystannanes: Color and Absorption Maxima

Polystannes are reported to exhibit a characteristic yellow or orange-yellow color leading to absorption maxima in UV-vis spectra at around 375-410 nm which are attributed to $\sigma \rightarrow \sigma^*$ band-gap transitions.[100,115,126,141] Long-chain polystannanes strongly absorb light in the UV, indicated by their high ε-values ranging from 4200 to 63000. Furthermore, those energies are independent of the polymer's phase, whether it is in solution or not.

2.3.5.3.2 Thermal Stability

Under common TGA conditions, i.e. heating rate of 10°C/min, thermal decomposition of poly(dialkylstannane)s, as well as for polystannanes with phenyl terminated alkly groups does not proceed below 200°C under inert conditions as well being exposed to the ambient.[126,134] However, the maximum decomposition rate regarding poly(alkylstannane)s could be detected in the range of 250-300°C under nitrogen and 240-300°C under oxygen containing atmosphere, respectively. There was no general systematic trend detectable referring to the dependency of decomposition and chain length. Regardless, it is established that poly(diphenylstannane)s exhibit more stability than poly(dialkylstannane)s. Concerning copolymers of butyl and phenyl moieties, the aromatic substituent did not improve thermal stability increasingly as shown on the example of poly(dibutylstannane-*ran*-diphenylstannane).[121]

2.3.5.3.3 Light Stability

Caseri *et al*. investigated the stability of polystannanes towards light under controlled exposure and compared results of the polymer in solution where a consistent illumination is more accessible then to the polymer in the solid state. The degradation process was monitored *via* NMR spectroscopy and GPC. A correlation between the length of the alkyl side groups and the stability of the polymer was not found, but indeed the used solvent exhibits a strong influence on the degradation rate. Hereby, chlorinated solvents as well as styrenes repressed the decomposition, whereas degradation proceeds rapidly in aromatic and aliphatic hydrocarbons.[141] Very recently, it was found that poly(diarylstannen)s exhibit a higher stability towards light than poly(dialkylstannane)s in THF as well as in dichloromethane.[142]

2.3.5.3.4 Processing and Orientation

Poly(dialklystannane)s (alkyl= butyl, octyl, dodecyl) were blended with ultrahigh molar mass polyethylene to afford blends containing typically about 10% or 25% w/w polystannane. The resulting blends were homogenous, but however opaque. Poly(alyklstannane)s exhibited

liquid-crystalline behavior at room temperature or even below. Hence, their orientation was achieved by shearing on a glass slide at ambient temperature or even at 60°C. Furthermore, they could be grown out of solution onto a glass slide coated with a PTFE layer. Depending on the procedure the polystannane backbone is either oriented parallel or perpendicular, evidenced by UV-vis spectra using polarized light.[143]

2.4 References

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3 Results and Discussion

3.1 Objective of the Project

The objective of the project can be defined as the synthesis and characterization of *ortho*-substituted aryltrichloro stannanes as well as their corresponding aryltrihydrido stannanes. The prepared tin trihydrides should serve as precursors for the generation of polyarylstannanes in the presence of TMEDA. The polymerization behavior of aryltin trihydrides should be investigated.

The synthetic scope was not only based on substituted phenyl derivatives, like *o*-tolyl, 2,4-xylyl and 2,6-xylyl compounds, but also on condensed aromatic rings like 1-naphthyl and 9-anthracenyl moieties. All synthesized aryltrihydrides have not been reported in thus far. Regarding the trichlorostannanes, only the *o*-tolyl and the 1-naphthyl derivative have been mentioned in the literature. The different substance classes are displayed in Figure 2, wherein Z stands for Cl or H respectively.

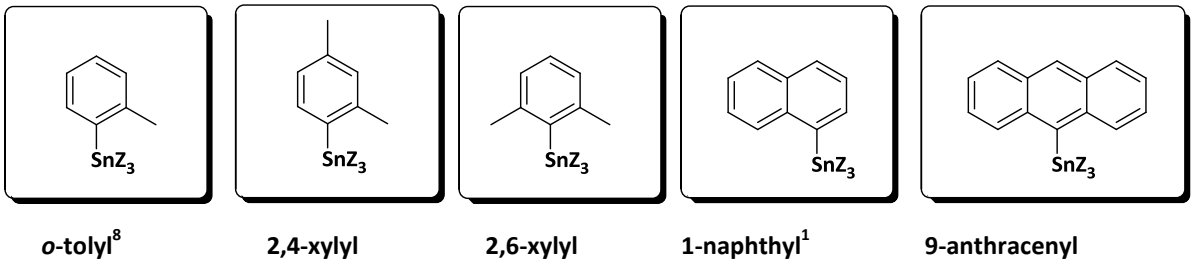
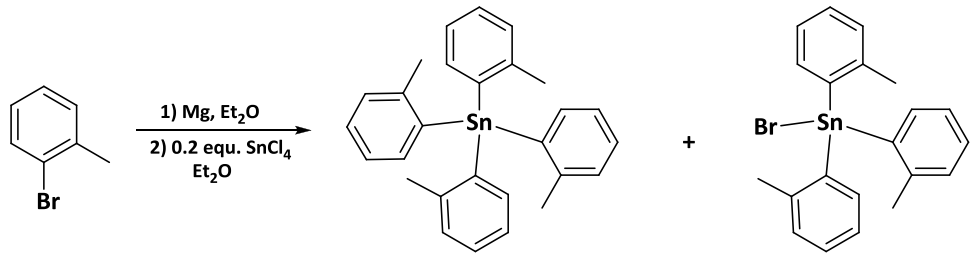


Figure 2: Synthetic scope

3.2 Synthesis of Tetraaryl Stannanes

The conversion of the arylhalides (*o*-tolyl, 2,4-xylyl, 2,6-xylyl) building up tetraaryl stannanes was carried out according to literature procedure.[2] Only the work up was modified slightly depending on the synthesized derivatives as described below.

3.2.1 Tetra-*o*-Tolylstannane 1

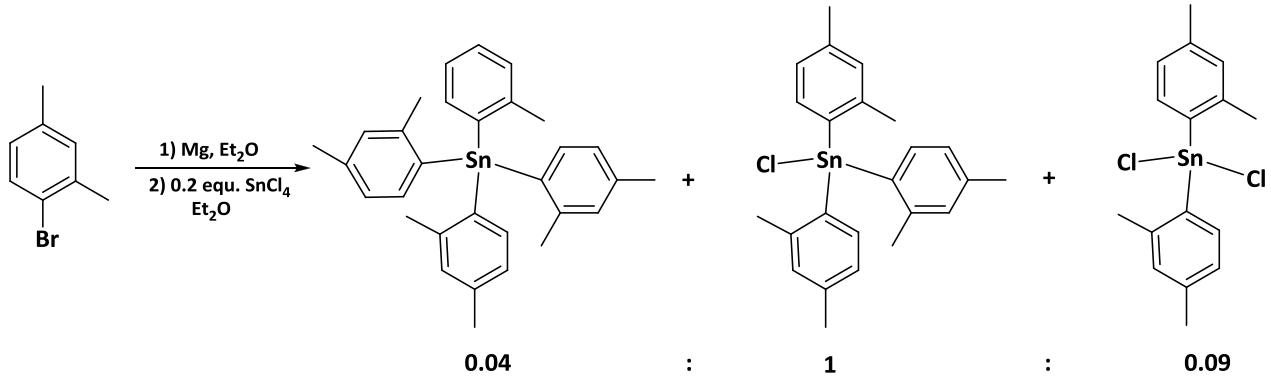


Scheme 40: Preparation of tetra-*o*-tolylstannane **1**

Compound **1** was synthesized *via* a Grignard route according to Scheme 40. The resulting greenish solid was subjected to a ^{119}Sn-NMR measurement in $CDCl_3$. Two signals could be found, the major signal at -54.5 ppm and a minor one -123.0 ppm. According to literature, the signals can be assigned as *o*-tol_3SnBr and the corresponding *o*-tol_4Sn in a ratio of 1:0.2.[3] Therefore only 20% of the resulting mixture refers to the desired product **1** leading to a theoretical yield of 18%. The mixture was not subjected to further purification procedures.

Onone hand Krause[4] synthesized compound **1** on the Grignard route with 35% yield, whereas on the other hand Srivastava[5], employing a Wurtz reaction in petrol-ether, also obtained **1** in the same yield. Additionaly, applying aryltin lithium[6] as educt only led to 4.2% yield of **1**. Consequently, the reaction might be limited by sterical factors yielding in a product mixture.

3.2.2 Tetra-2,4-Xylylstannane 2

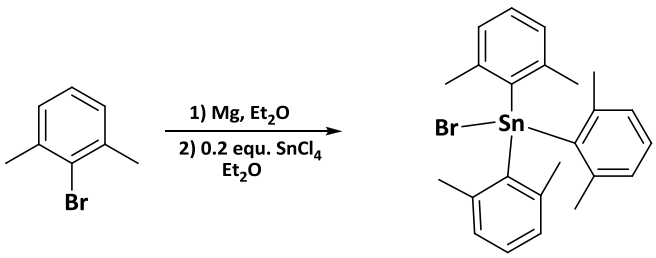


Scheme 41: Preparation of tetra-2,4-xylylstannane **2**

Compound **2** was synthesized *via* a Grignard route according to Scheme 41. The reaction afforded a yellow oil which was investigated *via* ^{119}Sn-NMR measurement in $CDCl_3$ revealing three different signals at -47.6 ppm, -73.3 ppm and -119.4 ppm. By comparison with already published compounds[3] from the substituted phenyl family as well with already in the literature mentioned shifts of the generated compounds[2], signals can be assigned as 2,4-xylyl$_3$Sn, 2,4-xylyl$_4$Sn and 2,4-xylyl$_2$SnCl$_2$ in a ratio of 1: 0.13: 0.16. Purification attempts *via* fractional distillation did not lead to full isolation of only one product, but minimized the ratio of Ar_2SnCl_2 and Ar_4Sn regarding R_3SnCl as the major product (0.09: 0.04: 1). That led to theoretical yield of 1.6% of the actually desired tetraaryl stannane, about 4% of 2,4-xylyl$_2$SnCl$_2$ and more than 94% of 2,4-xylyl$_3$SnCl.

In comparison to the product assignment gained during the synthesis of compound **1**, the same trend can be detected. The major product in both cases is the triaryl compound, but in this reaction also the disubstituted side product can be observed. The formation of the desired compound **2** is suppressed.

3.2.3 Tris-(2,6-xylyl)bromostannane 3



Scheme 42: Preparation of tris-(2,6-xylyl)bromostannane **3**

Compound **3** was synthesized *via* a Grignard route according to Scheme 42. When trying to synthesize the tetraaryl compound with a 2,6-xylyl substituent, the steric demand obviously was too elevated, so that the reaction did not afford the desired product. While monitoring the reaction progress *via* ^{119}Sn-NMR spectroscopy after overnight stirring at room temperature, one signal at -132.7 ppm was observed. After refluxing the reaction mixture for 2 h a second ^{119}Sn-NMR measurement was carried out in $CDCl_3$ giving rise to three different product signals at: -101.3 ppm, 132.2 ppm and -197.3 ppm. With the isolation method of choice, Soxhlet extraction using pentane, a white solid could be isolated, which then was subjected to an overnight ^{119}Sn-NMR (C_6D_6) measurement. The spectrum revealed that the major product with a ^{119}Sn-NMR shift of -131.6 can be found with a purity higher than 98% according to ^{119}Sn-NMR, which leads to a theoretical yield of 19%. **3** was subjected to recrystallization from pentane to yield colorless crystals (Figure 3).

Confirmation about structure of the main product synthesized was given by X-ray analysis, revealing that it is the triaaryl derivative tris-(2,6-xylyl)bromostannane. So far, only Bähr and Gelius[7] reported about the synthesis of tetramesityl stannane in the year 1958 without structural prove. Since the *para* substituent is considered to not have any influence on the steric demand on the tetravalent tin, the two organic moieties can easily be compared. Trisubstitution seems to be the maximum regarding bulky aryl substituents like mesityl and 2,6-xylyl.

Table 3 summarizes selected bond lengths and angles of **3**.

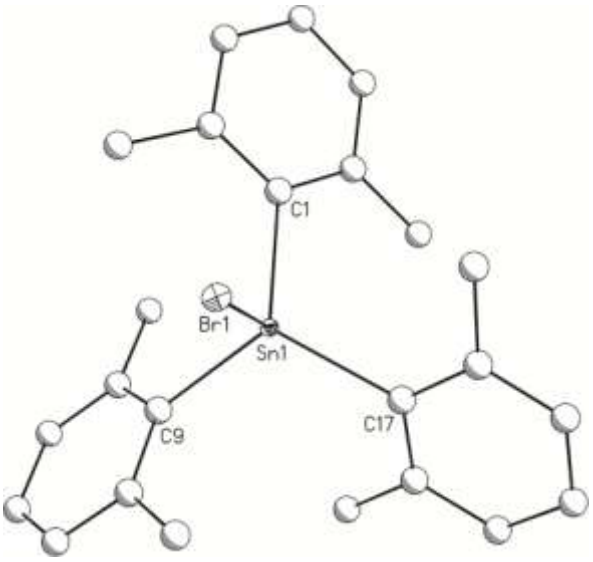


Figure 3: Crystal structure of tris-(2,6-xylyl)bromostannane **3**. All non-carbon atoms shown as 30% shaded ellipsoids. Hydrogen atoms removed for clarity.

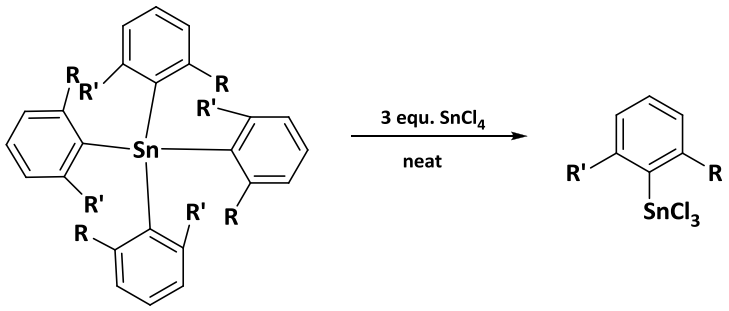
Table 3: Selected bond lengths and angles of tris-(2,6-xylyl)bromostannane **3**

	space group	**bond length av. [Å]**		**angle av. [°]**	
compound		*Sn-C*	*Sn-X*	*C-Sn-C*	*Br-Sn-C*
2,6-xylyl$_3$SnBr	P2$_1$/c	2.164(2)	2.547(3)	115.8(8)	102.0(6)

Tris-(2,6-xylyl)bromostannane, **3**, crystallizes in the monoclinic space group P2$_1$/c, whereas the tin can be found in a distorted tetrahedral environment coordinated to four different substituents as displayed in Figure 3. The tin is coordinated to three 2,6-xylyl ligands with an average bond length of 2.16 Å and to bromine with a bond length of 2.55(3) Å. The average C-Sn-C angle (115.8(8)°) is bigger, whereas the Br-Sn-C angle is smaller than the ideal tetrahedral one provoked by the steric demand of the 2,6-xylyl substituents. However, the values for bond lengths and angles lie in the expected area. Further discussion on the crystal structure will be given in chapter 3.5.

3.3 Synthesis of Trichloro Arylstannanes

All synthesized trichloro arylstannnes were prepared according to literature procedures by a Kozeschkow redistribution reaction if not otherwise stated (Scheme 43).[8]



Scheme 43: Kozeschkow redistribution reaction synthesizing aryltrichloro stannanes

3.3.1 Trichloro-*o*-tolylstannane 4

The product mixture gained within the preparation of compound **1** was treated with 3.1 equivalents of tin(IV) chloride leading to a liquid reaction mixture at room temperature, which was heated up to 150°C. The reaction progress was monitored by ^{119}Sn-NMR spectroscopy. Measurement after 1 h showed the formation of the intermediate *o*-tolyl$_2$SnCl$_2$. By adding another 3.1 equivalents of $SnCl_4$ after 1 h the reaction equilibrium should have promoted full conversion. Further monitoring after 1 h still showed a significant ratio increase of the intermediate dichloride. Before working up the reaction mixture, *o*-tolyl$_2$SnCl$_2$ and the desired *o*-tolylSnCl$_3$, **5**, were detected in a ratio of 1:0.08 according to the ^{119}Sn-NMR spectrum. For further purification the product mixture was distilled. However, **4** could not be gained without dichloride impurities (1:0.01), which in fact was not disturbing for subsequent conversion.

