



# Heteroleptic tin (II) dialkoxides stabilized by intramolecular coordination $\text{Sn}(\text{OCH}_2\text{CH}_2\text{NMe}_2)(\text{OR})$ ( $\text{R} = \text{Me}, \text{Et}, ^i\text{Pr}, ^t\text{Bu}, \text{Ph}$ ). Synthesis, structure and catalytic activity in polyurethane synthesis

Oleg V. Chernov<sup>a,b</sup>, Aleksandr Yu. Smirnov<sup>a</sup>, Ivan A. Portnyagin<sup>a,b</sup>, Victor N. Khrustalev<sup>c</sup>, Mikhail S. Nechaev<sup>a,b,\*</sup>

<sup>a</sup> Department of Chemistry, M.V. Lomonosov Moscow State University, Leninskie Gory 1/3, Moscow 119991, Russian Federation

<sup>b</sup> A.V. Topchiev Institute of Petrochemical Synthesis, RAS, Leninsky Prospekt, 29, Moscow 119991, Russian Federation

<sup>c</sup> A.N. Nesmeyanov Institute of Organoelement Compounds, RAS, Vavilov Str., 28, Moscow 119991, Russian Federation

## ARTICLE INFO

### Article history:

Received 10 April 2009

Received in revised form 6 May 2009

Accepted 8 May 2009

Available online 18 May 2009

### Keywords:

Tin (II)

Intramolecular coordination

Homogeneous catalysis

Polyurethane synthesis

## ABSTRACT

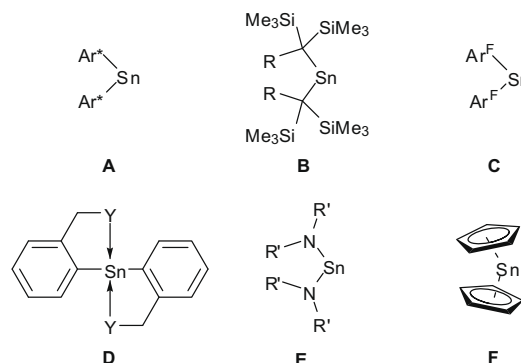
A straightforward method of synthesis of heteroleptic tin (II) alkoxides stabilized by one intramolecular coordination bond was developed. Addition of one equivalent of dimethylamino ethanol to diamide  $\text{Sn}(\text{N}(\text{SiMe}_3)_2)_2$  (**5**) yields alkoxy-amido derivative  $\text{Sn}(\text{OCH}_2\text{CH}_2\text{NMe}_2)(\text{N}(\text{SiMe}_3)_2)$  (**2**). Further addition of alcohol leads to corresponding heteroleptic dialkoxides  $\text{Sn}(\text{OCH}_2\text{CH}_2\text{NMe}_2)(\text{OR})$  ( $\text{R} = \text{Me}$  (**6**),  $\text{Et}$  (**7**),  $^i\text{Pr}$  (**8**),  $^t\text{Bu}$  (**9**),  $\text{Ph}$  (**10**)). Catalytic activity of tin (II) compounds in polyurethane formation was tested.

© 2009 Elsevier B.V. All rights reserved.

## 1. Introduction

Stannylenes  $\text{R}_2\text{Sn}$  are divalent tin compounds. Those bearing simple alkyl and aryl groups are reactive compounds that could not be isolated. They undergo rapid oligomerization and/or insertion in C–H, C–X and multiple bonds [1–3].

There are two approaches of stabilization of stannylenes in solution and in solid state. First is introduction of steric bulk – kinetic stabilization (types **A** [4–13] and **B** [14–21]). The alternative approach – thermodynamic stabilization stems from electronic effects: (i) introduction of acceptor substituents X to tin (type **C** [22–24]), (ii) formation of intramolecular coordination bonds  $\text{Y} \rightarrow \text{Sn}$  (Y – heteroatom bearing a lone electron pair, N, P, O, S; type **D** [25–32]), (iii) conjugation and delocalization (types **E** [33–47] and **F** [48–54]). In 2003 Zemlyansky et al. reported on the synthesis and solid state structure of stannylene  $\text{Sn}(\text{OCH}_2\text{CH}_2\text{NMe}_2)_2$  (**1**), stabilized by a combination of factors (i) and (ii) without the introduction of sterically bulky groups [55].

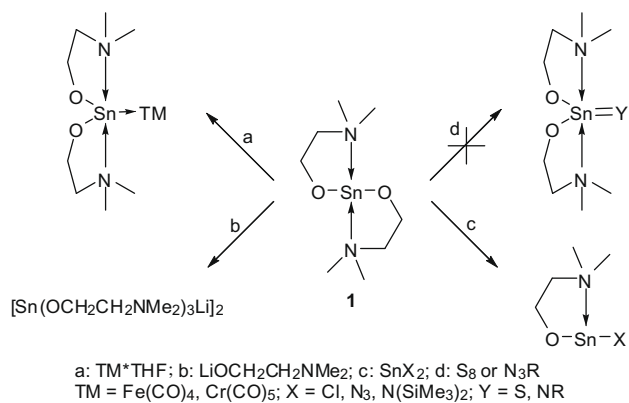


Ar\* – bulky aryl ligand  
 $\text{Ar}^{\text{F}}$  = 2,4,6-trifluoromethylphenyl  
 $\text{R} = \text{H}, \text{Alk}, \text{SiMe}_3$ ;  $\text{R}' = \text{Alk}, \text{Ar}, \text{SiMe}_3$   
 $\text{Y} = \text{donor group}$

\* Corresponding author. Address: Department of Chemistry, M.V. Lomonosov Moscow State University, Leninskie Gory 1/3, Moscow 119991, Russian Federation. Tel./fax: +7 495 9392677.

E-mail address: nechaev@nmr.chem.msu.ru (M.S. Nechaev).

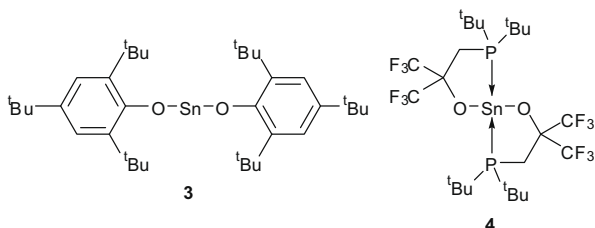
The key features of stannylene  $\text{Sn}(\text{OCH}_2\text{CH}_2\text{NMe}_2)_2$  (**1**) are: (i) lone electron pair, as well as (ii) partially occupied  $p_z$ -orbital on metal atom M, and (iii) labile strongly polarized M–O bonds (Scheme 1). This leads to unique chemical properties of stannylene **1**: addition of Lewis acids–transition metals [56], addition of strong Lewis bases



Scheme 1.

