

Bis(2,4,6-triisopropylphenyl)tin(IV) compounds: Synthesis, single-crystal X-ray characterization and reactivity toward ionizing species and polar monomers

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Abstract

The synthesis of new organotin compounds of general formula $\text{Tip}_2\text{SnRR}'$ (Tip = 2,4,6-triisopropylbenzene; $\text{R} = \text{R}' = \text{CH}_3$ (**1**); $\text{R} = \text{R}' = \text{CH}=\text{CH}_2$ (**2**); $\text{R} = \text{CH}_2\text{Ph}$, $\text{R}' = \text{Br}$ (**3**); $\text{R} = \text{R}' = \text{CH}_2\text{CH}=\text{CH}_2$ (**4**)) is described herein. The compounds have been characterized by ^1H , ^{13}C , ^{119}Sn NMR, mass spectroscopy and elemental analysis. Characterization by single-crystal X-ray diffraction analysis has been obtained for compounds **2**, **3** and **4**. The reactivity with ionizing agents has been studied by NMR spectroscopy. Compounds **2** and **4** underwent alkyl abstraction by $[(\text{CH}_3\text{CH}_2)_3\text{Si}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ affording stable cationic species (**2a**, **4a**). For the cationic specie **4a** a π -interaction of the benzyl group to the metal centre was recognized by solution NMR studies. A cationic species (**3a**) was generated from compound **3** using AgSbF_6 as ionizing agent. The cationic species (**2a**, **3a**) exhibited moderate activity as initiator in the cationic polymerization of 1,4-butadiene and good activity in the ring opening polymerization (ROP) of propylene oxide and ϵ -caprolactone.
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1. Introduction

The chemistry of stable and free cations of heavier group 14 elements is one of the most attractive topics in recent years [1]. Very recently tricoordinated stannylum cations have been obtained using weakly coordinating anions or strong electrophiles. For instance, in the presence of bulky weakly coordinating anions such as the permethylated carborane $\text{CB}_{11}\text{Me}_{12}^-$, Michl et al. reported the crystal structure of the species $n\text{-Bu}_3\text{Sn}^+\text{CB}_{11}\text{Me}_{12}^-$ [2]. Using aryl ligands with bulky substituents in the *ortho* positions, such as 2,4,6-triisopropylphenyl (Tip), the species $[(\text{Tip})_3\text{Sn}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ was successfully synthesized by Lambert

et al. [3]. Single-crystal X-ray diffraction analysis displayed a planar, tricoordinated cation fully free from interactions with either solvent or anion. Formation of the “free” cation required hydrocarbon solvents, strong electrophiles to abstract an appropriate leaving group, and very low nucleophilic anions such as tetrakis(pentafluorophenyl)borate $\text{B}(\text{C}_6\text{F}_5)_4^-$. Moreover, the three bulky aryl groups “cage” the central atom preventing access of external nucleophiles and protecting the positive charge.

Our recent research interest was devoted to the synthesis of octahedral bis(phenoxy-imine)dialkyl tin(IV) complexes bearing alkyl groups in a *cis* configuration. The obtained species underwent alkyl abstraction reaction with the carbenium salt $[\text{C}(\text{C}_6\text{H}_5)_3]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$. Interestingly, the obtained cationic species exhibited some activity in the ethylene oligomerization under mild conditions, producing oligomers with saturated end groups and methyl branches

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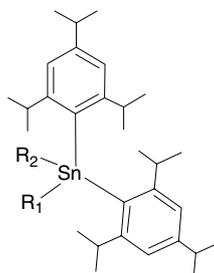
[4]. Such results prompted us to persist in exploring the reactivity of different cationic tin(IV) compounds bearing at least an alkyl group. Trusting in the protecting effect of the bulky 2,4,6-triisopropylphenyl ligands against nucleophilic agents, we have investigated the chemistry of di-aryl tin(IV) compounds of general formula Tip_2SnR_2 or Tip_2SnXR (Tip = 2,4,6-triisopropylbenzene; R = alkyl, X = halogen). Herein, we describe their synthesis and structural characterization, their reactivity with ionizing agents and the subsequent reactivity with olefins and polar monomers.