3.3.2 Trichloro-2,4-xylylstannane 5

The product mixture gained within the preparation of compound **2** was treated with 3.4 equivalents of $SnCl_4$ regarding the major product of the previous step (2,4-xylyl$_3$SnCl). The reaction was finished after 3 h reaction time resulting in a yellowish liquid. ^{119}Sn-NMR investigation in $CDCl_3$ showed a side product (2%) at -111.3 ppm, which could be identified

as a tin(IV) chloride water adduct, recrystallized from the deuterated solvent. A yield of 18% can be calculated over the two step reaction starting with the arylhalide. No further purification was carried out, because the impurity was not relevant for subsequent conversion.

3.3.3 Trichloro-2,6-xylylstannane 6

Compound **3** was treated with 3.4 equivalents tin(IV) chloride and heated up to 180°C. NMR measurements in $CDCl_3$ after 1.5 h showed the formation of the intermediate compound 2,6-xylyl$_2$SnCl$_2$ at -94.2 ppm in significant amount. The mixture was stirred and heated for another 2.5 h to afford the desired product without further impurities with shift of -87.7 ppm in ^{119}Sn-NMR spectrum in $CDCl_3$. To determine the first order coupling constants ^1J ^{119}Sn-^{13}C and $^1J^{117}$Sn-^{13}C in ^{13}C-NMR a relaxation delay of at least 25 sec was necessary. After distillation **6** was obtained as a white solid (44% yield), which was recrystallized from pentane (Figure 4).

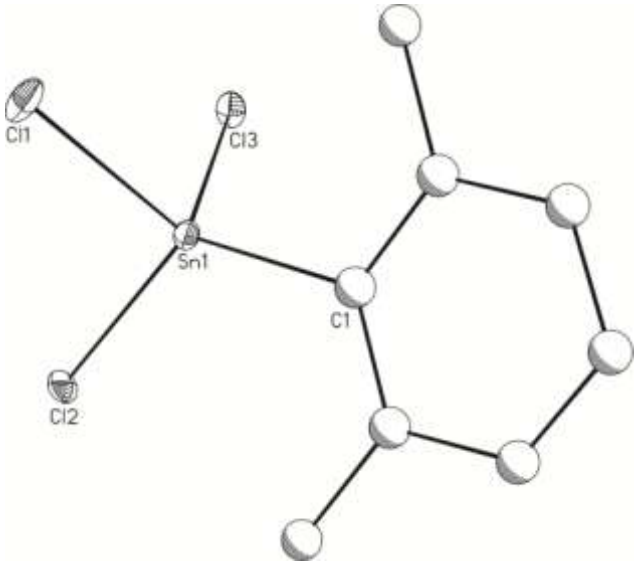


Figure 4: Crystal structure of trichloro-2,6-xylylstannane **6**. All non-carbon atoms shown as 30% shaded ellipsoids. Hydrogen atoms removed for clarity.

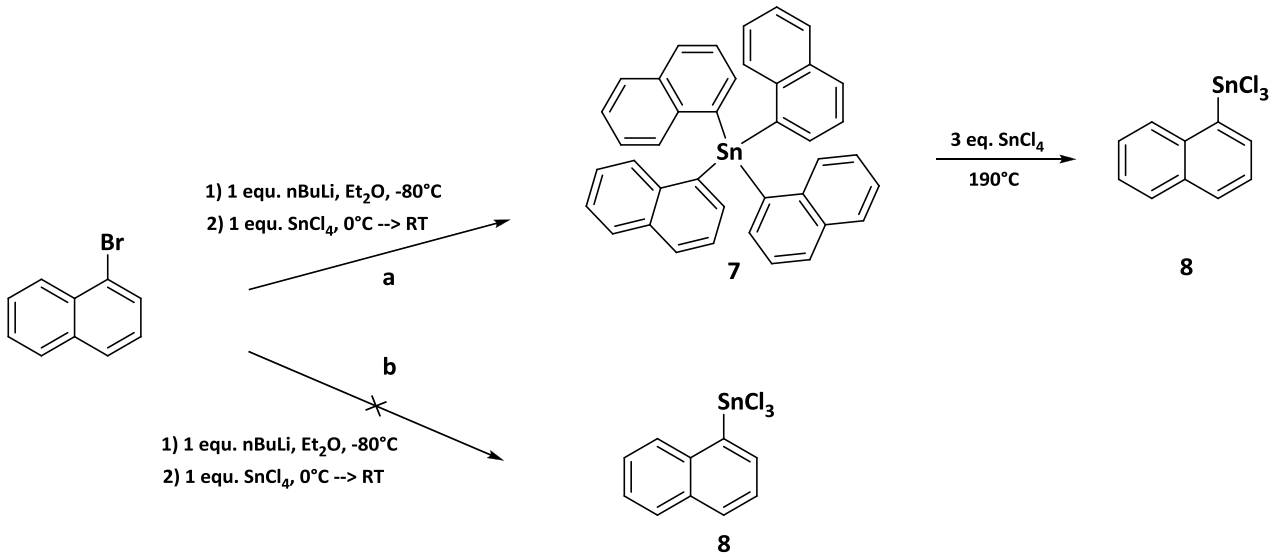
Table 4 summarizes selected bond lengths and angles of **6**.

Table 4: Selected bond lengths and angles of trichloro-2,6-xylylstannane **6**

	space Group	bond length av. [Å]		angle av. [°]	
compound		*Sn-C*	*Sn-Cl*	*C-Sn-Cl*	*Cl-Sn-Cl*
2,6-xylylSnCl$_3$	Pbcn	2.123(2)	2.332(6)	116.2(7)	101.8(2)

Trichloro-2,6-xylylstannen **6** crystallizes in the orthorhombic space group Pbcn. The tin can be found in a distorted tetrahedral environment, coordinated to four different substituents. As a central atom it is bonded to three chlorides and one 2,6-xylyl substituent (Figure 4). Due to the higher steric demand of the 2,6-methyl substituted phenyl group the average C-Sn-Cl angle (116.2(7)°) is significantly bigger than the average Cl-Sn-Cl (101.8(2)°) angle. However, the values for bond lengths and angles lie in the expected area. Further discussion on the crystal structure will be given in chapter 3.5.

3.3.4 Trichloro-1-naphthylstannane 8 and Tetra-1-naphthylstannane 7



Scheme 44: Preparation of tetra-1-naphthylstannane **7** and trichloro-1-naphthylstannane **8**

It was attempted to realize the formation of trichloro-1-naphthylstannane **8** on route **b** according to Scheme 44. Due to the applied equimolar stoichiometry of the lithiated naphthyl compound and the used tin(IV) chloride the formation of 1-naphthylSnCl$_3$ was expected, but surprisingly after work up 64% of the tetraaryl stannane **7** could be isolated. Furthermore, ^{119}Sn-NMR spectra showed no formation of any side products. Although the

steric demand resulting from fourfold substitution on the metal centre seems to be very high, the reaction proceeds with reasonably yields (64%). By recrystallization from pentane and toluene a crystal structure (Figure 5) could be obtained.

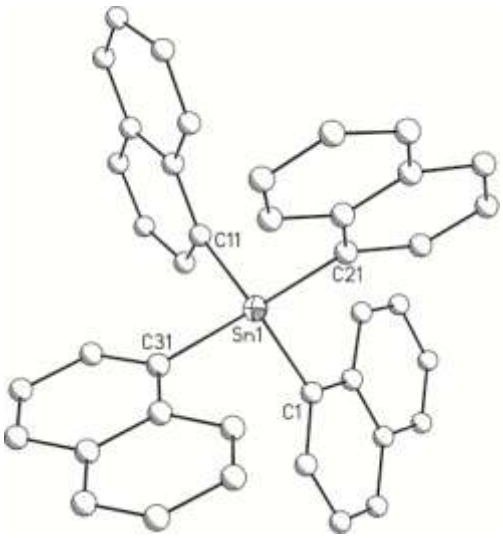


Figure 5: Crystal structure of tetra-1-naphthylstannane **7**. All non-carbon atoms shown as 30% shaded ellipsoids. Hydrogen atoms removed for clarity

Table 5 summarizes selected bond lengths and angles of **7**.

Table 5: Selected bond lengths and angles of tetra-1-naphthylstannane **7**

	space group	**bond length av. [Å]**	**angle av. [°]**
compound		*Sn-C*	*C-Sn-C*
1-naphthyl$_4$Sn	P2$_1$/n	2.154(6)	109.5(3)

Tetra-1-naphthylstannane **7** crystallizes in the monoclinic space group P2$_1$/n, whereas the tin can be found in a distorted tetrahedral environment coordinated to four naphthyl substituents (Figure 5). The average spanned C-Sn-C angle fits with the tetrahedral angle of 109.5(3)°. Further discussion on the crystal structure will be given in chapter 3.5.

Tetra-1-naphthylstannane, **7**, was subjected to a Kozeschkow redistribution reaction to yield in trichloro-1-naphthylstanne, **8**, as white crystals in 51% yield. It has to be taken into account that also for **8** a relaxation delay of at least 25 sec was necessary to detect the first

order coupling constants ^{1}J ^{119}Sn-^{13}C and $^{1}J^{117}$Sn-^{13}C in ^{13}C-NMR spectra. By recrystallization from toluene the following crystal structure could be obtained (Figure 6).

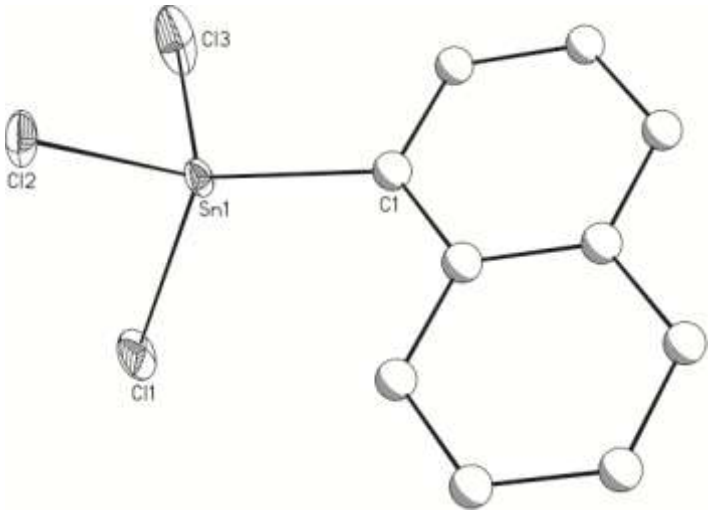


Figure 6: Crystal structure of trichloro-1-naphthylstannane **8**. All non-carbon atoms shown as 30% shaded ellipsoids. Hydrogen atoms removed for clarity.

Table 6 summarizes selected bond lengths and angles of **8**.

Table 6: Selected bond lengths and angles of trichloro-1-naphthylstannane **8**

	space group	**bond length av. [Å]**		**angle av. [°]**	
compound		*Sn-C*	*Sn-Cl*	*C-Sn-Cl*	*Cl-Sn-Cl*
1-naphthylSnCl$_3$	$P2_12_12_1$	2.131(19)	2.302(5)	114.9(5)	103.5(3)

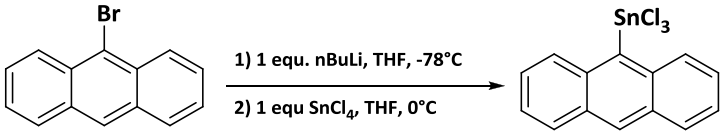
Trichloro-1-naphthylstannane **8** crystallizes in the orthorhombic space group $P2_12_12_1$, whereas the tin can be found in a distorted tetrahedral environment coordinated to four different substituents. The tin is bonded to three chlorides and one 1-naphthyl substituent (Figure 6). Due to the higher steric demand of the condensed aromatic ring system the average C-Sn-Cl angle (114.9(5)°) is significantly larger than the average Cl-Sn-Cl (103.5(3)°) angle. However, the values for bond lengths and angles lie in expected ranges. Further discussion on the crystal structure will be given in chapter 3.5.

3.3.5 9-Anthracenyl Systems

Various attempts to synthesize the challenging trichloro-9-anthracenylstannane were carried out and summarized in the following chapter.

3.3.5.1 Synthesis on the Lithiation Route

First a lithiation (*n*-BuLi) of the corresponding arylhalide was carried out and subsequent conversion with one equivalent $SnCl_4$ was used to afford trichloro-9-anthracenylstannane (Scheme 45).

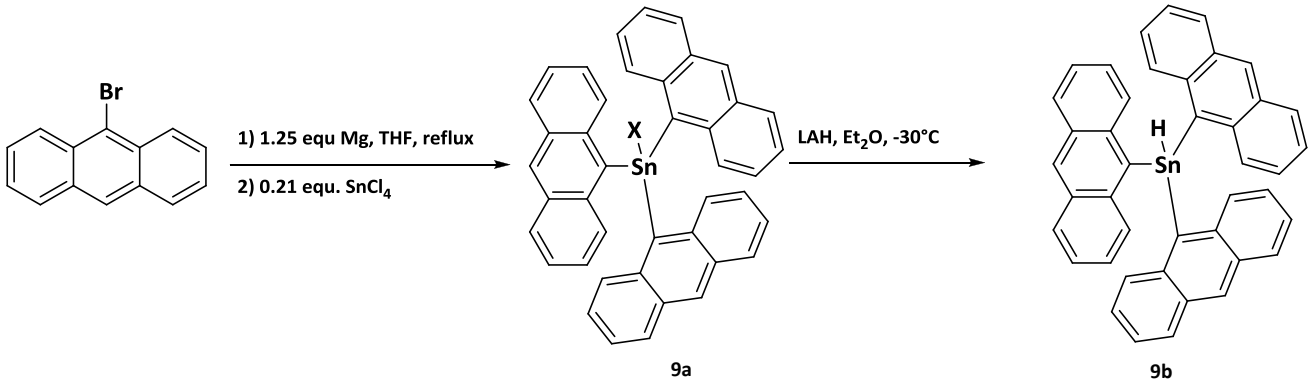


Scheme 45: Lithiation Route for the synthesis of trichloro-9-anthracenylstannane

The reaction resulted in a brown powder and showed a ^{119}Sn-NMR shift ($CDCl_3$) at -49 ppm. It has to be mentioned that at least 25 sec relaxation delay times were necessary to detect any Sn signals. Since the powder was hardly soluble in common organic solvents, recrystallization of the possible product failed. Furthermore, the same reaction was carried out using a twofold excess (2 eq.) of *n*-BuLi to avoid side products like $ArSnBu_3$, but no product formation could be detected. For that reason the lithiation route was neglected in the first place.

3.3.5.2 Synthesis on the Grignard Route

Consequently, attempts were made to isolate the desired product by subjecting 9-bromoanthracene to a traditional Grignard reaction. The Grignard reagent subsequently was treated with 0.2 eq. $SnCl_4$ to result in substituted products (Scheme 46).

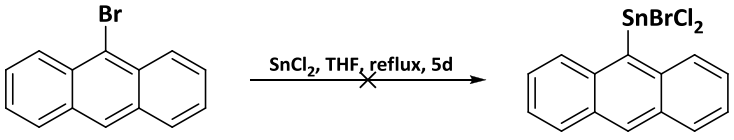


Scheme 46: Grignard route for the synthesis of 9-anthracenyl derivatives

The formation of a red and again badly soluble powder was observed, which showed two ^{119}Sn shifts at -124 ppm and -146 ppm ($CDCl_3$) after overnight measurement (25 sec of relaxation delay). Hence, only a small amount of product was formed. By comparison with known ^{119}Sn shifts, the peaks were considered to be 9-anth$_3$SnX or 9-anth$_2$SnX$_2$. In order to be able to specify the resulting signals, the product mixture was subjected to a hydrogenation with LAH and ether as solvent. Applying a hydrogen-coupled ^{119}Sn-NMR measurement (C_6D_6), a single duplet at -272 ppm was observed **9b**. Thus, the intermediate product could be identified as 9-anthr$_3$SnX **9a**. Once again, the resulting yellowish powder turned out to be badly soluble in common organic solvents making isolation difficult.