[57,58], facile substituent redistribution reactions to form Sn(OCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)X (X = N(SiMe<sub>3</sub>)<sub>2</sub> (**2**), Cl, F, N<sub>3</sub>) [59–61]. Due to efficient thermodynamic stabilization of stannylene **1** it is reluctant to form doubly bonded species [62].

Dibutyltin derivatives are known to catalyze different polycondensation reactions such as polyurethane synthesis, synthesis of polyesters, polylactides and organic polycarbonates [63]. Dialkyltin derivatives have toxicity issues [64,65] and the search for less toxic or non-toxic catalysts is an important task. A possible solution is utilization of inorganic tin derivatives that do not contain carbon–tin bonds and are virtually non-toxic. It was recently reported that sterically hindered phenoxide **3** [66] and divalent derivative, stabilized by intramolecular coordination, **4** [67] are active catalysts in polyurethane formation.



In this contribution we report on the stepwise synthesis of heteroleptic tin dialkoxides Sn(OCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)(OR) (R = Me, Et, <sup>i</sup>Pr, <sup>t</sup>Bu, Ph) via intermediate formation of alkoxy-amide Sn(OCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)(N(SiMe<sub>3</sub>)<sub>2</sub>) (**2**) and their application as catalysts for the formation of polyurethanes.

## 2. Results and discussion

### 2.1. Synthesis

A convenient way of preparation of alkoxy tin compounds is interaction of tin amides with alcohols. Interaction of halogenated tin derivatives with alcoholates of alkali metals is frequently hampered by formation of heterometallic alkoxides [68,69].

For synthesis of heteroleptic tin (II) dialkoxides we used the consecutive substitution of amido groups in stannylene **5**. Treatment of **5** with one equivalent of dimethylaminoethanol in THF yields alkoxy-amido derivative **2**. Reactions of **2** with a slight excess of alcohols give a series of heteroleptic tin (II) dialkoxides **6–10** (Scheme 2).

Compounds **6–10** are white crystalline solids sensitive to air and moisture. They are soluble in THF and benzene and moderately

soluble in hexane. Methyl, ethyl and isopropyl derivatives **6–8** are powders that decompose in air in several seconds. Compounds **9** and **10** bearing more bulky *tert*-butyl and phenyl substituents form large crystals that remain in air for several hours.

Compounds **6–10** were characterized by <sup>1</sup>H, <sup>13</sup>C and elemental analysis. In NMR spectra the signals of OCH<sub>2</sub>CH<sub>2</sub>N groups are broaden due to fast opening–closing of Me<sub>2</sub>N → Sn coordination bonds in solution [55,60,70]. Solid state structures of **9** and **10** were established by X-ray analysis.

### 2.2. X-ray

Crystals of **9** and **10** suitable for X-ray diffraction analysis were obtained from THF solution. The molecular structures of **9** and **10** are shown in Fig. 1. Selected bond lengths and angles are presented in Table 1.

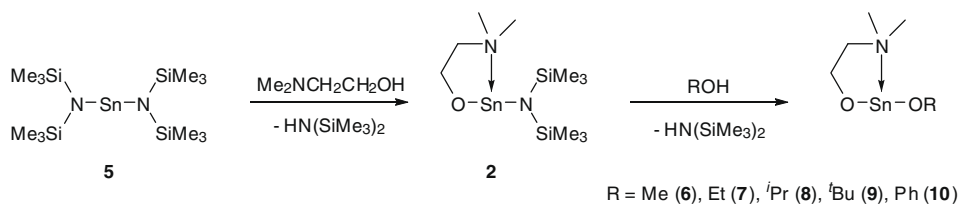
Compounds **9** and **10** were found to be centrosymmetric dimers via two intermolecular dative Sn ← O bonds. They consist of two Sn(OCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)(OR) units, sharing a Sn<sub>2</sub>O<sub>2</sub> four-membered ring. Molecular inversion center lies at the center of this ring relating the unprimed to primed atoms.

Tin atoms have a distorted trigonal bipyramidal configuration with a lone electron pair in the equatorial position. Stereochemically active lone pairs at Sn atoms push the atoms at the axial positions towards the equatorial bonded atoms. The resulting distortions towards a tetragonal pyramid are evident in the N(1) → Sn ← O(1A) bond angles of 140.79(4)° for **9** and 140.36(3)° for **10** (Table 1).

Sn–O bond lengths in the four-membered rings in both **9** and **10** (2.126(1) and 2.286(1) Å in **9**, and 2.118(1) and 2.245(1) Å in **10**, Table 1) are significantly different. In **10** they are more equalized than in **9**. We suppose that this is due to smaller steric effects of phenyl substituents in **10** in comparison with *tert*-butyl substituents in **9**. In contrast, Sn(1) ← N(1) coordination bond lengths in **9** (2.503(1) Å) and **10** (2.470(1) Å) are only slightly different and very close to those in Sn(OCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub> (2.458(2) Å) [55] and [Sn(OCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)(N(SiMe<sub>3</sub>)<sub>2</sub>)<sub>2</sub>] (2.505(5) Å [60]). Bridging oxygen atoms are practically planar (angles at O sum to 357.3° and 358.8° for **9** and **10**, respectively). Obtuse Sn–O–Sn angles together with the large Sn(1)···Sn(2) separation (3.6162(2) and 3.5918(2) Å) indicate there are no attractive interactions between the metal atoms. Apparently, the combination of electronic effects of the chelating β-dimethylaminoethoxy group and sterics of the terminal *tert*-butoxy- or phenoxy-groups is not enough to stabilize the monomeric species **9** and **10**.