2. Results and discussion

2.1. Synthesis

The synthesis strategies for the new di-aryl tin(IV) compounds (Chart 1) are described in Scheme 1. Compounds **1** and **2** were synthesized via metathesis reactions of the correspondent di-alkyl tin(IV) dichloride with a THF solution of TipMgBr in toluene. Reactions proceeded with good (compound **1**) or high (compound **2**) yields producing white solids. Suitable crystals for X-ray crystal structure determination were obtained for compound **2** from methyl alcohol at -20°C .

Compound **3** was prepared by reaction of SnBr_4 with two equivalent of TipMgBr in THF solution; the $(\text{Tip})_2\text{SnBr}_2$ product was allowed to react with a solution of benzylmagnesium bromide, producing compound **3** as a white solid (Yield: 73%). Suitable crystals for X-ray crystal structure determination were grown from hexane at -20°C . It is worth noting that even in the presence of more than two equivalent of benzyl Grignard, the only obtained product was the mono-benzylated tin(IV) derivative **3**. We were instead able to further alkylate compound (**3**) by metathesis reaction with allylmagnesiumbromide. The obtained allylbenzylbis[2,4,6-triisopropylphenyl] tin(IV) compound (**4**) was crystallized from methanol/hexane at -20°C .



- | | | |
|----------|--------------------------------------|---|
| 1 | $\text{R}_1 = \text{CH}_3$ | $\text{R}_2 = \text{CH}_3$ |
| 2 | $\text{R}_1 = \text{CH}=\text{CH}_2$ | $\text{R}_2 = \text{CH}=\text{CH}_2$ |
| 3 | $\text{R}_1 = \text{CH}_2\text{Ph}$ | $\text{R}_2 = \text{Br}$ |
| 4 | $\text{R}_1 = \text{CH}_2\text{Ph}$ | $\text{R}_2 = \text{CH}_2\text{CH}=\text{CH}_2$ |

Chart 1.

2.2. Characterization

All the synthesized compounds have been characterized by ^1H , ^{13}C , ^{119}Sn NMR, mass spectroscopy and elemental analysis (see Section 4). For the dialkyl compounds **1**, **2** and **4** the ^{119}Sn NMR spectra displayed a single resonance, appearing between -114 and -170 ppm, in the expected range for tetra-coordinated tin(IV) compounds, thus indicating the existence of a single species in solution. Compound **3** also displayed a single resonance, but at lower field (-56.1 ppm), as a consequence of the deshielding effect of the electron withdrawing bromine atom [5]. The ^1H NMR spectra resulted very clear, with useful information concerning the coordination deriving from the analysis of the proton-tin coupling constants. For instance, in all the compounds the meta hydrogen atoms on the aryl group exhibited coupling with tin with a $^4J(\text{Sn}-\text{H})$ value ranging between 17 and 25 Hz. In compound **1** the $\text{Sn}-\text{CH}_3$ proton resonance appears as singlet at 0.61 ppm, exhibiting coupling with tin with a $^2J(\text{Sn}-\text{H})$ of 53 Hz; using the equation developed by Lockhart for dimethyltin(IV) compounds the calculated angle for the $\text{C}-\text{Sn}-\text{C}$ was 108.6° , in the expected range for a tetrahedral structure [6]. In the benzyl derivative compounds, the observed $^2J(\text{Sn}-\text{H})$ for the $\text{Sn}-\text{CH}_2-\text{Ph}$ resonance was 58.7 Hz in compound **3** and 56.4 Hz in compound **4**.