3.3.5.3 Synthesis via Oxidative Addition

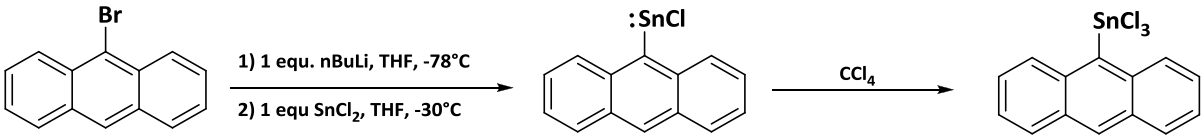
Furthermore, it was tried to realize the formation of the Ar-SnX$_3$ bond by oxidative addition of tin(II) chloride in THF at refluxing temperature (Scheme 47).[9] Unfortunately, no reaction took place.



Scheme 47: Oxidative addition of $SnCl_2$ on 9-bromoanthracene

3.3.5.4 Synthesis via the Formation of a Tin(II) Species

The next attempt to achieve the desired product was the formation of an activated Sn(II) intermediate, which subsequently should be reduced by CCl_4 as shown in Scheme 48.[10]



Scheme 48: Attempts towards the formation of trichloro-9-anthracene *via* an activated Sn(II) intermediate

The reaction mixture was subjected to a standard work-up procedure, removing the solvent under reduced pressure. The resulting solid was suspended in toluene to precipitate salts. However, the supernatant solution showed no signal in the ^{119}Sn-NMR spectrum, whereas in the precipitate (orange solid) a shift of -45 ppm applying a relaxation delay of 25 sec could be observed. As this signal was very similar to the one gained *via* the lithiation route (3.3.6.1), attempts to isolate the compounds were made. Hence, the orange residue was subjected to a solid phase extraction using heptane to afford 60 mg of a pale yellow powder. A second extraction fraction was gained utilizing ether to altogether obtain 0.31 g of a yellowish solid**.** The achieved compound was not soluble in a variety of organic solvents, therefore a characterization *via* NMR spectroscopy was not possible. Consequently, the thermal properties of the latter were investigated. Decomposition at around 248°C resulting in a dark green to black, amorphous solid and white, sublimating crystals was observed. To gain more information about the decomposition behavior a TGA, as well as a DTA were carried out. The results are displayed in Figure 7. First ideas about the formation of a tin(II) derivative could not be proven by TGA, elemental analysis and mass spectroscopy.

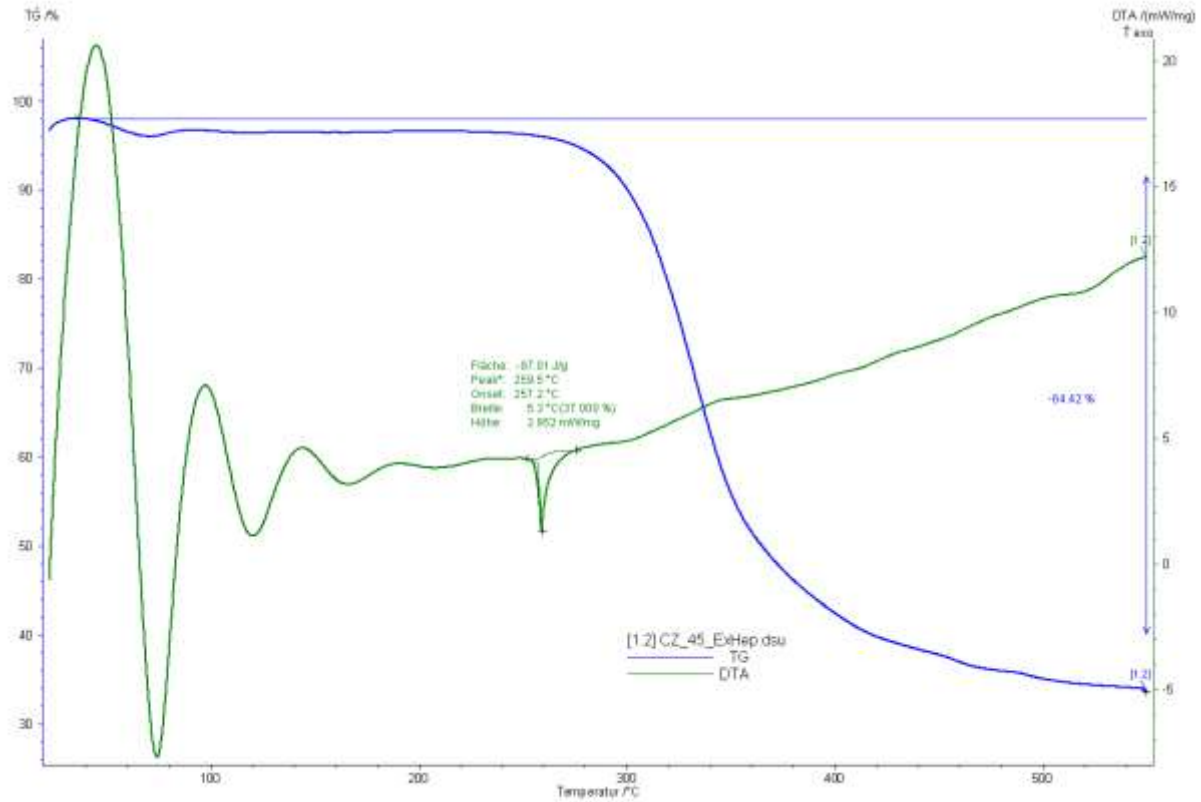


Figure 7: DTA and TGA of the anthracenyl derivative

Decomposition of the yellowish solid proceeds with a mass loss of 64.42 %. The percentage correlates with the loss of two anthracenyl groups regarding 9-anth$_2$SnCl$_2$.

Additionally, elemental analysis should reveal information about the composition of the substance. In Table 7, experimental values are compared with calculated results of possible compounds being formed during the reaction. Relevant data is presented in bold.

Table 7: Found and calculated C,H values [%] for anthracenyl derivatives

		C [%]	***H [%]***
experimental		**58.63**	**3.12**
calculated	$ArSnCl_3$	41.80	2.25
	ArSn:Cl	**50.74**	**2.74**
	Ar_2SnCl_2	**61.81**	**3.33**
	Ar_3SnCl	73.55	3.97
	$Ar_3Sn\text{-}SnAr_3$	69.11	3.73
	$Ar_2ClSn\text{-}SnClAr_2$	66.12	3.57
	$ArCl_2Sn\text{-}SnCl_2Ar$	45.84	2.47

Comparison of the values displays clearly that the gained substance is not a Sn(II) compound, because measured and calculated C,H values do agree. In fact, the found carbon ratio cannot be compared with any of the suggested products. However, the calculated values for dichloro-(bis-9-anthracenyl)stannane match most closely to the experimental data obtained as well as to with the TGA measurements.

Subsequently, the product was subjected to high resolution mass spectroscopy leading to following spectra (Figures 8 and 9).

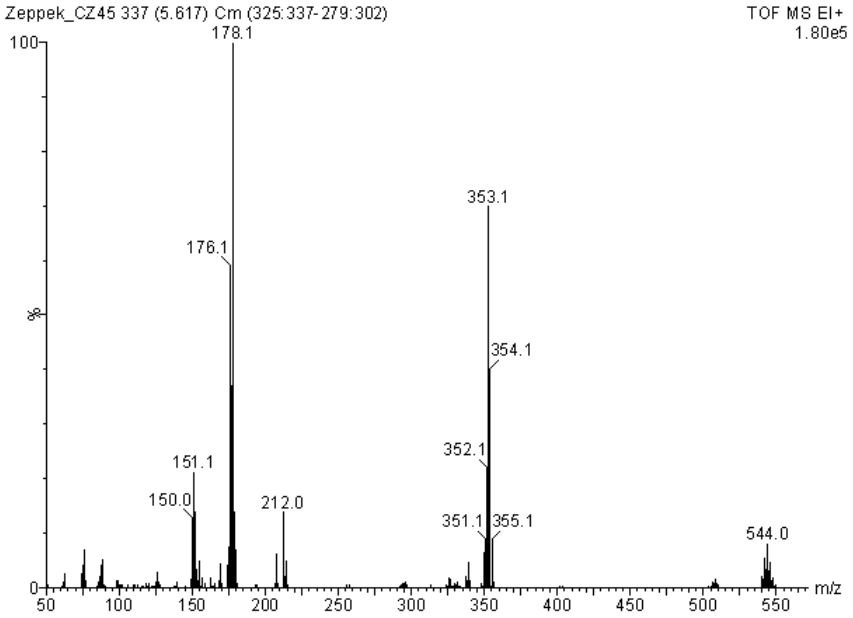


Figure 8: M/z fragmentation of dichloro-(bis-9-anthracenyl)stannane (DI-EI-TOF)

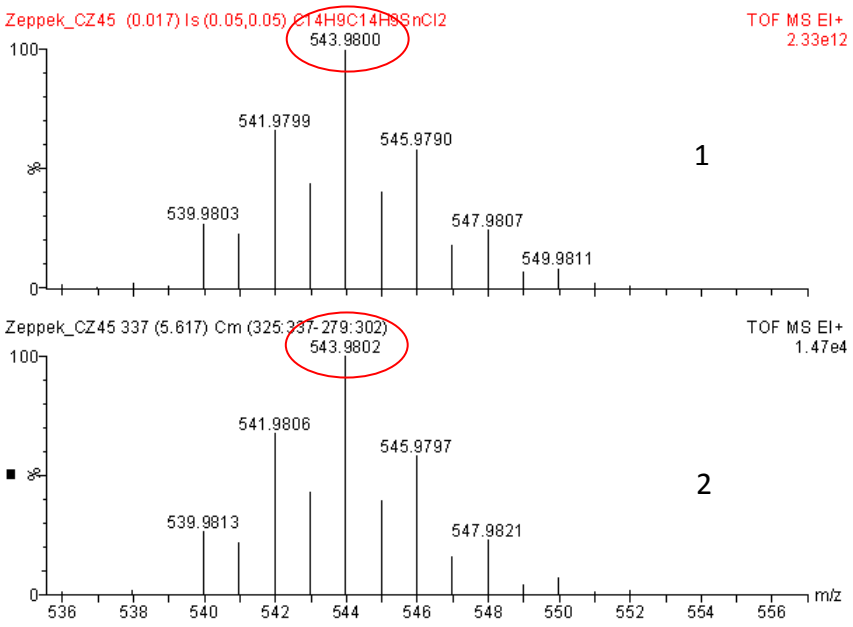


Figure 9: 1. Theoretical isotope pattern of M^+ **2.** Experimental isotope pattern of M^+

The found isotope pattern of M^+ indicates the formation of dichloro-(bis-9-anthracenyl)stannane **9**.

3.3.5.5 Temperature Study of the Lithiation Route

Because of a signal at -49 ppm (see chapter 3.3.6.1) in the ^{119}Sn-NMR spectrum the lithiation route was carried out again. The first step (lithiation) was always performed at -78°C, whereas the temperature profile of the second reaction (conversion with $SnCl_4$) was varied from -78°C to room temperature. In each case the reaction was monitored after a micro work-up in $CDCl_3$ with ^{119}Sn-NMR spectroscopy (25 sec relaxation delay). The temperature dependency of the generated product mixture is illustrated in Figure 10.

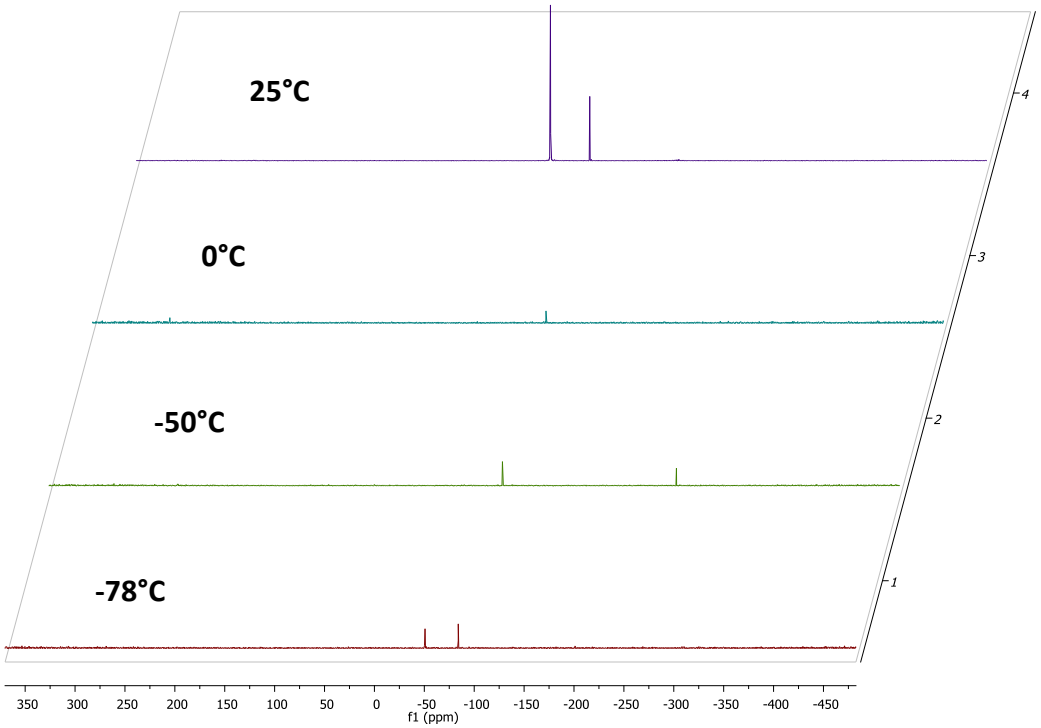


Figure 10: ^{119}Sn-NMRs ($CDCl_3$) from the temperature dependency study of the lithiation route

It can be concluded that in every case a signal at -82.3 ppm can be observed. When running the reaction at 0°C only a single peak at -85.2 ppm was detected. All gained product mixtures were subjected to a standard work up, removing the solvent under reduced pressure and precipitating the salts with toluene. Furthermore, the achieved products were subjected to recrystallization from toluene, which yielded rod like, orange crystals for the -78°C experiment (Figure 11). These crystals could be identified as 9-anth$_2$SnCl$_2$ with a ^{119}Sn-NMR chemical shift of -47.1 ppm. The second product with a ^{119}Sn-NMR chemical shift at -80.0 ppm could not be identified so far.

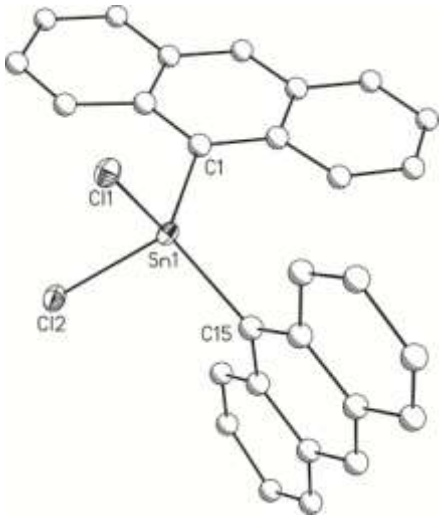


Figure 11: Crystal structure of dichloro-(bis-9-anthracenyl)stannane **9**. All non-carbon atoms shown as 30% shaded ellipsoids. Hydrogen atoms removed for clarity.

Table 8 summarizes selected bond lengths and angles of **9**.

Table 8: Selected Bond lengths and angles of dichloro-(bis-9-anthracenyl)stannane **9**

	space group	**bond length av. [Å]**		**angle av [°]**		
compound		*Sn-C*	*Sn-Cl*	*C-Sn-C*	*C-Sn-Cl*	*Cl-Sn-Cl*
9-anth$_2$SnCl$_2$	P2$_1$/c	2.134(6)	2.351(15)	119.68(2)	109.6(18)	96.24(5)

Dichloro-(bis-9-anthracenyl)stannane **9** crystallizes in the monoclinic space group P2$_1$/c, wherein the can be found in a distorted tetrahedral environment coordinated to four different substituents. The tin is bonded to two 9-anthracenyl substituents as well to two chlorides (Figure 12). Due to the higher steric demand of the condensed aromatic rings the average Cl-Sn-Cl angle is very compressed to only 96.24(5)°. In that manner it is possible that the anthracenyl moieties fit in the tetrahedral environment spanning an average C-Sn-C angle of 119.68(2)°, as well expected shorter C-Sn-Cl angle of 109.6(18)°. Further discussion on the crystal structure will be given in chapter 3.5.