It is interesting to note that the X-ray crystal structure of **9** reveals *tert*-butyl substituents turned away from the Sn<sub>2</sub>O<sub>2</sub> ring plane (torsion angle O(1)–Sn(1)–O(2)–C(5) is 133.0(1)°) while structural data for **10** show that phenyl groups occupy sites above the Sn<sub>2</sub>O<sub>2</sub> ring plane (the torsion angle O(1)–Sn(1)–O(2)–C(5) is 72.3(1)°, Fig. 2). The same disposition above the Sn<sub>2</sub>O<sub>2</sub> ring plane was observed for the azido-groups in the dimer [Sn(OCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)N<sub>3</sub>]<sub>2</sub> (torsion angle O(1)–Sn(1)–N(2)–N(3) is 49.0(5)° [59]). Such arrangement of the phenyl and azido moieties is presumably explained by the weak attractive interactions Sn···C=C (Sn1···C(5A) 3.960(1) and Sn(1)···C(10A) 3.634(1) Å) in **10** and Sn···N≡N (Sn(1)···N(3A) 3.653(5) and Sn(1)···N(4A) 3.532(5) Å) in [Sn(OCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)N<sub>3</sub>]<sub>2</sub>.

It is important to point out that the molecules of **9** and **10** could form the dimers via μ-bridging O atoms of the terminal *tert*-butoxy- or phenoxy-groups. To our best knowledge, the X-ray crystal structures of the divalent tin compounds containing terminal *tert*-butoxy- or phenoxy- ligands are unknown to date. The dimeric structures observed are obviously determined by the space-geometrical properties of the chelate β-dimethylaminoethoxy-ligand which facilitate the more favorable trigonal bipyramidal configura-



Scheme 2.

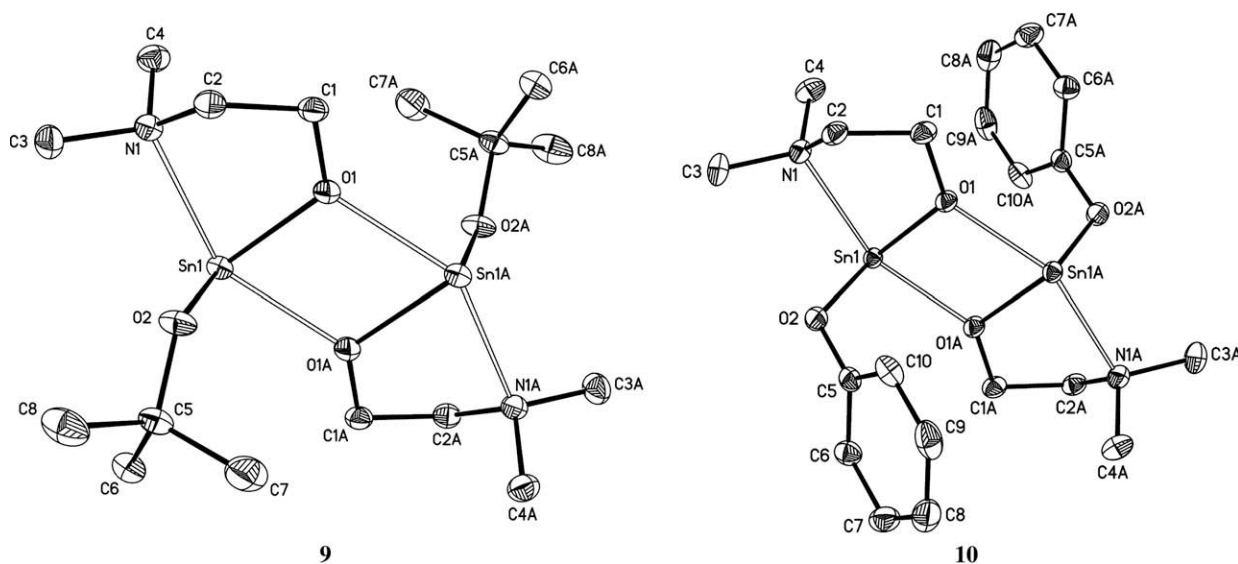


Fig. 1. Molecular structure of compounds **9** and **10** (50% probability ellipsoids; labeling A denotes symmetrically equivalent atom relative to the inversion center; hydrogen atoms are omitted for clarity; coordination bonds are shown by double lines).

tion of the tin atoms with the two axial coordination bonds ( $N \rightarrow Sn$  and  $Sn \leftarrow O(CH_2CH_2NMe_2)$ ).

### 2.3. Catalytic activity in polyurethane formation

Polyurethanes are usually produced via cross-linking of polyols and diisocyanates [71]. Catalytic activity of the compounds **1**, **2**, **9** and **10** in polyurethane formation was compared to industry standard catalyst – dibutyltin dilaurate (DBTDL). The test system was equimolar mixture of polyethylene glycol of average molecular weight 600 (PEG-600, Acros) and hexamethylene diisocyanate (HDI). “Gel time” was measured under argon ( $T_{Ar}$ ) and under air ( $T_{air}$ ). The “gel time” corresponds to the time at which flow is no

longer observed in polyol-diisocyanate mixture [72]. The results of catalytic tests are presented in Table 2, Figs. 3 and 4.

It was found that under argon compounds **1**, **2**, **9** and **10** are effective catalysts of polyurethane formation (Fig. 3). As it was expected, “gel time” decrease upon increase of catalyst concentration. In the region of low concentrations below 0.2 mol% the most active is alkoxy-amide **2**. In the region of higher concentrations the most active is DBTDL, although divalent tin compounds **1**, **2**, **9** and **10** exhibit relatively high activity. Compounds **1** and **10** are less active at high concentrations than amido derivative **2** and *tert*-butoxy deriv-

Table 1  
Selected bond lengths [Å] and angles [°] for **9** and **10**.

	<b>9</b>	<b>10</b>
Sn(1)?O(1)	2.126(1)	2.118(1)
Sn(1)?O(2)	2.030(1)	2.089(1)
Sn(1) ← N(1)	2.503(1)	2.470(1)
Sn(1) ← O(1A) <sup>*</sup>	2.286(1)	2.245(1)
O(1)?Sn(1)?O(2)	91.79(4)	93.03(4)
O(1)?Sn(1) ← O(1A)	69.93(4)	69.19(4)
O(2)?Sn(1) ← O(1A)	91.62(4)	88.39(3)
O(1)?Sn(1) ← N(1)	72.23(4)	73.14(3)
O(2)?Sn(1) ← N(1)	79.59(4)	81.60(4)
N(1) → Sn(1) ← O(1A)	140.79(4)	140.36(3)
Sn(1)?O(1) → Sn(1A)	110.07(4)	110.81(4)

<sup>\*</sup> The labeling A denotes symmetrically equivalent atom relative to the inversion center.