2.3. Single-crystal X-ray diffraction analysis

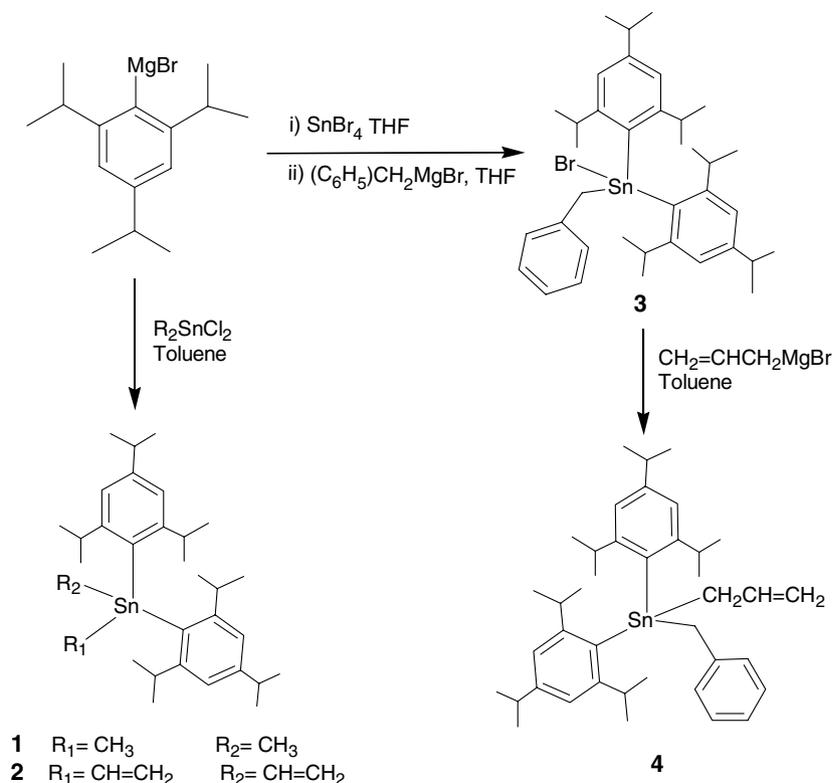
The molecular structures of compounds **2–4** are shown respectively in Figs. 1–3; selected bond lengths and angles are given in Table 1. The coordination environment about the Sn atom is approximately tetrahedral. In compounds **2** and **4** the vinyl and allyl ligands show $\text{Sn}-\text{C}$ distances similar to those observed in analogous vinyl and allyl compounds [7]. In compounds **3** and **4** the benzyl moiety displays η^1 coordination with $\text{Sn}-\text{C}1$ distances respectively 2.166(8) Å and 2.152(11) Å and $\text{Sn}-\text{C}1-\text{C}2$ angles respectively $113.5(6)^\circ$ and $110.2(8)^\circ$ [8b].

2.4. Generation of cationic species and their reactivity with olefins and polar monomers

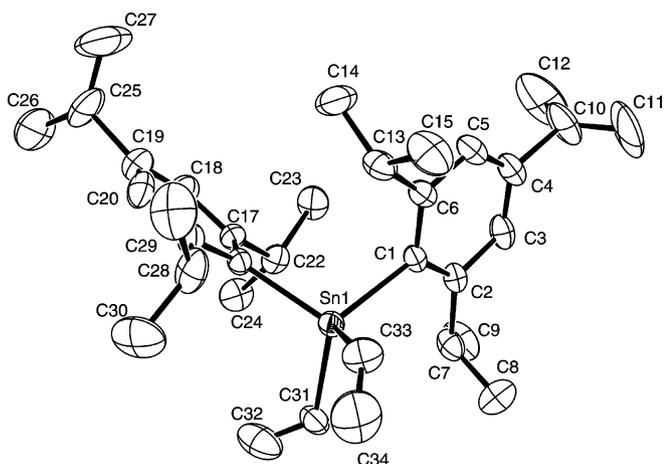
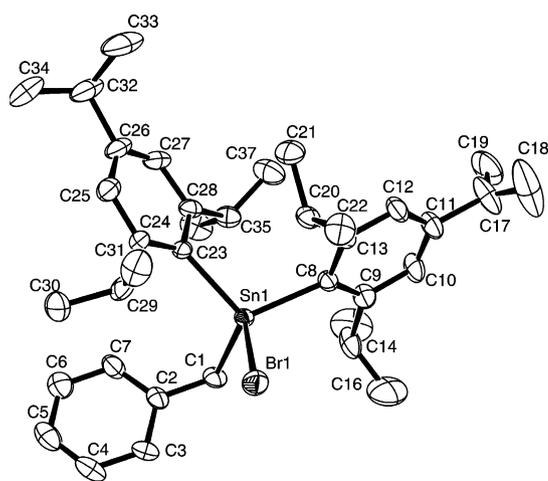
A main focus of our study has been the search of stannyl cations of general formula Tip_2SnR^+ (Tip = 2,4,6-triisopropylphenyl, R = vinyl, benzyl). Therefore, we studied, via NMR spectroscopy, the reactivity of the neutral compounds with different ionizing agents such as $[\text{C}(\text{C}_6\text{H}_5)_3]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$, $\text{B}(\text{C}_6\text{F}_5)_3$, $[(\text{CH}_3\text{CH}_2)_3\text{Si}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ and AgSbF_6 .