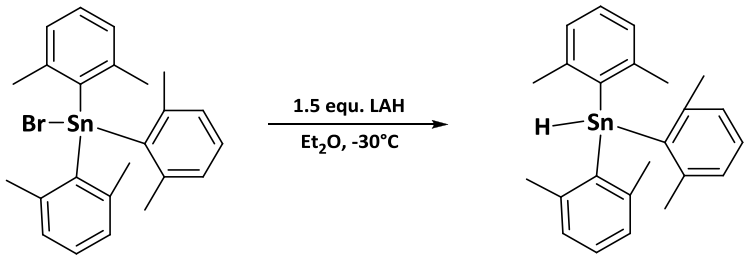
3.3.5.6 Conclusion

MS data confirmed that the product gained through the reaction *via* the activated Sn(II) compound is dichloro-(bis-9-anthracenyl)stannane **9** with an ^{119}Sn-NMR chemical shift at -45 ppm. This compound recrystallizes from toluene in the presence of an unidentified side product at -80.0 ppm regarding the temperature study. Herein, the product peak was found again at -47.1 ppm as shown in Figure 10.

3.4 Synthesis of Triarylstannanes

3.4.1 Tri-2,6-xylylstannane 10

The hydrogenation was carried out in the same way as for the trihydrides (chapter 3.6), but just 1.5 equivalents of LAH were used (Scheme 50).[11]



Scheme 50: Preparation of tri-2,6-xylylstannane

Tris-(2,6-xylyl)bromostannane **3** was subjected to reduction in order to better purify the product mixture, as well as to specify maginal side products of **3**, by subsequent hydrogen-coupled ^{119}Sn-NMR spectroscopy. However, the ^{119}Sn-NMR spectrum showed no side products, allowing isolation of 57% white solid, which was recrystallized from toluene yielding in colorless crystals. The crystal structure is displayed in Figure 12.

Similarly for the trichloro derivate, at least 25 sec of relaxation delay is also necessary to detect the first order coupling constants ^{1}J ^{119}Sn-^{13}C and $^{1}J^{117}$Sn-^{13}C in ^{13}C-NMR.

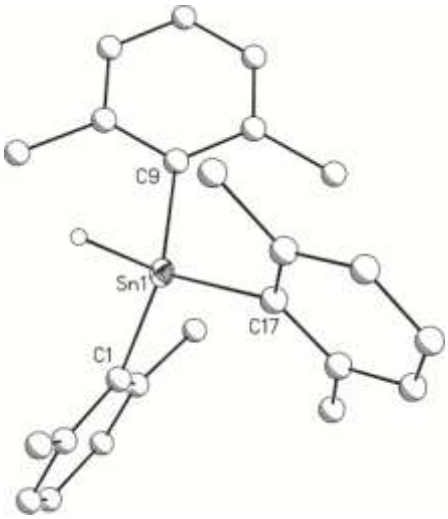


Figure 12: Crystal structure of tri-2,6-xylylstannane **10**. All non-carbon atoms shown as 30% shaded ellipsoids. Not relevant hydrogen atoms removed for clarity.

Table 9 summarizes selected bond lengths and angles of **10**.

Table 9: selected bond lengths and angles of tri-2,6-xylylstannane **10**

	space group	**bond length av. [Å]**		**angle av. [°]**	
compound		*Sn-C*	*Sn-H*	*C-Sn-C*	*H-Sn-C*
2,6-xylyl$_3$SnH	P-1	2.158(7)	n.o.	114.2(2)	n.o.

Tri-2,6-xylystannane **10** crystallizes in the triclinic space group P-1, whereas the tin can be found in a distorted tetrahedral environment coordinated to four different substituents. The tin is bonded to three 2,6-xylyl subtituents as well to one hydrogen, which was not able to be located *via* X-ray analysis (Figure 12). Due to the higher steric demand of the substituted aromatic ring the average C-Sn-C angle (114.2(2)°) is significantly wider than a tetrahedral angle. Unfortunately, there is no comparable literature data available about monohydrides, so that more information on the similar structures could not be given. Further discussion on the crystal structure will be given in chapter 3.5.

3.5 Comparison of Crystal Structures

This chapter provides a detailed overview of selected bond lengths and angles of published substances, as well as novel compounds which synthesized during this work. Furthermore, conclusions about the influence of increasing steric demand of substituents of the tetravalent tin on selected bond lengths and angles will be presented.

Table 10 summarizes selected bond lengths and angles for Ar_4Sn compounds.

Table 10: Comparison of selected bond lengths and angles for Ar_4Sn

Ar_4Sn	**space group**	**bond length av. [Å]**	**angle av. [°]**	**Ref.**
R		*Sn-C*	*C-Sn-C*	
Ph	$P42_1c$	2.139(5)	111.2(2)	12
o-Tol	$P42_1c$	2.152(5)	112.6(3)	11
3-Tol	$I4_1/a$	2.150(3)	109.3(4)	13
4-Tol	I4	2.147(6)	114.4(3)	14
3,5-Xylyl	P421c	2.134(5)	109.5(7)	15
2,4-Xylyl	P1	2.139(2)	109.4(9)	16
1-Naphthyl	$P2_1/n$	2.154(6)	109.5(3)	this work
2-Naphthyl	I-4	2.142(3)	107.3(6)	17

Comparison of published crystal structure data of tetraaryl stannane leads to the observation that average bond lengths and angles are not affected by the bulkiness of the organic substituent on the tetravalent tin. Sn-C bond lengths fall in a range of 2.13 - 2.15 Å, whereas C-Sn-C angles are about 107 - 114°.

Table 11 summarizes selected bond lengths and angles for Ar_3SnX compounds.

Table 11: Comparison of selected bond lengths and angles for Ar_3SnX

	Ar_3SnX	**space group**	**bond length av. [Å]**		**angle av [°]**		**Ref**
	R		*Sn-C*	*Sn-X*	*C-Sn-C*	*X-Sn-C*	
Br	Ph	P21/c	2.114(8)	2.495(2)	113.4(3)	105.2(2)	18
	2,6-xylyl	P21/c	2.164(8)	2.547(2)	115.8(3)	102.0(2)	this work
Cl	Ph	P21/c	2.116(4)	2.356(4)	113.3(2)	105.3(11)	19
	o-Tol	P21/n	2.132(3)	2.376(10)	114.3(13)	104.0(10)	20
	m-Tol	R3	2.123(1)	2.379(2)	114.0(14)	104.4(6)	3
	p-Tol	P-1	2.118(18)	2.373(6)	114.1(7)	104.4(5)	19
	3,5-Xylyl	R3c	2.124(2)	2.358(4)	111.9(2)	106.9(1)	3
	Mesityl	P21/n	2.158(5)	2.390(13)	115.4(17)	102.6(14)	21

For the Ar_3SnBr class only Ph_3SnBr can be compared, therefore the chloride analogues have been taken into account as well. The average Sn-C bond length falls in a range of 2.11 – 2.13 Å regarding all monosubstituted phenyl moieties as well as 3,5-xylyl. It has to be pointed out that the higher steric pressure of 2,6-xylyl and mesityl moieties leads to a slight increase of the average Sn-C bond up to 2.16(8) Å. However, the Sn-X bond is not affected by the organic substituent. The C-Sn-C angle is affected regarding the two biggest substituents leading to a maximum angle of 115.8(3)°, which in comparison to the general range of 113 - 114° is slightly increased. Therefore, corresponding X-Sn-C angles decrease a little bit with 2,6-xylyl and mesityl as organic groups.

Table 12 summarizes selected bond lengths and angles for Ar_3SnX compounds.

Table 12: Comparison of selected bond lengths and angles for Ar_3SnX

ArSnCl₃	**space group**	**bond length av. [Å]**		**angle av. [°]**		**Ref.**
R		*Sn-C*	*Sn-Cl*	*C-Sn-Cl*	*Cl-Sn-Cl*	
2,6-Xylyl	Pbcn	2.123(2)	2.332(6)	116.2(7)	101.8(2)	this work
1-Naphthyl	$P2_12_12_1$	2.131(19)	2.302(5)	114.9(5)	103.5(3)	this work
Mesityl	P21/c	2.128(6)	2.315(2)	117.3(2)	100.8(3)	22
Ph*	P1-n	2.155(5)	2.324(3)	117.1(14)	100.9(8)	23

It can be observed that starting from the 2,6-methyl substituted aromatic ligand, **6**, synthesized compounds are solid at room temperature. Therefore, it can be pointed out that changes in substitution position of the methyl groups, as seen in trichloro-2,4-xylylstannane **5** result in a liquid. Mono methyl-substituted aryltrichloro stannanes ,as e.g. trichloro-*o*-tolylstannane **4**, are liquid too. This can be explained by the decreased steric hindrance to the cental tin atom.

Average Sn-C and Sn-Cl bonds as well as C-Sn-Cl and Cl-Sn-Cl angles are not affected by the size of the substituents and fall in a range of 2.12 - 2.16 Å, 2.302 - 2.33 Å, 115 - 117° and 101 - 104°, respectively.

Table 13 summarizes selected bond lengths and angles for Ar_2SnCl_2 compounds.

Table 13: Comparison of selected bond lengths and angles for Ar_2SnCl_2

Ar_2SnCl_2	**space group**	**bond length av. [Å]**		**angle av. [°]**			**Ref.**
R		*Sn-C*	*Sn-Cl*	*C-Sn-C*	*C-Sn-Cl*	*Cl-Sn-Cl*	
Ph	P-1	2.112(5)	2.345(2)	123.9(4)	107.3(2)	101.7(1)	24
p-Biphenyl	P21/n	2.130(9)	2.386(3)	130.8(3)	105.6(2)	99.72(9)	25
Mesityl	Pbcn	2.117(4)	2.414(4)	119.7(5)	108.9(3)	100.3(3)	26
(2,4,6*i*Pr)Ph	C2/c	2.147(4)	2.353(2)	119,7(2)	109.8(2)	96.20(1)	27
Supermesityl	P21/c	2.198(2)	2,371(4)	117.0(4)	111.0(2)	94.48(1)	28
2-Naphthyl	P21/n	2.111(2)	2.355(5)	119.3(3)	109.2(4)	101.3(7)	16
9-Anthracenyl	P21/c	2.134(6)	2.351(15)	119,7(2)	109.6(18)	96.24(5)	this work

By comparison with already published data it is obvious, that the Sn-C bond of dichloro-(bis-9-anthracenyl)stannane **9** falls within the range of 2.11 - 2.15 Å. Only the Sn-C bond of the supermesityl derivative slightly differs with a value of 2.198(2) Å. Regarding the average C-Sn-C, Ph_2SnCl_2 surprisingly shows the widest angle with 130.8(3)° in comparison to a usual range of 119 - 124°. Dichloro-(bis-9-anthracenyl)stannane **9** exhibits a decreased Cl-Sn-Cl bond (96.24(5)°) in comparison to the 2-naphthyl derivative (101.3(7)°) containing only two condensed aromatic rings due to the higher steric pressure of the anthracenyl ligands.

Table 14 summarizes selected bond lengths and angles for aryltin hydrides.

Table 14: Comparison of selected bond lengths and angles for aryltin hydrides

Ar_3SnH	**space group**	**bond length av. [Å]**		**angle av. [°]**			**Ref**
R		*Sn-C*	*Sn-H*	*C-Sn-C*	*H-Sn-C*	*H-Sn-H*	
2,6-xylyl	P-1	2.158(7)	n.o.	114.2(2)	n.o.	-	this work
Ar_2SnH_2							
R							
Mesityl	C2/c	2.154(1)	1.669(2)	111.1(4)	110.6(7)	105.3(1)	29

Unfortunately, there is no crystallographic data available for tin monohydrides, so that crystal data of Mes_2SnH_2 is also displayed in Table 14.

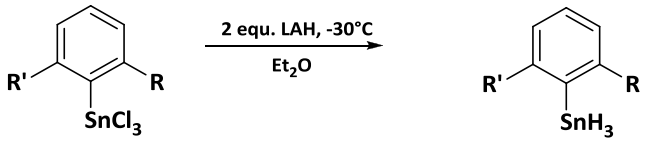
All in all it can be pointed out, that C-Sn-C in the tetraaryl case as well as C-Sn-Cl angles for all other compounds can be ranked in the following manner.

$$Ar_2SnCl_2 < Ar_4Sn < Ar_3Snx < ArSnCl_3$$

This clearly shows, that the spanned angle is not only a question of the steric demand of the substituent but also of the electron repulsion induced by electron rich halides. In case of the bond lengths, Sn-X remains unaffected by other substituents.[21]

3.6 Synthesis of Trihydrido Arylstannanes

The synthesis and work up for all trihydrido stannanes (**11**, **12**, **13**, **14**) proceeded in the same manner by employing 2 equivalents of LAH (scheme 51) resulting in moderate to high yields as shown in table 15.[11]



Scheme 51: Hydrogenation of aryltrichlorostannanes resulting in aryltin trihydrides

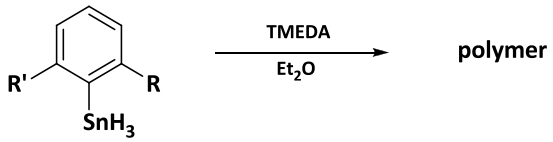
Table 15: Yields for all synthesized trihydrido arylstannanes

R	yield [%]
o-Tol **11**	50
2,4-Xylyl **12**	68
2,6-Xylyl **13**	86
1-Naphthyl **14**	75

All synthesized trihydrides were stored at -80°C, under nitrogen atmosphere. Slow decomposition over several months under the formation of a yellowish to brownish solid, which is not soluble in common organic solvents could be detected.

3.7 Polymerization Attempts

Polymerization attempts of the aryltin trihydrides in the presence of TMEDA using ether as solvent were carried according the conditions described by Lechner.[30]



Scheme 52: Polymerization of aryltrihydrido stannanes in the presence of TMEDA

To a colorless solution of *o*-tolylstannane **11** in ether 1 equivalent of TMEDA was added at room temperature which immediately led to a color change to slightly orange and the formation of hydrogen. The color change was also reported in several publications[31-34] dealing with the visible properties of polystannanes induced by $\sigma \rightarrow \sigma^*$ and $\sigma \rightarrow \pi$ transitions. Already after 1 h reaction time the mixture turned black. In order to isolate the amorphous solid the solvent was removed under reduced pressure and the remaining product extracted with THF to separate soluble parts. ^{119}Sn-NMR investigation of the supernatant THF solution showed no signal. The resulting product can be described as amorphous solid, insoluble in organic solvents. Furthermore, the substance decomposes at ambient conditions under the formation of a white to yellowish solid. This decomposed substance is also not soluble in common organic solvents. In order to know whether there are organic groups left in the polymer, the black substance was subjected to elemental analysis to determine the carbon, as well as hydrogen content. To gain qualitative information about the percentage of Sn in the polymer, also EDX measurements were carried out. Experimental C,H values are compared with calculated ones referring to different polymerization degrees (Table 16).

Table 16: Elemental analysis (C,H) and EDX (Sn) measurements of the polymerization product

polymer composition		***element***		
		C [%]	**H [%]**	**Sn [%]**
calculated	$(RSnH_2)_2$	39.68	4.28	56.03
	$RSnH_n$	39.87	3.82	56.30
	RSn_x	40.07	3.36	56.57
found		29.87	2.59	60.04

Elemental analysis (C,H values) does not exactly fit with a polymer of the type $(RSn)_x$. Hence, it can be suspected that during the reaction organic moieties got lost besides H_2. Furthermore, EDX measurement reveals a Sn ratio of 60%, suggesting the formation of a polymer composition of $(R_{0.95}Sn)_x$.

An addition polymerization reaction was also carried out using 2,4-xylylstannane. In order to investigate the temperature dependency of the reaction process, six different reactions where carried at -30°C, -20°C, -10°C, 0°C, 10°C and ambient temperature. All of them were stirred for 1 h and then subjected to ^{119}Sn-NMR measurements using a $CDCl_3$ capillary tube to reference the spectra. It could be found out that, the reaction even starts at -40°C immediately under the formation of hydrogen and a color change to slightly orange. After 1 h stirring time, the reaction carried out at -30°C was dark red, color change at 35 min was observed for the reaction maintained at 0°C and at 20 min for the reaction at 10°C. In all of the red colored suspensions a remaining hydride signal in the ^{119}Sn-NMR could be detected. Again, the reaction which was carried out at room temperature neither showed the educt signal, or other signals due to solubility problems. However, a black precipitate was obtained. Based on these findings, further investigations are ongoing.

3.8 Comparison of ^{119}Sn-NMR Data of Ar_4Sn, Ar_3SnX, Ar_2SnCl_2, $ArSnCl_3$, Ar_3SnH and $ArSnH_3$

This chapter gives an overview on the ^{119}Sn-NMR data overview of relevant compounds presented in literature and in this work. If nor otherwise stated values are listed for $CDCl_3$ as NMR solvent.