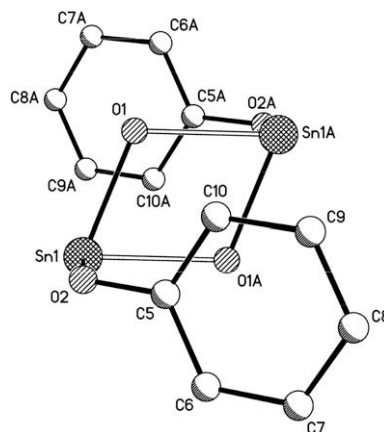


Fig. 2. A fragment of crystal structure **10** indicating disposition of phenyl groups relative to  $Sn_2O_2$  ring plane.

**Table 2**Gel times under argon ( $T_{Ar}$ ) and under air ( $T_{air}$ ) for compounds **1**, **2**, **9**, **10** and DBTDL (min).

Entry	Compound	Catalyst (mol%)	$T_{Ar}$	$T_{air}$
1	1	1.00	8.1	8.2
2	1	0.50	10.3	17.8
3	1	0.20	20.1	90.7
4	1	0.10	60.3	–
5	1	0.05	–	–
6	2	1.00	5.7	8.8
7	2	0.50	7.7	23.3
8	2	0.20	10	–
9	2	0.10	11.2	–
10	2	0.05	16.2	–
11	9	1.00	3.7	4.8
12	9	0.50	6.8	13.5
13	9	0.20	15	–
14	9	0.10	70.1	–
15	9	0.05	–	–
16	10	1.00	9.8	22.3
17	10	0.50	10.1	–
18	10	0.20	45.2	–
19	10	0.10	90.5	–
20	10	0.05	–	–
21	DBTDL	1.00	2.0	2.1
22	DBTDL	0.50	2.6	2.5
23	DBTDL	0.20	4.5	4.5
24	DBTDL	0.10	31.8	30.1
25	DBTDL	0.05	66.9	65.4
26	No catalyst	N/A	–	–

ative **9**. We suppose that this is due to chelating effect of dimethylamino alkoxy group in **1** and lower basicity (comparing to amido and *tert*-butoxy groups) of phenoxy group in **10**.

In case of diamide **5** we were unable to reliably determine “gel times” because the spread of results was too high. We suppose that in absence of supporting dimethylamino ethoxy ligand **5** interacts with mixture components giving associates of low catalytic activity. As a result, the “gel time” is dependent on small deviations in experiment conditions and rates of addition and mixing of the reagents.

Under aerobic conditions the activity of DBTDL is the same to anaerobic conditions (Fig. 4). The activity of divalent compounds **1**, **2**, and **9** at 1 mol% concentration slightly decreases, although remains high. The decrease of activity of **10** is more pronounced. At lower concentrations the activity of divalent derivatives decrease more rapidly than for anaerobic conditions. At concentrations below 0.2 mol% “gel times” were not reached (>180 min). We suppose that this is due to oxidation and hydrolysis of divalent derivatives under moist air.

### 3. Conclusions

A straightforward method of synthesis of heteroleptic tin (II) dialkoxides (**6–10**) stabilized by one intramolecular coordination bond was developed. Dialkoxides **9** and **10** are surprisingly stable (at least for several hours) in solid state under aerobic conditions. Compounds **1**, **2**, **9** and **10** are active catalysts in polyurethane formation under anaerobic conditions.

### 4. Experimental

#### 4.1. General procedures

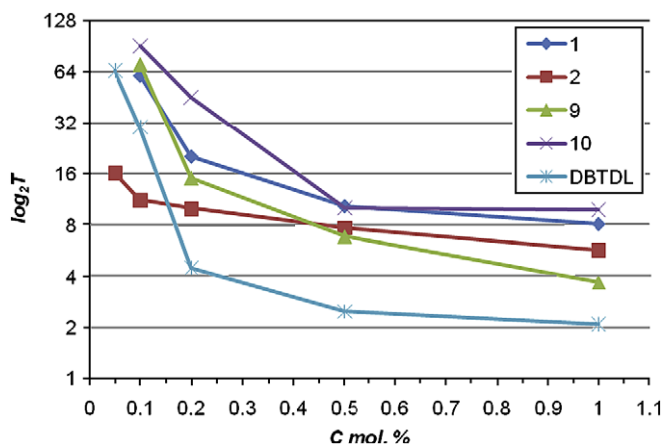
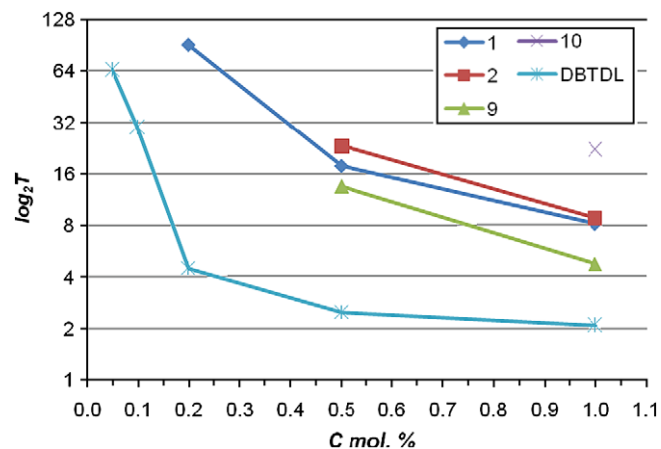
All manipulations with air and moisture sensitive compounds were carried out under purified argon using standard Schlenk and high-vacuum-line techniques. The commercially available solvents were purified by conventional methods and distilled immediately prior to use [73].  $\text{Sn}(\text{N}(\text{SiMe}_3)_2)_2$  (**5**) was synthesized using published procedure [74]. NMR spectra were recorded on an AVANCE-400 NMR spectrometer at 400.13 MHz ( $^1\text{H}$ ) and 100.62 MHz ( $^{13}\text{C}$ ) in  $\text{THF-d}_8$  or  $\text{C}_6\text{D}_6$ . Chemical shifts are indirectly referenced to tetramethylsilane ( $\text{SiMe}_4$ ) via the solvent signals. The accuracy of chemical shift measurements is  $\pm 0.01$  ppm ( $^1\text{H}$ ) and  $\pm 0.05$  ppm ( $^{13}\text{C}$ ). Elemental analyses were performed on a Carlo Erba EA1108 CHNS-O elemental analyzer.