Compound **1** resulted non-reactive with all the used ionizing agents. The species $[\text{C}(\text{C}_6\text{H}_5)_3]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ and $\text{B}(\text{C}_6\text{F}_5)_3$ did not react with all the synthesized compounds, at least under the explored experimental conditions.

On the contrary, the species $[(\text{CH}_3\text{CH}_2)_3\text{Si}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ was able to remove an alkyl group from compounds **2** or **4**, affording cationic species (**2a**, **4a**) (Scheme 2). These



Scheme 1.

Fig. 1. Molecular structure of **2**. Thermal ellipsoids are drawn at 20% probability level. Hydrogen atoms have been omitted for clarity.Fig. 2. Molecular structure of **3**. Thermal ellipsoids are drawn at 20% probability level. Hydrogen atoms have been omitted for clarity.

reactions were performed in the NMR tube, in C_6D_6 solvent, and produced two benzene layers. The oily bottom layer revealed the presence of the cationic species, which were stable for weeks. This behaviour was already observed by Lambert for tricoordinated silyl, germyl and stannyl cations in aromatic solvents, and it is characteristic of the formation of liquid clathrates [1b]. It is reasonable to hypothesize that our ionic compounds also exist as liquid clathrates in benzene solution. It is well known that liquid clathrates usually present low lattice energy [9]; as matter of fact, compounds **2a** and **4a** did not crystallize, even after

prolonged standing at low temperature, and, as a consequence, were characterized in situ by ^1H , ^{13}C , and ^{119}Sn NMR analysis.

As described above, reaction of compound **2** with 1 equiv. of $[(\text{CH}_3\text{CH}_2)_3\text{Si}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ in C_6D_6 (Scheme 2), produced two layers. In the upper layer, ^1H NMR analysis evidenced the presence of the sideproduct $\text{CH}_2=\text{CHSi}(\text{CH}_2\text{CH}_3)_3$. In the bottom layer, ^1H NMR analysis (Fig. 4) displayed a new organometallic species, different from the starting compound **2**, and characterized by the upfield shift of the signals and by the aryl signals/vinyl

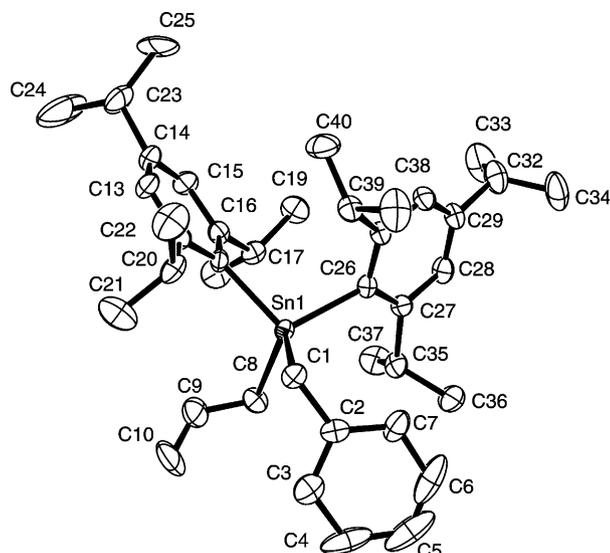


Fig. 3. Molecular structure of **4**. Thermal ellipsoids are drawn at 20% probability level. Hydrogen atoms have been omitted for clarity.