Table 17 summarizes ^{119}Sn-NMR shifts of Ar_4Sn, Ar_3SnCl, Ar_3SnBr and $RSnH_3$ compounds in $CDCl_3$.

Table 17: ^{119}Sn-NMR Data (ppm) for Ar_4Sn, Ar_3SnCl, Ar_3SnBr, $ArSnCl_3$ and $RSnH_3$ in $CDCl_3$

	Ar_4Sn	**Ar_3SnCl**	**Ar_3SnBr**	**$ArSnCl_3$**	**$RSnH_3$[a]**
Ph	-128.8[3]	-44.81[3]	-60.01[3]	-65[35]	-320[35]
o-Tol	-122.6	-32.28[3]	-53.98[3]	-54,4	-358
m-Tol	-128.0[3]	-42.33[3]	-56.87[3]		
p-Tol	-124.6[2]	-35.91[36]	-52.17[36]		
2,4-Xylyl	-119.3	-40.55		-57,03	-352,4
2,6-Xylyl			-131.6	-88,18	-417,5
3,5-Xylyl	-127.5[3]	-39.68[3]	-53.55[3]		
Mes		-84.39[3]	-121.0[3]	-85,5[37]	
1-Naph	-118.8[a]	-37,20 [16]		-55.0	-358,9
2-Naph	-117.6 [a,16]				

a… C_6D_6 was used as a solvent

For these compounds the bulkiness of the organic substituents does not affect the range of the ^{119}Sn-NMR signal, whereas electronegative substituents like halides lead to down field shifts due to the shielding of the external magnetic field.

Table 18 summarizes coupling constants of Ar_4Sn, Ar_3SnX, Ar_2SnCl_2, Ar_3SnH and $ArSnH_3$ compounds.

Table 18: Coupling Constants Overview

	Organic moiety	$^1J^{13}C$-^{119}Sn*	$^1J^{13}C$-^{117}Sn*	$^1J^1H$-^{119}Sn**	^1J1H-^{117}Sn**	Ref.
Ar_4Sn	Ph	531				3
	o-Tol	521				3
	m-Tol	527				3
	p-Tol	537				38
	2,4-Xylyl	529	504			15
	3,5-Xylyl	522				3
	1-Naph	520	497			this work
	2-Naph	529	505			16
Ar_3SnCl	Ph	616				3
	o-Tol	604				3
	m-Tol	608				3
	p-Tol	625				36
	3,5-Xylyl	603				3
	Mes	596				3
Ar_3SnBr	Ph	596				3
	o-Tol	586				3
	m-Tol	591				3
	p-Tol	607				36
	2,6-Xylyl	570	544			this work
	3,5-xylyl	580				3
	Mes	580				3
Ar_2SnCl_2	1-Naph	770	736			16
	2-Naph	788	753			16
$ArSnCl_3$	Ph	1118				35
	o-Tol	1087	1039			this work
	2,4-Xylyl	1101	1052			this work
	2,6-Xylyl	1062	1015			this work
	1-Naph	1127	1074			this work
Ar_3SnH	Ph			1936		35
	2,6-Xylyl	534	512	1776	1697	this work
Ar_2SnH_2	Ph			1928		35
	1-Naph	544	520	1937	1851	16
	2-Naph	543	518	1947	1855	16
$ArSnH_3$	Ph			1920		35
	o-Tol	568	543	1908	1824	this work
	2,4-Xylyl	580	555	1898	1814	this work
	2,6-Xylyl	582	558	1896	1812	this work
	1-Naph	not found	not found	1934	1849	this work

* Data from ^{13}C spectra, ** Data from ^1H spectra

As a general trend the following sequence of $^1J^{13}C$-^{119}Sn coupling can be detected:

$$ArSnCl_3 > Ar_2SnCl_2 > Ar_3SnCl > Ar_3SnBr \approx ArSnH_3 > Ar_2SnH_2 \geq Ar_3SnH > Ar_4Sn$$

Additionally, it can be shown that the coupling constants differ only slightly regarding tetraarylstannes and values lie in a range of 521 - 537 Hz ($^{1}J^{13}$C-^{119}Sn). Regarding Ar_3SnCl, *ipso* coupling constants can be found in a range of 596 - 625 Hz. For the corresponding bromo derivative (Ar_3SnBr) values are observed to be slightly decreased, lying in a range from 570 - 607 Hz. Furthermore, it can be observed that all *para*-substituted aryl ligands exhibit the highest ^{119}Sn-^{13}C coupling constants. Moreover, it is obvious that substituents harboring high electronegativity, like halides, lead to an increase of ^{1}J-values so that a growing number of chloro atoms bond to the tin leads to maximum ^{13}C-^{119}Sn coupling constants up to 1127 Hz ($ArSnCl_3$). Tinhydrides do not show a significant difference of carbon-tin coupling constants from Ar_4Sn compounds, but slightly increase with the number of hydrogen bond to the tin from 534 - 582 Hz. However, ^{1}H-^{119}Sn coupling constants of all mentioned hydrides range from 1776 - 1937 Hz, where neither an influence of the organic substituent's size nor of the number of hydrogens bond can be detected so far.

3.9 Conclusion and Outlook

During this work novel trichloro arylstannanes where successfully synthesized by Kozeschkow[8] redistribution reactions serving as starting compounds for the preparation of hitherto quite neglected and little described aryltin trihydrides. Synthesis of *ortho* substituted aryltin trihydrides as a novel family of tin compound was realized using LAH in ether.[11] Additionally, unpublished aryltin di- and monohalides were prepared and characterized. A better understanding of synthetic and structural factors influencing the synthesis and characterization of those organostannanes was achieved. Furthermore, initial polymerization attempts of generated aryltin trihydrides was carried out in the presence of TMEDA described by Lechner[31] resulting in black, amorphous solids. The generated polymers are insoluble in common organic solvents and decompose at ambient conditions. Elemental analysis showed that organic moieties get lost during the reaction progress. Additionally, first measurements *via* EDX showed a Sn ratio of 60% and suggest a polymer composition of $(R_{0.95}Sn)_x$. Based on these findings further investigation on the polymerization behavior, as well as on the properties can be declared as future goals.

3.10 References

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4 Experimental Section

4.1 General and Used Chemicals

All reactions, unless otherwise stated were carried out under inert conditions using Schlenk technique and nitrogen as inert gas. In order to ensure dry atmosphere the used nitrogen passed a molecular sieve (4Å) to remove residual moisture. All dried and deoxygenated solvents were obtained from a solvent drying plant (Innovative Technology, inc). Other organic solvents for synthesis were purchased at VWR and Lactan.

All chemicals from commercial source were utilized without further purification, unless otherwise mentioned.

4.1.1 Chemicals Used in Synthesis

Table 19: Used chemicals and commercial sources

compound	provider
1-bromo-2-methyl-benzene	Sigma Aldrich
1-bromo-2,4-dimethylbenzene	Alfa Aeser
2-bromo-1,3-dimethylbenzene	Alfa Aeser
magnesium tunings	Sigma Aldrich
LAH pellets	Sigma Aldrich
zinc powder	Acros Organics
tributyl tinhydride	Merck
*n*BuLi 2.5 M in hexane	Sigma Aldrich
9-bromoanthracene	Sigma Aldrich
tin dichloride	Fischer Chemical
1-bromonaphtaline	Merck
LDA	Sigma Aldrich

4.2 Analytics

4.2.1 NMR-Spectroscopy

^{1}H-, ^{13}C- and ^{119}Sn-NMR spectra were recorded on a Mercury 300 MHz spectrometer from Varian at 25°C not otherwise mentioned.

Table 20: frequencies of observed nuclei (300 MHz spectrometer)

nucleus	frequency [MHz]
^{1}H	300.22
^{13}C	75.5
^{119}Sn	111.92

Only for one compound ^{1}H and ^{13}C-NMR spectra were recorded on a Varian Inova 500 MHz spectrometer at 25°C . The applied software was VNMRJ 2.2 D.

Table 21: Frequencies of observed nuclei (500 MHz spectrometer)

nucleus	frequency [MHz]
^{1}H	499.98
^{13}C	125.69

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). The spectra were processed and analyzed in MestReNova 5.2.5. As solvents C_6D_6 or $CDCl_3$ are used if not otherwise mentioned.

4.2.2 Elemental Analysis

All elemental analysis were performed with an Elementar Vario EL using sulfanilic acid as standard.

4.2.3 X-Ray Analysis

XRD data collection was performed on a Bruker Apex II diffractometer with use of Mo Kα radiation (λ=0.71073 Å) and a CDD area detector. Empirical absorption corrections were applied using SADABS.[1,2] 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.[3,4] Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located in calculated positions corresponding to standard bond lengths and angles.

4.2.4 ICP-AES Measurements

Microwave assisted chemical combustion was carried out with 6 ml HCl conc. suprapur and 0.5 ml HNO_3 using a Multiwave 3000, 1400 W during 15 minutes. ICP-AES were carried out with a Spectro Cyros Vision EOP end on plasma.

4.2.5 SEM and EDX Measurments

SEM measurements were carried out in a Vega 3 SBU SEM from Tescan equipped with a wolfram cathode. For qualitative assignment of the sample composition EDX on an Oxford Instruments, model INCA x-act was carried out.

4.2.6 Melting Point Measurements

For these measurements a Stuart Scientific SMP 10 (up to 300°C) was used and a threefold determination carried out.

4.2.7 ATR Measurments

For ATR measurements a Bruker Alpha-P was used.

4.2.8 MS-Measurements

Compounds were ionized *via* electron impact (70 eV) ionization. Mass spectra were recorded on a Waters GCT Premier equipped with direct insertion (DI).

4.2.9 TGA and DTA Measurements

TGA and DTA measurements were carried out using a STA 449C Jupiter from Netzsch. The performed temperature program lay between 20-550°C with a heating rate of 10°C/min. As purge gas helium was used.

4.3 Synthesis

For all naphtyl and anthracenyl moieties the NMR assignment for carbon and hydrogen atoms is according to the IUPAC numbering.

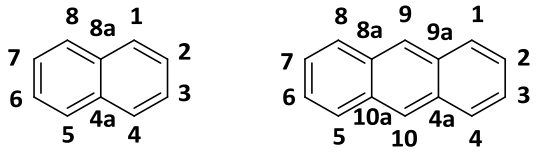
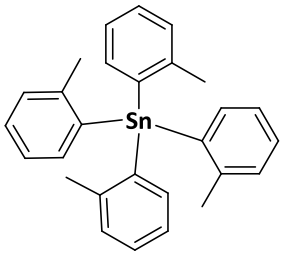


Figure 13: IUPAC numbering of naphthyl and anthracenyl substituents

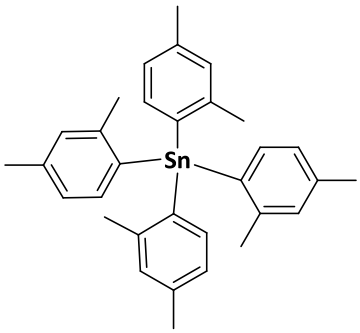
Tetra-*o*-tolylstannane (1)[5]



A flask equipped with a dropping funnel and a reflux condenser was charged with 15.19 g (1.25 eq., 0.63 mol) magnesium tunings in 500 ml Et_2O as well as the dropping funnel was filled with a solution of 60.1 ml 1-bromo-2-methyl-benzene (1 eq., 0.5 mol, 85.51 g) in 60 ml Et_2O. The Grignard reaction started after addition of 2 ml dibromoethane and the ethereal solution was added drop wise so that gentle reflux continued. After completion of the addition the reaction mixture was stirred overnight. A second flask furnished with a mechanical stirrer and a reflux condenser was charged with 12.3 ml $SnCl_4$ (0.21 eq., 27.35 g) in 350 ml Et_2O under ice cooling. Then the Grignard solution was added *via* a cannula and the mixture stirred at room temperature overnight and subsequently refluxed for 2 h to obtain a slightly yellow suspension. The solvent was evaporated to give a greenish solid which was suspended in toluene and filtered hot through celite. Again the solvent was removed under reduced pressure to obtain 50.73 g of a pale green solid. According to the NMR spectra measured in $CDCl_3$ the side product can be defined as *o*-tol_3SnBr. Hence, **1** is gained with a purity of 21% and yield of 18% (10.65 g, 22 mmol).

^{119}Sn-NMR ($CDCl_3$) δ: -122.6 (**1**), -54.0 (*o*-tol_3SnBr)

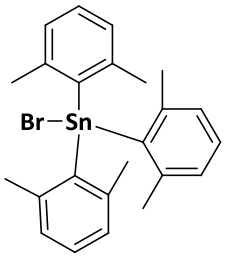
Tetra-2,4-xylylstannane (2)[5,6]



A flask equipped with a dropping funnel and a reflux condenser was charged with 15.19 g (1.25 eq., 0.63 mol) magnesium tunings in 350 ml Et_2O as well as the dropping funnel was filled with a solution of 67.5 ml 1-bromo-2,4-dimethylbenzene (1 eq., 0.5 mol, 92.53 g) in 100 ml Et_2O. The Grignard reaction started after addition of 2 ml dibromoethane and the ethereal solution was added drop wise so that gentle reflux continued. After completion of the addition the reaction mixture was refluxed for 3.5 h and then stirred overnight at room temperature. A second flask furnished with a mechanical stirrer and a reflux condenser was charged with 12.3 ml $SnCl_4$ (0.21 eq., 0.11 mol, 27.4 g) in 500 ml Et_2O under ice cooling. Then the Grignard solution was added *via* a cannula and the mixture stirred at room temperature overnight. Subsequently, the reaction mixture was refluxed for 2 h to obtain a pale brown suspension. The solvent was evaporated to afford a yellowish syrup which was taken up in pentane in order to precipitate the salt. The mixture was then filtered through celite and the solvent evaporated to give a pale yellow solid, which was subjected to fractionated distillation. The purification afforded 27.67 g of a brownish solid which according to the NMR spectra measured in $CDCl_3$ can be assigned as followed: 87% Ar_3SnCl, 9% Ar_2SnCl_2 as well as 4% of the desired product **2**, which was not further isolated. A theoretical yield of 4% (1.1 g, 2 mmol) can be calculated.

^{119}Sn-NMR ($CDCl_3$) δ: -119.3 (**2**),-40.55 (2,4-xylyl$_3$SnCl), -73.27 (2,4-xylyl$_2$SnCl$_2$)

Tribromo-2,6-xylylstannan (3)[5]



A flask equipped with a dropping funnel and a reflux condenser was charged with 7.59 g (1.25 eq., 0.31 mol) magnesium tunings in 300 ml Et_2O as well as the dropping funnel was filled with a solution of 33.3 ml 2-bromo-1,3-dimethylbenzene (1 eq., 0.25 mol, 46.27 g) in 60 ml Et_2O. The Grignard reaction started after addition of 1 ml dibromoethane and the ethereal solution was added drop wise so that gentle reflux continued. After completion of the addition the reaction mixture was refluxed for 1 h and then stirred at room temperature over night. Subsequently it was again refluxed for 3 h. A second flask furnished with a mechanical stirrer and a reflux condenser was charged with 4.68 ml $SnCl_4$ (0.16 eq., 0.04 mol, 10.42 g) in 500 ml Et_2O under ice cooling. Then the Grignard solution was added *via* a cannula and the mixture stirred at room temperature over night. Subsequently it was refluxed for further 2 h to obtain a pale yellow suspension. The solvent was evaporated to afford a white solid which then was Soxhlet extracted during 2 d using pentane to afford 16.88 g of a white solid, which subsequently was subjected to recrystallization from pentane to afford colorless crystals. The crystals were identified by X-ray analysis as tribromo-2,6-xylylstannane in 19% yield (16.54 g, 32 mmol).