#### 4.2. X-ray structure determination

Data were collected on a Bruker SMART APEX II CCD diffractometer ( $\lambda(\text{Mo K}\alpha)$ -radiation, graphite monochromator,  $\omega$  and  $\varphi$  scan mode) and corrected for absorption [75]. For details, see Table 3. The structures were determined by direct methods and refined by full-matrix least squares technique with anisotropic thermal parameters for non-hydrogen atoms. The hydrogen atoms were placed in calculated positions and refined in riding model with fixed thermal parameters ( $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$  for the  $\text{CH}_3$ -groups and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  for the other groups). All calculations were carried out by use of the SHELXTL PLUS (Version 6.12) program package [76].

#### 4.3. $\text{Sn}(\text{OCH}_2\text{CH}_2\text{NMe}_2)(\text{N}(\text{SiMe}_3)_2)$ (**2**)

To a solution of  $\text{Sn}(\text{N}(\text{SiMe}_3)_2)_2$  (45.7 g, 0.104 mol) in 50 ml THF 9.28 g (0.104 mol) of *N,N*-dimethylaminoethanol was added. After stirring for 30 min the solvent was removed in vacuo at 0.1 mm Hg, and the residue was recrystallized from hexane. Yield of

Fig. 3. Gel time for **1**, **2**, **9** and **10** and DBTDL under argon ( $T_{Ar}$ , min).Fig. 4. Gel time for **1**, **2**, **9** and **10** and DBTDL in air ( $T_{air}$ , min).

**Table 3**  
Crystallographic data for **9** and **10**.

	<b>9</b>	<b>10</b>
Empirical formula	C <sub>16</sub> H <sub>38</sub> N <sub>2</sub> O <sub>4</sub> Sn <sub>2</sub>	C <sub>20</sub> H <sub>30</sub> N <sub>2</sub> O <sub>4</sub> Sn <sub>2</sub>
Formula weight	559.86	599.84
Temperature (K)	100(2)	100(2)
Crystal size (mm)	0.25 × 0.25 × 0.20	0.20 × 0.15 × 0.12
Crystal system	Monoclinic	Orthorhombic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>Pbca</i>
<i>a</i> (Å)	10.9437(4)	13.0745(4)
<i>b</i> (Å)	9.0826(4)	12.9669(7)
<i>c</i> (Å)	11.9307(5)	13.6824(7)
$\alpha$ (°)	90	90
$\beta$ (°)	106.907(1)	90
$\gamma$ (°)	90	90
Volume (Å <sup>3</sup> )	1134.62(8)	2319.66(19)
<i>Z</i>	2	4
<i>D</i> <sub>calc</sub> (g/cm <sup>3</sup> )	1.639	1.718
<i>F</i> (000)	560	1184
$\mu$ (1/mm)	2.220	2.179
2 $\theta$ <sub>max</sub> (°)	60	60
Index range	−15 ≤ <i>h</i> ≤ 15 −12 ≤ <i>k</i> ≤ 12 −16 ≤ <i>l</i> ≤ 16	−18 ≤ <i>h</i> ≤ 18 −18 ≤ <i>k</i> ≤ 18 −19 ≤ <i>l</i> ≤ 19
No. of reflections collected	14 327 ( <i>R</i> <sub>int</sub> = 0.0250)	77 220 ( <i>R</i> <sub>int</sub> = 0.0312)
No. of unique reflections	3285	3341
No. of reflections with <i>I</i> > 2 $\sigma$ ( <i>I</i> )	2968	2807
Data/restraints/parameters	3285/0/114	3341/0/129
<i>R</i> <sub>1</sub> ; <i>wR</i> <sub>2</sub> ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	0.0162; 0.0196	0.0147; 0.0201
<i>R</i> <sub>1</sub> ; <i>wR</i> <sub>2</sub> (all data)	0.0363; 0.0375	0.0341; 0.0372
Goodness-of-fit (GOF) on <i>F</i> <sup>2</sup>	1.002	1.016
<i>T</i> <sub>min</sub> ; <i>T</i> <sub>max</sub>	0.586; 0.646	0.666; 0.777

Sn(OCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)(N(SiMe<sub>3</sub>)<sub>2</sub>) was 25.8 g (67%) as a white solid. Anal. Calc. for C<sub>10</sub>H<sub>28</sub>N<sub>2</sub>OSi<sub>2</sub>Sn (mol wt 367.22): C, 32.71; H, 7.69; N, 7.63. Found: C, 32.94; H, 7.87; N, 7.46%. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  0.43 (s, <sup>2</sup>*J*<sub>SiH</sub> = 5.8 Hz, 18H, Me<sub>3</sub>Si), 1.98 (s, 6H, Me<sub>2</sub>N), 2.23 (br. t, <sup>3</sup>*J*<sub>HH</sub> = 5.3 Hz, 2H, CH<sub>2</sub>N), 3.71 (t, <sup>3</sup>*J*<sub>HH</sub> = 5.3 Hz, 2H, CH<sub>2</sub>O). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.41 (<sup>1</sup>*J*<sub>SiC</sub> = 54.6, <sup>3</sup>*J*<sub>SnSiC</sub> = 37.3, Me<sub>3</sub>Si), 44.3 (Me<sub>2</sub>N), 57.88 (CH<sub>2</sub>N), 61.1 (CH<sub>2</sub>O).

#### 4.4. Sn(OCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)(OMe) (**6**)

To a solution of 1.36 g Sn(OCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)(N(SiMe<sub>3</sub>)<sub>2</sub>) (3.71 mmol) in 10 ml of THF 0.130 g (4.07 mmol) of methanol was added. After stirring for 30 min the solvent was removed in vacuo at 0.1 mmHg, and the residue was recrystallized from hexane. Yield of Sn(OCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)(OMe) was 0.710 g (81%) as a white solid. Anal. Calc. for C<sub>5</sub>H<sub>13</sub>N<sub>2</sub>O<sub>2</sub>Sn (mol wt 237.87): C, 25.25; H, 5.51; N, 5.89. Found: C, 25.12; H, 5.57; N, 5.73%. <sup>1</sup>H NMR (THF-*d*<sub>8</sub>):  $\delta$  2.27 (s, 6H, Me<sub>2</sub>N), 2.49 (t, *J*<sub>HH</sub> = 5.3 Hz, 2H, CH<sub>2</sub>N), 3.58 (br. s, 3H, MeO), 3.87 (t, *J*<sub>HH</sub> = 5.3 Hz, 2H, CH<sub>2</sub>O). <sup>13</sup>C NMR (THF-*d*<sub>8</sub>):  $\delta$  43.7 (Me<sub>2</sub>N), 50.8 (MeO), 58.6 (CH<sub>2</sub>N), 61.0 (CH<sub>2</sub>O).