^{1}H-NMR (C_6D_6) δ: 7.01-6.92 (t, 1H, $J_{5,4}$= 7.5 Hz, H5), 6.86-6.78 (d, 2H, $J_{4,5}$= 7.5 Hz, H4), 2.41 (s, 6H, H3)

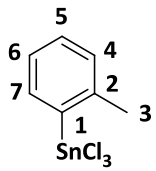
^{13}C-NMR (C_6D_6) δ: 144.62 ($^1J(^{119}Sn\text{-}^{13}C)$= 570 Hz, $^1J(^{117}Sn\text{-}^{13}C)$= 544 Hz, C1), 144.13 ($^2J(^{119/117}Sn\text{-}^{13}C)$= 43 Hz, C2), 129.75 ($^4J(^{119/117}Sn\text{-}^{13}C)$= 11 Hz, C5), 128.23 ($^3J(^{119/117}Sn\text{-}^{13}C)$= 53 Hz, C4), 25.67 ($^3J(^{119/117}Sn\text{-}^{13}C)$= 41 Hz, C3)

^{119}Sn-NMR ($CDCl_3$) δ: -131.6

CHN-analysis: found (C: 54.67 %, H: 5.48 %), required (C: 56.07 %, H: 5.29 %)

Mp: 175°C

Trichloro-*o*-tolylstannane (4)[7]



48.14 g of the mixed product **1** were combined with 22.8 ml $SnCl_4$ (50.67 g, 1.3 mol, 6.2 eq. calculated for **1**) in a Schlenk flask furnished with a reflux condenser. The mixture was heated up to 150°C using an oil bath and stirred for 2 h to obtain complete conversion which was monitored *via* ^{119}Sn-NMR spectroscopy. The excess of $SnCl_4$ was removed under reduced pressure to obtain a dark brown liquid. Subsequently the mixture was subjected to fractionated distillation under reduced pressure to afford 12.19 g of a product mixture containing **4** in 99% purity and 1% dichloro-(bis-*o*-tolylstannane) as side product. A theoretical yield of 7% (12.07 g, 38 mmol) referring to 2-bromotoluene can be calculated.

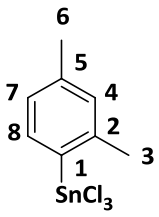
^{1}H-NMR ($CDCl_3$) δ: 7.69-7.53 (m, 2H, H5, H7), 7.50-7.42 (m, 2H, H4, H6), 2.70 (m,3H, CH_3)

^{13}C-NMR ($CDCl_3$) δ: 143.1 ($^2J(^{119}Sn\text{-}^{13}C)$= 75 Hz, $^2J(^{117}Sn\text{-}^{13}C)$= 72 Hz, C2 or C7),136.9 ($^1J(^{119}Sn\text{-}^{13}C)$= 1087 Hz, $^1J(^{117}Sn\text{-}^{13}C)$= 1039 Hz, C1), 134.41 (($^2J(^{119}Sn\text{-}^{13}C)$= 77 Hz, $^1J(^{119}Sn\text{-}^{13}C)$= 74 Hz, C2 or C7), 135.53 ($^4J(^{119/117}Sn\text{-}^{13}C)$= 24 Hz, C5), 131.71 ($^3J(^{119}Sn\text{-}^{13}C)$= 119 Hz, $^3J(^{117}Sn\text{-}^{13}C)$= 114 Hz, C4 or C6), 127.34 ($^3J(^{119}Sn\text{-}^{13}C)$= 122, $^3J(^{117}Sn\text{-}^{13}C)$=125 Hz, C4 od. C6), 24.71 (($^3J(^{119/117}Sn\text{-}^{13}C)$=54 Hz, C3)

^{119}Sn-NMR ($CDCl_3$) δ: -54.4 (**4**), - 114.6 *o*-tol_2SnCl_2

Total Sn-determination *via* ICP-AES: found (Sn: 33.4 %) required (Sn: 37.5%)

Trichloro-2,4-xylylstannane (5)[7]



22.55 g of the mixed product **2** were combined with 16.85 ml $SnCl_4$ (37.52 g, 0.14 mol, 3.4 eq. calculated for 2,4-xylyl$_3$SnCl in a Schlenk flask furnished with a reflux condenser. The mixture was heated up to 170°C using an oil bath and stirred for 3h to obtain complete conversion which was monitored *via* ^{119}Sn-NMR spectroscopy. The dark brown mixture was then subjected to fractionated distillation under reduced pressure to afford 30.24 g of **5** in 98% purity (18% yield related to 4-bromo-m-xylol) as a yellowish liquid.

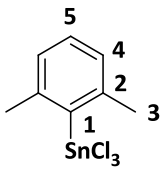
^{1}H-NMR ($CDCl_3$) δ: 7.53 (d, 1H, $J_{7,8}$=7.6 Hz, H8), 7.29-7.23 (m, 2H, H7, H4), 2.66 (s, 3H, C3H_3), 2.46 (s, 3H, C6H_3)

^{13}C-NMR ($CDCl_3$) δ: 144.23 ($^4J(^{119/117}Sn\text{-}^{13}C)$= 24 Hz, C5), 142.81 ($^2J(^{119/117}Sn\text{-}^{13}C)$= 78 Hz, C2), 134.21 ($^2J(^{119/117}Sn\text{-}^{13}C)$= 80 Hz, C8), 133.48 ($^1J(^{119}Sn\text{-}^{13}C)$= 1101 Hz, $^1J(^{117}Sn\text{-}^{13}C)$= 1052 Hz, C1), 132.50 (C4 or C7), 128.01 ($^4J(^{119/117}Sn\text{-}^{13}C)$= 127 Hz, C4 or C7), 24.44 (C3), 21.70 (C6)

^{119}Sn-NMR ($CDCl_3$) δ: -57.03

CHN-analysis: found (C: 28.38 %, H: 2.64 %), required (C: 29.10 %, H: 2.75 %)

Trichloro-2,6-xylylstannane (6)[7]



9.28 g of **3** were combined with 7.05 ml $SnCl_4$ (15.69 g, 60 mmol, 3.4 eq) in a Schlenk flask furnished with a reflux condenser which immediately leads to a deep red color change. The mixture was heated up to 190°C using an oil bath and stirred for 4h to obtain complete conversion which was monitored *via* ^{119}Sn-NMR spectroscopy. The excess of $SnCl_4$ was removed under reduced pressure and the remaining mixture was subjected to distillation under reduced pressure to afford 10.53 g of **6** as white crystals (0.03 mol, 44%).

^{1}H-NMR ($CDCl_3$) δ: 7.42-7.37 (1H, t, $J_{5,4}$= 7.5 Hz, H5), 7.32-7.08 (2H, d, $J_{4,5}$=7.5 Hz, H4), 2.72 - 2.68 (6H, m, CH_3)

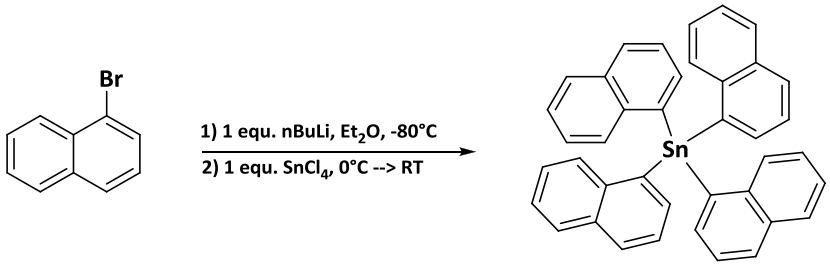
^{13}C-NMR ($CDCl_3$) δ: 143.29 ($^{2}J(^{119}Sn\text{-}^{13}C)$= 76, $^{2}J(^{117}Sn\text{-}^{13}C)$= 72 Hz, C2), 138.10 ($^{1}J(^{119}Sn\text{-}^{13}C)$= 1062 Hz, $^{1}J(^{117}Sn\text{-}^{13}C)$= 1015, C1), 132.48($^{4}J(^{119/117}Sn\text{-}^{13}C)$= 23 Hz, C5), 129.92 ($^{3}J(^{119}Sn\text{-}^{13}C)$= 123 Hz, $^{3}J(^{117}Sn\text{-}^{13}C)$= 117 Hz, C4), 24.47 ($^{3}J(^{119}Sn\text{-}^{13}C)$= 57 Hz, $^{3}J(^{117}Sn\text{-}^{13}C)$= 55 Hz, C3)

^{119}Sn-NMR ($CDCl_3$) δ: -88.18

Melting range: 56-59°C

CHN-analysis: found (C: 29.45 %, H: 2.66 %), required (C: 29.10 %, H: 2.75 %)

Tetra-1-naphthylstannane (7)



To a solution of 5 ml 1-bromonaphthalene (7.4 g, 35 mmol, 1 eq.) in 50 ml Et_2O 14.3 ml of a 2.5 M *n*-BuLi solution in hexane (1 eq, 0.035 mol) was added *via* a syringe at -80° to immediately obtain an orange reaction mixture. The solution was stirred under cooling for 2 h and then allowed to warm to room temperature. A second Schlenk flask was charged with 4.18 ml $SnCl_4$ (1 eq., 9.31 g, 0.035 mol) in 20 ml Et_2O at ice cooling and the lithiated solution was added *via* a cannula. The resulting suspension was stirred at room temperature over the weekend and subsequently the solvent was removed under reduced pressure. The obtained residue was taken up in 50 ml toluene and the salts were filtered. Then the solvent was evaporated to obtain a light brown solid which was taken up in 250 ml CH_2Cl_2 and 150 ml H_2O dest. were added. The phases were separated and the aqueous phase extracted twice with 100 ml CH_2Cl_2. The combined organic phases were dried over Na_2SO_4 and the solvent was removed under reduced pressure to afford a grey solid which was recrystallized from ethylacetate. 3.58 g **7** (5.7 mmol, 64%) as white crystals.

^{1}H-NMR (C_6D_6) δ: 8.34-8.25 (d, 1H, $J_{8,9}$=8.3 Hz, H8), 8.21-7.95 (d, 1H, $J_{2,3}$= 6.5 Hz, $^{3}J(^{119}Sn\text{-}^{1}H)$= 68 Hz, $^{3}J(^{117}Sn\text{-}^{1}H)$= 54 Hz, H2), 7.64-7.55 (d, 1H, $J_{6,7}$=8.1 Hz, H5), 7.55-7.47 (d, 1H, $J_{3,4}$=8.0 Hz, H4), 7.08-6.94 (m, 2H, H6, H7), 6.84-6.74 (dd, 1H, H3)

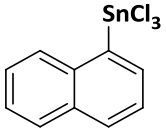
^{13}C-NMR (C_6D_6) δ: 140.35 ($^{1}J(^{119}Sn\text{-}^{13}C)$=520 Hz, $^{1}J(^{117}Sn\text{-}^{13}C)$= 497 Hz, C1), 139.02 ($^{3}J(^{119/117}Sn\text{-}^{13}C)$= 34 Hz, C4a), 137.20 ($^{2}J(^{119}Sn\text{-}^{13}C)$= 38 Hz, $^{2}J(^{117}Sn\text{-}^{13}C)$= 47 Hz, C2), 134.16 ($^{2}J(^{119/117}Sn\text{-}^{13}C)$= 37 Hz, C8a), 130.23 ($^{3}J(^{119/117}Sn\text{-}^{13}C)$= 32 Hz, C8), 130.00 ($^{4}J(^{119/117}Sn\text{-}^{13}C)$= 12 Hz, C4), 129.00 (C5), 126.43 (C6 or C7), 126.07 (C6 or C7), 125.72 (C3).

^{119}Sn-NMR (C_6D_6) δ: -118.8.

Melting range: 246-248°C.

CHN-analysis: found (C: 75.36 %, H: 4.40 %), required (C: 76.58 %, H: 4.50 %)

Trichloro-1-naphthylstannane (8)[7]



3.00 g of **7** (4.78 mmol) were combined with 1.67 ml $SnCl_4$ (3.73 g, 14.3 mmol, 3 eq.) in a Schlenk flask furnished with a reflux condenser. The mixture was heated up to 190°C using an oil bath and stirred for 1.5 h to obtain complete conversion which was monitored *via* ^{119}Sn-NMR spectroscopy. The excess of $SnCl_4$ was removed under reduced pressure and the remaining black solid was taken up in 50 ml CH_2Cl_2. The suspension was filtered through celite and the solvent was evaporated under reduced pressure. The obtained white solid was recrystallized from toluene to afford 3.43 g **8** as white crystals (9.73 mmol, 51%).

^{1}H-NMR ($CDCl_3$) δ: 8.13-8.06 (d, 1H, $J_{3,4}$=8.3 Hz, H3), 8.06-7.95 (m, 2H, H8a, H7), 7.93-7.88 (d, 1H, $J_{5,6}$=7.0 Hz, H5), 7.75-7.59 (2dd, 3H, H4,H4a,H8).

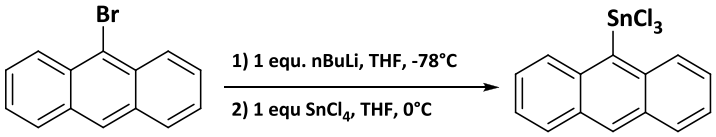
^{13}C-NMR ($CDCl_3$) δ: 136.89 ($^1J(^{119}Sn\text{-}^{13}C)$= 1127, $^1J(^{117}Sn\text{-}^{13}C)$= 1074, C1), 134.91 ($^3J(^{119/117}Sn\text{-}^{13}C)$= 84 Hz, C6), 134.70 ($^2J(^{119/117}Sn\text{-}^{13}C)$= 102 Hz, C2), 134.42 ($^5J(^{119/117}Sn\text{-}^{13}C)$= 61 Hz, C5), 133.36 ($^2J(^{119/117}Sn\text{-}^{13}C)$= 28 Hz, C3), 129.4 ($^4J(^{191/117}Sn\text{-}^{13}C)$= 21 Hz, C7), 128.56 ($^4J(^{119/117}Sn\text{-}^{13}C)$=7 Hz, C4a), 127.48 ($^4J(^{119/117}Sn\text{-}^{13}C)$= 59 Hz, C8a), 127.38 (C4), 125.81 ($^1J(^{119}Sn\text{-}^{13}C)$= 142, $^1J(^{117}Sn\text{-}^{13}C)$= 136 Hz, C8)

^{119}Sn-NMR ($CDCl_3$) δ: -55.0

CHN-analysis: found (C: 33.99 %, H: 1.87 %), required (C: 34.10 %, H: 2.00 %)

Attempts towards Dichloro-(bis-9-anthracenyl)stannane (9)

a) Synthesis *via* the lithiation route



4 g 9-bromoanthracene (15.6 mmol) in 150 ml THF were treated with 1.8 ml *n*-BuLi (2.5 M in hexane, 15.6 mmol) at -70°C. The reaction mixture immediately turned orange. After 2 h stirring at -70°C the solution was transferred *via* a cannula into a suspension of $SnCl_4$ (1 eq., 15.6 mmol, 4.05 g, 1.8 ml) in 30 ml THF at 0°C. The mixture turned amber colored and was allowed to warm up to room temperature. After stirring for 3 h the solvent was removed under reduced pressure and the resulting solid taken up in toluene to precipitate salts. The supernatant red solution was filtered of and again the solvent removed under reduced pressure to obtain 2.68 g of a brownish powder.

^{119}Sn-NMR ($CDCl_3$) δ: -49.4

b) Temperature study (lithiation route)

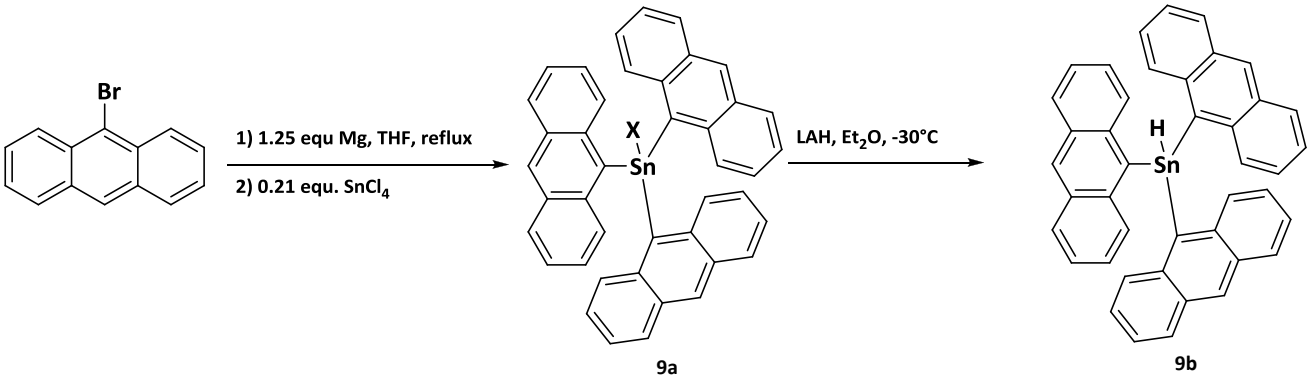
The temperature study was carried out regarding the lithiation route as described in **a**. Lithiation was always carried out at -78°C, whereas the temperature profile of the subsequent reaction (conversion with $SnCl_4$) was varied from -78°C to room temperature (-78°C, -50°C, 0°C, 25°C). In each experiment 2 g 9-bromoathracene (7.8 mmol) in 15 ml THF were cooled down to -78°C. Subsequently, 3.1 ml *n*-BuLi solution (2.5 M in hexane, 1 eq., 7.8 mmol) was added drop wise *via* a syringe to obtain an orange suspension. The reaction mixture was stirred for 1 h and then transferred *via* a cannula into a suspension of $SnCl_4$ (1 eq., 7.8 mmol, 2.03 g, 0.9 ml) in 15 ml THF at the appropriate temperature. The reaction mixture was stirred at the certain temperature for 2 h and then allowed to warm to room temperature. The reaction progress was monitored *via* ^{119}Sn-NMR spectroscopy applying a microwork-up with $CDCl_3$. Therefore, 5 ml of the reaction mixture were transformed into a separate flask, the solvent removed under reduced pressure, and the resulting yellow syrup

taken up in $CDCl_3$ to precipitate salts. The supernatant liquid was subjected to ^{119}Sn-NMR spectroscopy.

-78°C: ^{119}Sn-NMR ($CDCl_3$) δ: -80-02, -47.11; **-50°C**: ^{119}Sn-NMR ($CDCl_3$) δ: -255.5, -81.4; **0°C**: ^{119}Sn-NMR ($CDCl_3$) δ: -81.8; **-25°C**: ^{119}Sn-NMR ($CDCl_3$) δ: -81.7, -41.3

Furthermore, all reaction mixtures were subjected to a standard work up with toluene, removing the solvent and adding toluene to precipitate the salts. Then the supernatant liquid was separated and the solvent again removed under reduced pressure. In case of the reaction carried out at -78°C orange, rod like crystals of dichloro-(bis-9-anthracenyl)stannane **9** were obtained. The resulting green product of the reaction carried out at 0°C was solid phase extracted with ether leading to no reasonable isolation.

c) Synthesis *via* the Grignard route 9a and subsequent hydrogenation 9b



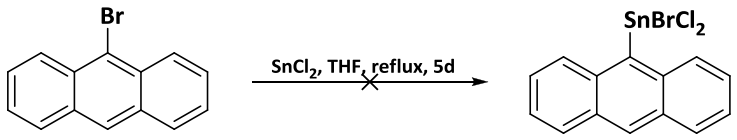
A flask equipped with a dropping funnel and a reflux condenser was charged with 1.18 g magnesium tunings (1.25 eq., 48.6 mmol) in 60 ml THF as well as the funnel was filled with a solution of 10 g 9-bromoanthracene (1 eq., 38.9 mmol) in 60 ml THF. The reaction started after addition of 0.6 ml dibromoethane and the ethereal solution was added drop wise so that gentle reflux continued. The reaction was refluxed for 2 h. A second flask furnished with a reflux condenser was charged with 0.83 ml $SnCl_4$ (1.86 g, 7.2 mmol, 0.23 eq.) in 150 ml THF under ice cooling, Then the Grignard solution was added *via* a cannula and the reaction mixture stirred at room temperature for 2 d. The supernatant solution was decanted and the solvent removed under reduced pressure to afford 13.74 g of a red powder **9a**.

^{119}Sn-NMR ($CDCl_3$) δ: -124.3, -146.0

A flask furnished with reflux condenser and a dropping funnel was charged with 0.10 g LAH pellets (27.6 mmol) and 20 ml Et_2O. The suspension was stirred at room temperature until all of the LAH was dissolved. A solution of 1 g **9a** in 35 ml Et_2O was added slowly *via* the dropping funnel under cooling to -30°C. The reaction mixture turned slightly orange and was stirred for 2 h and then allowed to warm up to room temperature. Subsequently 25 ml of oxygen free water was added. Then the phases were separated *via* a cannula and the aqueous layer washed twice with 15 ml Et_2O. The combined organic phases were extracted with 25 ml saturated sodium tartrate in oxygen free water and the resulting organic phase dried over $CaCl_2$. Then the solvent was evaporated under reduced pressure to obtain 0.87 g of a yellowish powder **9b**.

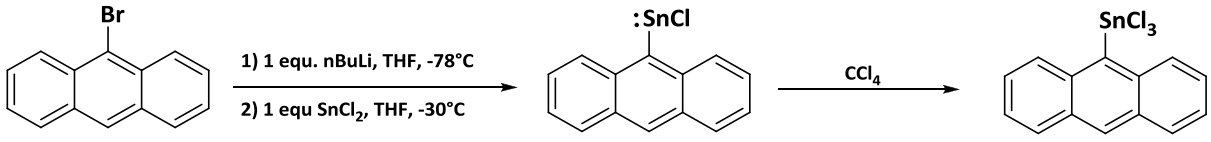
^{119}Sn-NMR (C_6D_6) δ: -272.2

d) Synthesis *via* oxidative addition[8]



0.5 g 9-bromoanthracene (19.4 mmol) in 10 ml THF were treated with 0.37 g $SnCl_2$ (1 eq., 19.4 mmol) and refluxed for 5 days. The reaction progress was monitored *via* ^{119}Sn-NMR spectroscopy, showing no conversion at all.

e) Synthesis *via* activated tin(II) species 9[9]



5 g 9-bromoanthracene (19.4 mmol) in 30 ml THF were cooled to -78°C and 8.5 ml *n*-BuLi solution (2.5 M in hexane, 1.1 eq., 21.4 mmol) were added slowly *via* a syringe to obtain an orange suspension which was stirred for 1 h and then allowed to warm up to -30°C. Then, a

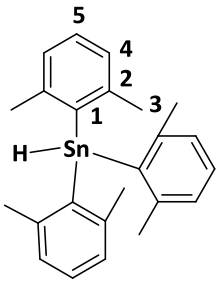
solution of 4.1 g $SnCl_2$ (1.1 eq., 21.4 mmol) in 25 ml was added *via* a syringe to result in a dark red, clear solution which was stirred for 2 h and allowed to warm up to room temperature. Subsequently 25 ml CCl_4 were added to obtain a slight orange solution which was stirred overnight at room temperature. The solvent was evaporated and the afforded orange syrup taken up in toluene to precipitate salts (orange solid). The supernatant solution was separated, and again the solvent removed under reduced pressure. ^{119}Sn-NMR in $CDCl_3$ showed no signal, whereas the filtered orange solid showed a Sn signal at -45.4 ppm in $CDCl_3$. Therefore, it was subjected to a solid phase extraction using heptane to afford 60 mg of a pale yellow powder. Subsequent extraction with Et_2O led to a total amount of 0.31 g product. No characterization *via* NMR spectroscopy was possible due to its insolubility in CDCl3, C_6D_6, toluene, heptane, hexane, pentane, Et_2O, CCl_4, acetone, THF, DCM and ethyl acetate. A mass spectrum confirmed the formation of dichloro-(bis-9-anthracenyl)stannane **9**.

HRMS calculated for $C_{28}H_{18}Cl_2Sn$ [M^+]: 543.9800; found: 543.9802

Decomposition temperature (*via* DTA): 259.5 °C

CHN-analysis: found (C: 58.63 %, H: 3.12 %) required (C: 61.81.10 %, H: 2.74 %)

Tri-2,6-xylylstannane (10)



A flask furnished with reflux condenser and a dropping funnel was charged with 0.60 g LAH pellets (1.5 eq., 15.7 mmol) and 40 ml Et_2O. The suspension was stirred at room temperature until all of the LAH was dissolved. A solution of 5.38 g **3** (1 eq, 10.5 mmol) in 40 ml Et_2O was added slowly *via* the dropping funnel under cooling to -30°C. The reaction mixture was stirred for 2 h and allowed to warm up to room temperature. Subsequently 50 ml of oxygen free water was added. Then the phases were separated *via* a cannula and the aqueous layer washed twice with 40 ml Et_2O. The combined organic phases were extracted with 40 ml saturated sodium tartrate in oxygen free water and the resulting organic phase dried over $CaCl_2$. Then the solvent was evaporated under reduced pressure to obtain a white solid which was recrystallized from toluene to afford 2.59 g **10** (59.5 mmol, 57 %) as white crystals.

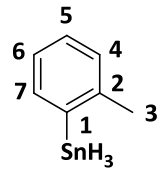
^{1}H-NMR (C_6D_6) δ: 7.06-6.95 (t, 1H, $J_{5,4}$=7.6 Hz, H5), 6.91-6.84 (d, 2H, $J_{4,5}$= 7.6 Hz, $^{3}J(^{119/117}Sn\text{-}^{1}H)$= 28Hz, H4), 6.83 (s, $^{1}J(^{119}Sn\text{-}^{1}H)$=1776 Hz, $^{1}J(^{117}Sn\text{-}^{1}H)$=1697 Hz, SnH), 2.29 (s, 6H, C3)

^{13}C-NMR (C_6D_6) δ: 144.58 ($^{2}J(^{119/117}Sn\text{-}^{13}C)$= 32 Hz, C2), 142.48 ($J(^{119}Sn\text{-}^{13}C)$= 534 Hz, $^{1}J(^{117}Sn\text{-}^{13}C)$= 512 Hz, C1), 128.89 ($^{4}J(^{119/117}Sn\text{-}^{13}C)$= 9 Hz, C5), 119.32 (*C4*), *25.43* ($^{3}J(^{119/117}Sn\text{-}^{13}C)$= 42 Hz).

^{119}Sn-NMR (C_6D_6) δ: -286.60 ($^{1}J(^{119}Sn\text{-}^{1}H)$=1765 Hz)

CHN-analysis: found (C: 67.94 %, H: 6.78 %), required (C: 66.24 %, H: 6.49 %)

_o_-Tolylstannane (11)[10]



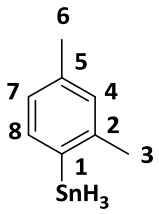
A flask furnished with reflux condenser and a dropping funnel was charged with 15.8 ml LAH-solution (2 eq., 2M in Et_2O, 31.6 mmol) and 40 ml Et_2O. A solution of 4 g **4** (1 eq., 12.1 mmol) in 50 ml Et_2O was added slowly *via* the dropping funnel under cooling to -30°C. The reaction mixture was stirred for 3.5 h and allowed to warm up to room temperature. Subsequently 50 ml of oxygen free water was added. Then the phases were separated *via* a cannula and the aqueous layer washed twice with 40 ml Et_2O. The combined organic phases were extracted with 40 ml saturated sodium tartrate in oxygen free water and the resulting organic phase dried over $CaCl_2$. Then the solvent was evaporated gently at 200 mbar and subsequently the product distilled at room temperature at 10^{-4} mbar to obtain 1.68 g **11** (7.89 mmol, 50 %) as a colorless liquid.

^{1}H-NMR (C_6D_6) δ: 7.53-7.27 (d, 1H, $J_{6,7}$=6.1 Hz $^2J(^{119}Sn\text{-}^1H)$=70 Hz, $^2J(^{117}Sn\text{-}^1H)$= 57 Hz, H7), 7.22-7.07 (t, 1H, H5), 7.07-6.95 (m, 2H, H6, H4), 5.02 (s, 1H, $^1J(^{119}Sn\text{-}^1H)$= 1908 Hz, $^1J(^{117}Sn\text{-}^1H)$= 1824 Hz, SnH_3), 2.21 (s, 3H, H3).

^{13}C-NMR (C_6D_6) δ: 144.40 ($^2J(^{119/117}Sn\text{-}^{13}C)$=32 Hz, C2), 138.67 ($^3J(^{119}Sn\text{-}^{13}C)$=45 Hz, $^3J(^{117}Sn\text{-}^{13}C)$=44 Hz, C7), 134.04 ($^1J(^{119}Sn\text{-}^{13}C)$=568 Hz, $^1J(^{117}Sn\text{-}^{13}C)$=543 Hz, C1), 129.42 ($^4J(^{119/117}Sn\text{-}^{13}C)$=12 Hz, C5), 128.95 ($^3J(^{119}Sn\text{-}^{13}C)$=43 Hz, $^3J(^{117}Sn\text{-}^{13}C)$=42 Hz, C4 or C6), 125.58 ($^3J(^{119}Sn\text{-}^{13}C)$=59 Hz, $^3J(^{117}Sn\text{-}^{13}C)$=56 Hz, C4 or C6), 25.35 ($^3J(^{119}Sn\text{-}^{13}C)$=41 Hz, $^3J(^{117}Sn\text{-}^{13}C)$= 40 Hz, C3).

^{119}Sn-NMR (C_6D_6) δ: -357.99 ($^1J(^{119}Sn\text{-}^1H)$= 1911 Hz)

2,4-Xylylstannane (12)[10]



A flask furnished with reflux condenser and a dropping funnel was charged with 15.1 ml LAH-solution (2 eq., 2M in Et_2O, 30.3 mmol) and 50 ml Et_2O. A solution of 5 g **5** (1 eq., 15.1 mmol) in 50 ml Et_2O was added slowly *via* the dropping funnel under cooling to -30°C. The reaction mixture was stirred for 2 h and allowed to warm up to room temperature. Subsequently 50 ml of oxygen free water was added. Then the phases were separated *via* a cannula and the aqueous layer washed twice with 40 ml Et_2O. The combined organic phases were extracted with 40 ml saturated sodium tartrate in oxygen free water and the resulting organic phase dried over $CaCl_2$. Then the solvent was evaporated gently at 200 mbar and subsequently the product was distilled at room temperature at 10^{-4} mbar to obtain 2.33 g **12** (7.89 mmol, 68 %) as a pale yellow liquid.

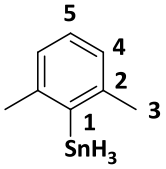
^{1}H-NMR (C_6D_6) δ: 7.34—7.11 (d, 1H, $J_{7,8}$=7.4 Hz $^2J(^{119}Sn\text{-}^1H)$=69 Hz, $^2J(^{117}Sn\text{-}^1H)$= 56 Hz, H8), 6.83-6.74 (m, 2H, H7, H4), 4.93 (s, $^1J(^{119}Sn\text{-}^1H)$= 1898 Hz, $^1J(^{117}Sn\text{-}^1H)$= 1814 Hz, SnH_3), 2.14 (s, 3H, H3), 2.09 (s, 3H, H6).

^{13}C-NMR (C_6D_6) δ: 144.17 ($^4J(^{119/117}Sn\text{-}^{13}C)$=34 Hz, C5), 138.86 (C2), 138.60 (C8), 130.05 ($^3J(^{119/117}Sn\text{-}^{13}C)$=43 Hz, C7 or C4), 130.00 ($^1J(^{119}Sn\text{-}^{13}C)$= 580 Hz, $^1J(^{117}Sn\text{-}^{13}C)$= 555 Hz, C1), 126.46 (C3), 25.35 (C3), 21.09 (C6).

^{119}Sn-NMR (C_6D_6) δ: -352.43 ($^1J(^{119}Sn\text{-}^1H)$= 1877 Hz)

CHN-analysis: found (C: 42.10 %, H: 5.22 %), required (C: 42.35 %, H: 5.33 %)

2,6-Xylylstannane (13)[10]



A flask furnished with reflux condenser and a dropping funnel was charged with 0.86 g LAH pellets (2 eq., 22.8 mmol) and 40 ml Et_2O. The suspension was stirred at room temperature until all of the LAH was dissolved. A solution of 3.76 g **6** (1 eq, 11.4 mmol) in 40 ml Et_2O was added slowly *via* the dropping funnel under cooling to -30°C. The reaction mixture was stirred for 2 h and allowed to warm up to room temperature. Subsequently 50 ml of oxygen free water was added. Then the phases were separated *via* a cannula and the aqueous layer washed twice with 40 ml Et_2O. The combined organic phases were extracted with 40 ml saturated sodium tartrate in oxygen free water and the resulting organic phase dried over $CaCl_2$. Then the solvent was evaporated gently at 200 mbar and subsequently the product was distilled at room temperature at 10^{-4} mbar to obtain 2.70 g **13** (11.9 mmol, 86 %) as a colorless liquid.

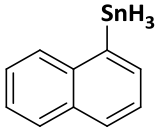
^{1}H-NMR (C_6D_6) δ: 7.01-6.09 (m, 1H, H5), 6.89-6.74 (d, 2H, $J_{4,5}$=4.5 Hz, H4), 4.78 (s, 3H, $^1J(^{119}Sn\text{-}^1H)$= 1896 Hz, $^1J(^{117}Sn\text{-}^1H)$= 1812 Hz, SnH_3), 2.19 (s, 6H, C3).