#### 4.5. Sn(OCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)(OEt) (**7**)

The compound was prepared according to the procedure for **6** from 1.727 g (4.71 mmol) of Sn(OCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)(N(SiMe<sub>3</sub>)<sub>2</sub>) and 0.232 g (4.95 mmol) of ethanol to give 0.890 g (75%) of white solid. Anal. Calc. for C<sub>6</sub>H<sub>15</sub>N<sub>2</sub>O<sub>2</sub>Sn (mol wt 251.90): C, 28.61; H, 6.00; N, 5.56. Found: C, 28.52; H, 6.07; N, 5.48%. <sup>1</sup>H NMR (THF-*d*<sub>8</sub>):  $\delta$  1.13 (t, *J*<sub>HH</sub> = 5.4 Hz, 3H, CH<sub>3</sub>CH<sub>2</sub>O), 2.27 (s, 6H, Me<sub>2</sub>N), 2.53 (t, *J*<sub>HH</sub> = 5.4 Hz, 2H, CH<sub>2</sub>N), 3.83 (t, *J*<sub>HH</sub> = 5.4 Hz, 2H, OCH<sub>2</sub>CH<sub>2</sub>N), 3.88 (m, 2H, CH<sub>3</sub>CH<sub>2</sub>O). <sup>13</sup>C NMR (THF-*d*<sub>8</sub>):  $\delta$  22.2 (CH<sub>3</sub>CH<sub>2</sub>O), 43.7 (Me<sub>2</sub>N), 58.7 (CH<sub>2</sub>N), 60.1 (CH<sub>3</sub>CH<sub>2</sub>O), 61.6 (OCH<sub>2</sub>CH<sub>2</sub>N).

#### 4.6. Sn(OCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)(*O*<sup>*i*</sup>Pr) (**8**)

The compound was prepared according to the procedure for **6** from 1.410 g (3.84 mmol) of Sn(OCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)(N(SiMe<sub>3</sub>)<sub>2</sub>) and

0.242 g (4.03 mmol) of *i*-propanol to give 0.685 g (67%) of white solid. Anal. Calc. for C<sub>7</sub>H<sub>17</sub>N<sub>2</sub>O<sub>2</sub>Sn (mol wt 265.93): C, 31.62; H, 6.44; N, 5.27. Found: 31.55; H, 6.56; N, 5.20%. <sup>1</sup>H NMR (THF-*d*<sub>8</sub>):  $\delta$  1.09 (d, *J*<sub>HH</sub> = 5.9 Hz, 6H, Me<sub>2</sub>CH), 2.28 (s, 6H, Me<sub>2</sub>N), 2.59 (br. s, 2H, CH<sub>2</sub>N), 3.83 (t, *J*<sub>HH</sub> = 5.2 Hz, 3H, CH<sub>2</sub>O), 4.27 (sept., *J*<sub>HH</sub> = 5.9 Hz, 1H, CH). <sup>13</sup>C NMR (THF-*d*<sub>8</sub>):  $\delta$  29.6 (Me<sub>2</sub>CH), 43.5 (Me<sub>2</sub>N), 59.8 (CH<sub>2</sub>N), 61.0 (CH<sub>2</sub>O), 64.0 (CH).

#### 4.7. Sn(OCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)(*O*<sup>*t*</sup>Bu) (**9**)

The compound was prepared according to the procedure for **6** from 1.390 g (3.79 mmol) of Sn(OCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)(N(SiMe<sub>3</sub>)<sub>2</sub>) and 0.296 g (4.00 mmol) of *tert*-butanol to give 0.764 g (72%) of white solid. The structure was proven by X-ray analysis. Anal. Calc. for C<sub>8</sub>H<sub>19</sub>N<sub>2</sub>O<sub>2</sub>Sn (mol wt 279.95): C, 34.32; H, 6.84; N, 5.00. Found: C, 34.25; H, 6.90; N, 5.14%. <sup>1</sup>H NMR (THF-*d*<sub>8</sub>):  $\delta$  1.24 (s, 9H, Me<sub>3</sub>C), 2.28 (s, 6H, Me<sub>2</sub>N), 2.50 (br. t, *J*<sub>HH</sub> = 5.2 Hz, 2H, CH<sub>2</sub>N), 3.85 (br. t, *J*<sub>HH</sub> = 5.2 Hz, 2H, CH<sub>2</sub>O). <sup>13</sup>C NMR (THF-*d*<sub>8</sub>): 31.8 (Me<sub>3</sub>C), 35.7 (Me<sub>2</sub>N), 43.7 (CH<sub>2</sub>N), 61.3 (CH<sub>2</sub>O).

#### 4.8. Sn(OCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)(*O*Ph) (**10**)

The compound was prepared according to the procedure for **6** from 1.850 g (5.05 mmol) of Sn(OCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)(N(SiMe<sub>3</sub>)<sub>2</sub>) and 0.498 g (5.30 mmol) of phenol. The product was recrystallized from THF to give 1.12 g (74%) of white solid. The structure was proven by X-ray analysis. Anal. Calc. for C<sub>8</sub>H<sub>19</sub>N<sub>2</sub>O<sub>2</sub>Sn (mol wt 299.94): C, 40.04; H, 5.04; N, 4.67. Found: C, 39.95; H, 5.07; N, 4.58%. <sup>1</sup>H NMR (THF-*d*<sub>8</sub>):  $\delta$  2.20 (s, 6H, Me<sub>2</sub>N), 2.55 (t, *J*<sub>HH</sub> = 5.3 Hz, 2H, CH<sub>2</sub>O), 3.62 (t, *J*<sub>HH</sub> = 5.3 Hz, 2H, CH<sub>2</sub>N), 6.54 (t, *J*<sub>HH</sub> = 7.1 Hz, 1H, *p*-Ph), 6.66 (d, *J*<sub>HH</sub> = 8.1 Hz, 2H *o*-Ph), 7.01 (t, *J*<sub>HH</sub> = 8.1 Hz, 2H, *m*-Ph). <sup>13</sup>C NMR (THF-*d*<sub>8</sub>):  $\delta$  43.2 (Me<sub>2</sub>N), 59.0 (CH<sub>2</sub>N), 60.4 (CH<sub>2</sub>O), 117.1 (*o*-Ph), 121.3 (*p*-Ph), 129.6 (*m*-Ph).

#### 4.9. Standard polymerization procedure

All test samples were prepared under an argon atmosphere. Samples were prepared by taking a known mass of the precatalyst and diluting it with THF until it reached the desired percent concentration. The starting materials for the gel time were measured with 1.68 g (10 mmol) of hexamethylene diisocyanate (HMDI) and 6.00 g (10 mmol) of polyethyleneglycol (PEG-600). To this mixture was added 0.25 ml of stock solution to produce the desired concentration of the precatalyst, and the contents were mixed. From this, two samples are produced: one is left stirring under an argon atmosphere and the other is left stirring exposed to air. The samples were checked frequently, and the time it took for the samples to gel is recorded for both.

### 5. Supplementary material

CCDC 709480 and 709481 contain the supplementary crystallographic data for **9** and **10**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

### References

- [1] W.P. Neumann, Chem. Rev. 91 (1991) 311.
- [2] M.P. Egorov, P.P. Gaspar, Encyclopedia of Inorganic Chemistry, Wiley, New York, 1995.
- [3] J. Barrau, G. Rima, Coord. Chem. Rev. 593 (1998) 178.
- [4] R. Okazaki, M. Unno, N. Inamoto, Chem. Lett. (1987) 2293.
- [5] R. Okazaki, M. Unno, N. Inamoto, G. Yamamoto, Chem. Lett. (1989) 493.
- [6] R. Okazaki, M. Unno, N. Inamoto, Chem. Lett. (1989) 791.
- [7] N. Tokitoh, M. Saito, R. Okazaki, J. Am. Chem. Soc. 115 (1993) 2065.
- [8] N. Tokitoh, T. Matsumoto, K. Manmaru, R. Okazaki, J. Am. Chem. Soc. 115 (1993) 8855.
- [9] N. Tokitoh, K. Manmaru, R. Okazaki, Organometallics 13 (1994) 167.