^{13}C-NMR (C_6D_6) δ: 144.56 ($^3J(^{119/117}Sn\text{-}^{13}C)$= 30 Hz, C2), 134.97 ($^1J(^{119}Sn\text{-}^{13}C)$= 582 Hz, $^1J(^{117}Sn\text{-}^{13}C)$= 558 Hz, C1), 129.00 ($^4J(^{119/117}Sn\text{-}^{13}C)$= 9 Hz, C5), 126.57 ($^1J(^{119/117}Sn\text{-}^{13}C)$= 44 Hz, C4), 26.33 ($^3J(^{119/117}Sn\text{-}^{13}C)$= 47 Hz, C3).

^{119}Sn-NMR (C_6D_6) δ: -417.53 ($^1J(^{119}Sn\text{-}^1H)$= 1899 Hz)

CHN-analysis: found (C: 43.08 %, H: 5.29 %), required (C: 42.35 %, H: 5.33 %)

1-Naphthylstannane (14)[10]



A flask furnished with reflux condenser and a dropping funnel was charged with 0.67 g LAH pellets (2 eq., 17.6 mmol) and 30 ml Et_2O. The suspension was stirred at room temperature until all of the LAH was dissolved. A solution of 3.10 g **8** (1 eq, 10.5 mmol) in 20 ml Et_2O was added slowly *via* the dropping funnel under cooling to -30°C. The reaction mixture was stirred for 2 h and allowed to warm up to room temperature. Subsequently 50 ml of oxygen free water was added. Then the phases were separated *via* a cannula and the aqueous layer washed twice with 40 ml Et_2O. The combined organic phases were extracted with 40 ml saturated sodium tartrate in oxygen free water and the resulting organic phase dried over $CaCl_2$. Then the solvent was evaporated gently at 200 mbar and subsequently the product was distilled at 10^{-4} mbar and slight heating (~ 50°C) to obtain 1.64 g **14** (6.59 mmol, 75 %) as a colorless liquid.

^{1}H-NMR (C_6D_6, 500 MHz) δ: 7.41-7.36 (dd, 1H, $^3J^{119}$Sn-^{1}H= 259 Hz, $^3J^{117}$Sn-^{1}H= 245 Hz, H2), 7.31-7.25 (m, 2H, H5, H4), 7.22-7.19 (d, 1H, $^1J_{7,8}$= 6.87 Hz), 6.94-6.91 (m, 2H, H6, H7), 6.86-6.81 (dd, 1H, H3), 4.84 (s, 3H, $^1J(^{119}Sn\text{-}^1H)$= 1934 Hz, $^1J(^{117}Sn\text{-}^1H)$= 1849 Hz, SnH_3)

^{13}C-NMR (C_6D_6) δ: 138.81 ($^2J(^{119/117}Sn\text{-}^{13}C)$= 36 Hz, C8a), 137.88 ($^3J(^{11/1179}Sn\text{-}^{13}C)$= 39 Hz, C8), 134.07 ($^1J(^{119}Sn\text{-}^{13}C)$= n.o., $^1J(^{117}Sn\text{-}^{13}C)$= n.o., C1), 133.75 ($^3J(^{119/117}Sn\text{-}^{13}C)$= 31 Hz, C4a), 130.41 ($^2J(^{119/117}Sn\text{-}^{13}C)$= 42 Hz, C2), 129.61 ($^4J(^{119/117}Sn\text{-}^{13}C)$= 13 Hz, C4 or C5), 128.81 ($^4J(^{119/117}Sn\text{-}^{13}C)$= 7 Hz, C4 or C5), 126.23 (C3), 125.64 (C6), 125.58 ($^4J(^{119/117}Sn\text{-}^{13}C)$= 62 Hz, C7)

CHN-analysis: found (C: 49.06 %, H: 3.98 %), required (C: 48.26 %, H: 4.05 %)

^{119}Sn-NMR (C_6D_6) δ: -353.86 ($^1J(^{119}Sn\text{-}^1H)$= 1927 Hz)

Polymerization of *o*-tolylstannane 1[11]

0.23 g **11** (11 mmol) where mixed with 7 ml Et_2O to obtain a colorless solution which was then treated with 0.16 ml TMEDA (1 eq, 11 mmol, 0.13 g) at room temperature. The reaction mixture immediately changed its color to dark orange and the formation of hydrogen could be detected. After 45 min reaction time the solution was dark brown and reaction monitoring using a D_2O capillary did not show any signal in ^{119}Sn-NMR. After another 15 min stirring, the solvent of the black reaction mixture was removed under reduced pressure, and the residual black solid extracted with 15 ml THF, to remove soluble parts. Also the supernatant THF solution was subjected to ^{119}Sn-NMR , whereas no tin signal could be observed. The separated black, amorphous solid was further subjected to elemental analysis and total Sn determination *via* EDX measurements.

CHN-analysis: found (C: 29.87 %, H: 2.59 %)

Total Sn- determination *via* EDX: 60.04%

Polymerization of 2,4-xylylstannane 12, Temperature study[11]

0.29 g **1** (13 mmol) where mixed with 4 ml Et_2O to obtain a colorless solution which was then treated with 0.19 ml TMEDA (1 eq., 13 mmol, 0.14 g) at -40°C. The reaction mixture immediately changed its color to slight orange and the formation of hydrogen could be observed. Subsequently six times 0.4 ml of the reaction mixture where transferred in 6 different NMR tubes, separately cooled to -30°C, -20°C, -10°C, 0°C and room temperature. Then each reaction was stirred at its specific temperature and for 1h. The reaction progress was investigated by color change of the mixture as well as ^{119}Sn-NMR where run using $CDCl_3$ capillaries to reference the spectra.

4.4 References

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5 Appendix

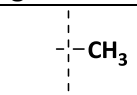
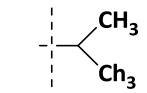
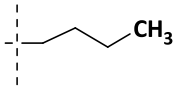
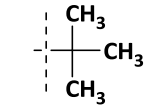
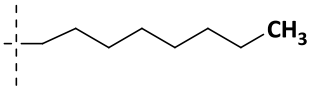
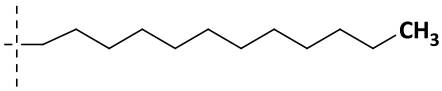
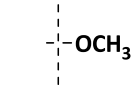
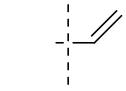
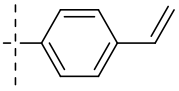
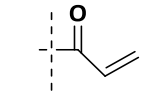
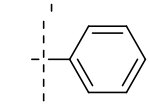
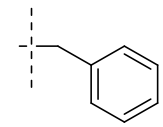
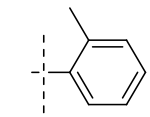
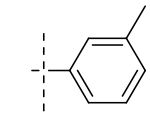
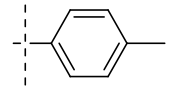
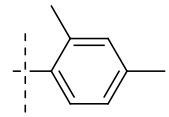
5.1 Abbreviations

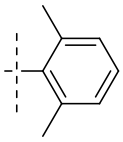
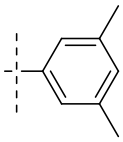
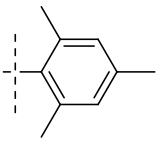
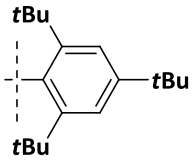
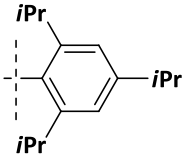
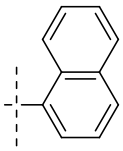
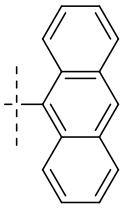
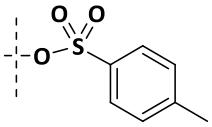
Table 22: Abbreviations

EE	ethylacetate
ACN	acetonitrile
av.	average
DCM	dichloromethane
DIBAL	diisobutylaluminium hydride
DI-EI-TOF-MS	direct insertion electron impact ionization time of flight mass spectroscopy
DTA	differential thermo analysis
EDX	energy dispersive X-ray spectroscopy
eq.	equivalent
GC-MS	gas chromatography-mass spectroscopy
GPC	gel permeation chromatography
HCl	hydrochloric acid
HRMS	high resolution mass spectroscopy
LAH	lithium aluminum hydride
LD50	median lethal dose
LDA	lithium diisopropylamide
Mp	melting point
n. o.	not observed
NA	not available
OTC	organotin compound
PTFE	polytetrafluoroethylene
Ref	reference
SEM	scanning electron microscopy
R	organic residue
S_N2	bimolecular nucleophilic substitution
TBT	tributyltin hydride
TGA	thermogravimetric analysis
THF	tetrahydrofuran
TMEDA	tetramethylethylene diamine
TMS	tetramethylsilane
UV	ultra violet
X	halide

5.2 Chemical Short Names

Table 23: Chemical short names

abbreviation	fragment name	fragment structure
Me	methyl	
i-Pr	iso-propyl	
n-Bu	*n*-butyl	
t-Bu	tert-butyl	
Oct	octyl	
Doc	dodecyl	
OMe	methoxy	
	allyl	
	vinyl	
	acryl	
Ph	phenyl	
Bz	benzyl	
o-Tol	*ortho*-tolyl	
m-Tol	*metha*-tolyl	
p-Tol	*para*-tolyl	
2,4-Xyl	2,4-xylyl	

abbreviation	fragment Name	fragment Structure
2,6-Xyl	2,6-xylyl	
3,5-Xyl	3,5-xylyl	
Mes	mesityl	
Supermes	supermesityl	
Ph*		
1-naph	1-naphthyl	
9-anth	9-anthracenyl	
Tos	tosylate	

5.3 Crystal Structure Analysis Data

Table 24: Crystallographic data for **3** and **7**

compound	**$C_{24}H_{27}BrSn$ (3)**	**$C_{40}H_{28}Sn$ (7)**
Formula weight	514.06	627.31
Temperature [K]	100(2)	100(2)
Wavelength [Å]	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	P(2)1/c	P2(1)/n
Unit cell dimensions	a = 7.9774(3) Å	a = 11.0020(3) Å
	b = 18.6305(6) Å	b = 12.3126(4) Å
	c = 14.5078(4) Å	c = 21.3522(6) Å
	α= 90°	α = 90°
	β= 94.68(10)°	β = 90.79(10)°
	γ = 90°	γ = 90°
Volume [$Å^3$]	2149.00(12)	2892.16(15)
Z	4	4
Density (calculated) [mg/m^3]	1.589	1.441
Absorption coefficient [mm^{-1}]	3.053	0.911
F(000)	1024	1272
Crystal size [mm^3]	0.20 x 0.18 x 0.17	0.14 x 0.10 x 0.05
Theta range for data collection	1.78 to 26.77°	1.91 to 27.16°
Index ranges	-10≤h≤10	-13≤h≤14
	-23≤k≤23	-15≤k≤15
	-18≤l≤15	-20≤l≤27
Reflections collected	27788	64496
Independent reflections	4448 [R(int) = 0.0300]	6390 [R(int) = 0.1505]
Completeness to Θ= 26.77° [%]	97.3	99.5
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.74 and 0.56	0.7455 and 0.3421
Refinement method	Full-matrix least-squares on F2	Full-matrix least-squares on F2
Data / restraints / parameters	4448 / 0 / 277	6390 / 0 / 358
Goodness-of-fit on F2	1032	1035
Final R indices [I>2σI)]	R1 = 0.0193, wR2 = 0.0458	R1 = 0.0639 wR2 = 0.1450
R indices (all data)	R1 = 0.0250 wR2 = 0.0481	R1 = 0.1076 wR2 = 0.1660
Largest diff. peak and hole	0.416 and -0.777 $e.Å^{-3}$	1.915 and -1.102 $e.Å^{-3}$

Table 25: Crystallographic data for **6** and **8**

compound	***$C_8H_9Cl_3Sn$ (6)***	***$C_{10}H_7ClSn$ (8)***
Formula weight	330.19	449.95
Temperature [K]	100(2)	100(2)
Wavelength [Å]	0.71073	0.71073
Crystal system	Orthorhombic	Orthorhombic
Space group	Pbcn	P2(1)2(1)2(1)
Unit cell dimensions	a = 8.2836(4) Å	a = 7.2140(2)
	b = 15.1421(7) Å	b = 17.8056(5)
	c = 17.9066(8) Å	c = 45.7927(13)
	a= 90°	a= 90°
	b= 90°	b= 90°
	g = 90°	g = 90°
Volume [$Å^3$]	2246.04(18)	5882.1(3)
Z	8	2
Density (calculated) [mg/m^3]	1.953	0.254
Absorption coefficient [mm^{-1}]	2.936	0.262
F(000)	1264	448
Crystal size [mm^3]	0.19 x 0.17 x 0.10	0.23 x 0.17 x 0.15
Theta range for data collection	2.27 to 30.03°	0.89 to 19.83°
Index ranges	-11≤h≤11 -21≤k≤20 -24≤l≤25	-6≤h≤6, -16≤k≤16 -43≤l≤43
Reflections collected	22034	131161
Independent reflections	3273 [R(int) = 0.0348]	5343 [R(int) = 0.1235]
Completeness to Θ= 26.77° [%]	99.6	100.0
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.7460 and 0.5875	0.7444 and 0.4744
Refinement method	Full-matrix least-squares on F2	Full-matrix least-squares on F2
Data / restraints / parameters	3273 / 0 / 111	5343 / 0 / 631
Goodness-of-fit on F2	1.068	0.635
Final R indices [I>2σI)]	R1 = 0.0265 wR2 = 0.0725	R1 = 0.0388 wR2 = 0.1091
R indices (all data)	R1 = 0.0313 wR2 = 0.0748	R1 = 0.0520 wR2 = 0.1299
Largest diff. peak and hole	1.281 and -1.195 e.Å-3	1.278 and -0.660 e.Å-3

Table 26: Crystallographic Data for **9** and **13**

compound	***$C_{28}H_{18}Cl_2Sn$ (9)***	***$C_{24}H_{27}Sn$ (13)***
Formula weight	544.01	434.15
Temperature [K]	100(2)	100(2)
Wavelength [Å]	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	P2(1)/c	P-1
Unit cell dimensions	a = 13.6349(9) Å	a = 6.9410(4) Å
	b = 9.3541(5) Å	b = 11.9702(7) Å
	c = 18.0168(12) Å	c = 12.8302(8) Å
	a= 90°.	a= 108.671(2)°.
	b= 106.799(3)°.	b= 91.290(2)°.
	g = 90°.	g = 95.961(2)°.
Volume [$Å^3$]	2199.8(2)	1002.68(10)
Z	4	2
Density (calculated) [mg/m^3]	1.643	1.438
Absorption coefficient [mm^{-1}]	1.418	1.277
F(000)	1080	442
Crystal size [mm^3]	na	0.24 x 0.19 x 0.15
Theta range for data collection	1.56 to 29.85°	1.81 to 26.79°
Index ranges	-18≤h≤19	-8≤h≤8
	-12≤k≤13	-15≤k≤15
	-25≤l≤24	-15≤l≤16
Reflections collected	43268	21602
Independent reflections	6281 [R(int) = 0.0983]	4227 [R(int) = 0.0766]
Completeness to Θ= 26.77° [%]	99.3	98.4
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.70 and 0.34	0.7454 and 0.3773
Refinement method	Full-matrix least-squares on F2	Full-matrix least-squares on F2
Data / restraints / parameters	6281 / 0 / 300	4227 / 0 / 232
Goodness-of-fit on F2	2.736	1.094
Final R indices [I>2σI)]	R1 = 0.0912	R1 = 0.0709
	wR2 = 0.2008	wR2 = 0.1860
R indices (all data)	R1 = 0.0987	R1 = 0.0732
	wR2 = 0.2025	wR2 = 0.1877
Largest diff. peak and hole	4.303 and -2.020 e.Å-3	3.369 and -1.010 e.Å-3

5.4 Indices

5.4.1 Index of Tables

5.4.2 Index of Schemes

5.4.3 Index of Figures

Deutsche Fassung:

Beschluss der Curricula-Kommission für Bachelor-, Master- und Diplomstudien vom 10.11.2008

Genehmigung des Senates am 1.12.2008

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I declare that I have authored this thesis independently, that I have not used other than the declared sources / resources, and that I have explicitly marked all material which has been quoted either literally or by content from the used sources.

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