- [10] N. Tokitoh, K. Kishikawa, T. Matsumoto, R. Okazaki, *Chem. Lett.* (1995) 827.
- [11] P. Jutzi, H. Schmidt, B. Neumann, H.G. Stammler, *Organometallics* 15 (1996) 741.
- [12] M. Saito, N. Tokitoh, R. Okazaki, *Organometallics* 15 (1996) 4531.
- [13] R.S. Simons, L. Pu, M.M. Olmstead, P.P. Power, *Organometallics* 16 (1997) 1920.
- [14] P.J. Davidson, M.F. Lappert, *J. Chem. Soc. Chem. Comm.* (1973) 317.
- [15] D.E. Goldberg, D.H. Harris, M.F. Lappert, K.M. Thomas, *J. Chem. Soc. Chem. Commun.* (1976) 261.
- [16] J.D. Cotton, P.J. Davidson, M.F. Lappert, *J. Chem. Soc., Dalton Trans.* (1976) 2275.
- [17] J.D. Cotton, P.J. Davidson, M.F. Lappert, J.D. Donaldson, *J. Chem. Soc., Dalton Trans.* (1976) 2286.
- [18] P.J. Davidson, D.H. Harris, M.F. Lappert, *J. Chem. Soc., Dalton Trans.* (1977) 2268.
- [19] P. Jutzi, A. Becker, H.G. Stammler, B. Neumann, *Organometallics* 10 (1991) 1647.
- [20] M. Kira, R. Yauchibara, R. Hirano, C. Kabuto, H. Sakurai, *J. Am. Chem. Soc.* 113 (1991) 7785.
- [21] M. Kira, S. Ishida, T. Iwamoto, M. Ichinohe, C. Kabuto, L. Ignatovich, H. Sakurai, *Chem. Lett.* (1999) 263.
- [22] M.P. Bigwood, P.J. Corvan, J.J. Zuckerman, *J. Am. Chem. Soc.* 103 (1981) 7643.
- [23] H. Gruetzmacher, H. Pritzkow, F.T. Edelman, *Organometallics* 10 (1991) 23.
- [24] J. Bender IV, M.M.B. Holl, J.W. Kamp, *Organometallics* 16 (1997) 2743.
- [25] K. Angermund, K. Jonas, C. Kniger, J.L. Latten, Y.-H. Tsay, *J. Organomet. Chem.* 353 (1988) 17.
- [26] J.T.B.H. Jastrzebski, P.A.v.d. Schaaf, G. Boersma, G.v. Koten, D. Heijdenrijk, K. Goubitz, D.J.A.d. Ridder, *J. Organomet. Chem.* 367 (1989) 55.
- [27] C. Drost, P.B. Hitchcock, M.F. Lappert, L.J.-M. Pierssens, *Chem. Commun.* (1997) 1141.
- [28] W.-P. Leung, W.-H. Kwok, L.-H. Weng, L.T.C. Law, Z.Y. Zhou, T.C.W. Mak, *J. Chem. Soc., Dalton Trans.* (1997) 4301.
- [29] H. Schmidt, S. Keitemeyer, B. Neumann, H.-F. Stammler, W.W. Schnoeller, P. Jutzi, *Organometallics* 17 (1998) 2149.
- [30] P. Jutzi, S. Keitemeyer, B. Neumann, H.-G. Stammler, *Organometallics* 18 (1999) 4778.
- [31] M. Mehring, C. Loew, M. Schuermann, F. Uhlig, K. Jurkschat, B. Mahieu, *Organometallics* 19 (2000) 4613.
- [32] P. Jutzi, S. Keitemeyer, B. Neumann, A. Stammler, H.-G. Stammler, *Organometallics* 20 (2001) 42.
- [33] J.D. Cotton, C.S. Cundy, D.H. Harris, A. Hudson, M.F. Lappert, P.W. Lednor, *J. Chem. Soc. Chem. Commun.* (1974) 651.
- [34] D.H. Harris, M.F. Lappert, *J. Chem. Soc. Chem. Commun.* (1974) 895.
- [35] C.D. Schaeffer, J.J. Zuckerman, *J. Am. Chem. Soc.* 96 (1974) 7160.
- [36] M. Veith, *Angew. Chem., Int. Ed. Engl.* 14 (1975) 263.
- [37] D.H. Harris, M.F. Lappert, J.B. Pedley, G.J. Sharp, *J. Chem. Soc., Dalton Trans.* (1976) 945.
- [38] H. Fußstetter, H. Nöth, *Chem. Ber.* 112 (1979) 3672.
- [39] W. Sander, A. Patyk, G. Bucher, *J. Mol. Struct.* 222 (1990) 21.
- [40] M.V. Andreocci, C. Cauletti, S. Stranges, B. Wrackmeyer, C. Stader, *Z. Naturforsch.* 46 (1991) 39.
- [41] M. Veith, E. Werle, R. Lisowsky, R. Koeppel, H. Schnoekel, *Chem. Ber.* 125 (1992) 1375.
- [42] W.A. Hermann, M. Denk, J. Behm, W. Scherer, F.-R. Klingan, H. Bock, B. Solouki, M. Wagner, *Angew. Chem., Int. Ed. Engl.* 31 (1992) 1485.
- [43] H. Braunschweig, B. Gehrhus, P.B. Hitchcock, M.F. Lappert, *Z. Anorg. Allg. Chem.* 621 (1995) 1922.
- [44] R. West, M. Denk, *Pure Appl. Chem.* 68 (1996) 785.
- [45] S. Veprek, J. Prokop, F. Glatz, R. Merica, F.R. Klingan, W.A. Hermann, *Chem. Mater.* 8 (1996) 825.
- [46] J.R. Babcock, C. Incarvito, A.L. Rheingold, J.C. Fettinger, L.R. Sita, *Organometallics* 18 (1999) 5729.
- [47] N. Gans-Eischler, D. Guetat, M. Nieger, *Angew. Chem. Int. Ed.* 41 (2002) 1888.
- [48] J. Almlif, L. Fernholt, K.J. Faegri, B.R. Schilling, R. Seip, K. Taugbol, *Acta Chem. Scand.* A37 (1983) 131.
- [49] P. Jutzi, B. Hielscher, *Organometallics* 5 (1986) 1201.
- [50] C. Janiak, H. Schumann, C. Stader, B. Wrackmeyer, J.J. Zuckerman, *Chem. Ber.* 121 (1988) 1745.
- [51] P. Jutzi, R. Dickbreder, *J. Organomet. Chem.* 373 (1989) 301.
- [52] D.J. Burke, T.P. Hanusa, *Organometallics* 14 (1995) 11.
- [53] H. Sitzmann, R. Boese, P. Stellberg, *Z. Anorg. Allg. Chem.* 622 (1996) 751.
- [54] P. Jutzi, N. Burford, *Chem. Rev.* 99 (1999) 969.
- [55] N.N. Zemlyansky, I.V. Borisova, M.G. Kuznetsova, V.N. Khrustalev, Y.A. Ustynyuk, M.S. Nechaev, V.V. Lunin, J. Barrau, G. Rima, *Organometallics* 22 (2003) 1675.
- [56] V.N. Khrustalev, I.A. Portnyagin, M.S. Nechaev, S.S. Bukalov, L.A. Leites, *Dalton Trans.* (2007) 3489.
- [57] V.N. Khrustalev, M.Y. Antipin, N.N. Zemlyansky, I.V. Borisova, Y.A. Ustynyuk, V.V. Lunin, J. Barrau, G. Rima, *J. Organomet. Chem.* 689 (2004) 478.
- [58] V.N. Khrustalev, O.V. Chernov, R.R. Aysin, I.A. Portnyagin, M.S. Nechaev, S.S. Bukalov, *Dalton Trans.* (2008) 1140.
- [59] V.N. Khrustalev, I.A. Portnyagin, N.N. Zemlyansky, I.V. Borisova, Y.A. Ustynyuk, M.Y. Antipin, *J. Organomet. Chem.* 690 (2005) 1056.
- [60] V.N. Khrustalev, I.A. Portnyagin, N.N. Zemlyansky, I.V. Borisova, M.S. Nechaev, Y.A. Ustynyuk, M.Y. Antipin, V.V. Lunin, *J. Organomet. Chem.* 690 (2005) 1172.
- [61] V.N. Khrustalev, N.N. Zemlyansky, I.V. Borisova, M.G. Kuznetsova, E.B. Krut'ko, M.Y. Antipin, *Russ. Chem. Bull., Int. Ed.* 56 (2007) 267.
- [62] M.S. Nechaev, *J. Mol. Struct.: THEOCHEM* 862 (2008) 49.
- [63] A.G. Davies, *Organotin Chemistry*, Second ed., Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2004.
- [64] DOSE, *Dictionary of Substances and Their Effects*, Royal Society of Chemistry, Cambridge, 1999.
- [65] R.J. Lewis, *Sax's Dangerous Properties of Industrial Materials*, Wiley, New York, 2000.
- [66] A.S. Ionkin, United States Patent Application Publication, No. 0243390, 2007.
- [67] A.S. Ionkin, W.J. Marshall, B.M. Fish, *Organometallics* 25 (2006) 4170.
- [68] J. Barrau, G. Rima, T. El Amraoui, *Organometallics* 17 (1998) 607.
- [69] V.N. Khrustalev, M.Y. Antipin, N.N. Zemlyansky, I.V. Borisova, Y.A. Ustynyuk, V.V. Lunin, J. Barrau, G. Rima, *J. Organomet. Chem.* 689 (2004) 478.
- [70] N.N. Zemlyansky, I.V. Borisova, V.N. Khrustalev, M.Y. Antipin, Y.A. Ustynyuk, M.S. Nechaev, V.V. Lunin, *Organometallics* 22 (2003) 5441.
- [71] Z.S. Petrovic, in: H.R. Kricheldorf, O. Nuyken, G. Swift (Eds.), *Handbook of Polymer Synthesis*, second ed., Marcel Dekker, New York, 2005.
- [72] J.-M. Bernard, J.-M. Frances, B. Jousseume, N. Noiret, M. Pereyre, *PCT Int. Appl.* (1995) 37. WO 9521694 A1 19950817.
- [73] W.L.F. Armarego, C.L.L. Chai, *Purification of Laboratory Chemicals*, Elsevier Science, Burlington, 2003.
- [74] M.J.S. Gynane, D.H. Harris, M.F. Lappert, P.P. Power, P. Rivière, M. Rivière-Baudet, *J. Chem. Soc., Dalton Trans.* (1977) 2004.
- [75] G.M. Sheldrick, *SADABS*, V2.03, Bruker/Siemens Area Detector Absorption Correction Program, Bruker AXS, Madison, Wisconsin, USA, 2003.
- [76] G.M. Sheldrick, *SHELXTL PLUS* (Version 6.12) Structure Determination Software Suite, Bruker AXS, Madison, Wisconsin, 1998.