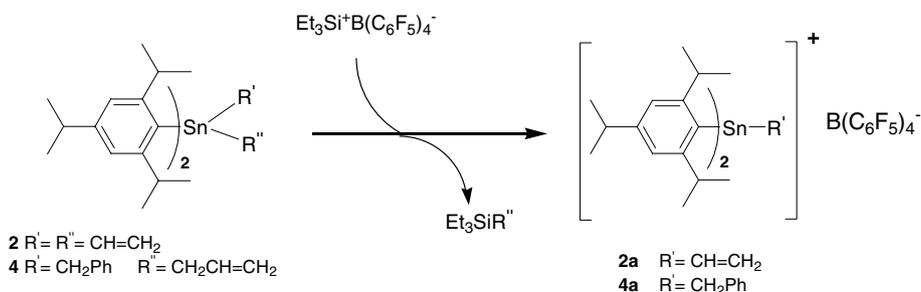
signals integrals ratio consistent with a 2:1 formulation. A very high down-field shift of ^{119}Sn NMR signal (760 ppm) was observed, which is likely due to tin atom deshielding, according to literature data concerning free tricoordinate stannylum cations [1b,3].

Analogously, when compound **4** was reacted with 1 equiv. of $[(\text{CH}_3\text{CH}_2)_3\text{Si}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ in C_6D_6 , the allyl group was abstracted (Scheme 2), and two layers were formed. In the upper layer, NMR analysis evidenced the presence of $\text{CH}_2=\text{CHCH}_2\text{Si}(\text{CH}_2\text{CH}_3)_3$. Consequently, in

the ^1H NMR spectrum of the bottom layer the resonances of the allyl group are absent, with the residual signals appearing very broad. However, the ^{119}Sn NMR spectrum showed one signal at 599.9 ppm, thus indicating the existence of a single tin species in solution. The very high downfield shift observed is consistent with the formation of a cationic species. A better resolution of the spectrum was obtained in the presence of few drops of ClC_6D_5 . The subsequently recorded ^1H NMR spectrum (Fig. 5) displayed the benzylic CH_2Ph hydrogen atoms at 3.4 ppm ($^2J^{119}\text{Sn}-^1\text{H} = 56.2$) and an upfield shift of the CH of the isopropyl substituents on the aryl group in *ortho* position at 1.8 ppm, if compared with the corresponding resonances of the neutral compound **4**. Interesting information came from careful analysis of the aromatic region. As matter of fact, it is well known that the benzyl ligand differs from the simple alkyls in its potential ability to interact with electron-deficient metal centers through the π -aromatic system. Coordination $\eta^n(n > 1)$ is typical of transition metal and has been observed in solid state [10]; among main group elements, η^3 interaction has been observed, in solid state, for benzyl lithium [11]. Latesky found NMR spectroscopic evidence that also in solution is possible to detect this type of interaction. In particular, η^n benzyl ligands are characterized by a high-field shift for the *ortho* hydrogen resonance ($\delta < 6.8$ ppm) in the ^1H NMR spectrum, and by large $^1J_{\text{CH}}$ values for CH_2 group ($J > 130$ Hz). The increase of the coupling constant can be explained with an increasing “ sp^2 ” character of α -carbon, involving a decrease of the $\text{Mt}-\text{C}-\text{Ph}$ angle. It is worth nothing that in these studies tetrabenzyltin $\text{Sn}(\text{CH}_2\text{C}_6\text{H}_5)_4$ was taken as a model for

Table 1
Selected bond lengths (Å) and angles (°) for compounds **2–4**

| 2 | | 3 | | 4 | |
|----------------|----------|--------------|-----------|--------------|-----------|
| Sn–C(1) | 2.163(3) | Sn–C(8) | 2.159(8) | Sn–C(11) | 2.174(11) |
| Sn–C(16) | 2.169(4) | Sn–C(23) | 2.157(8) | Sn–C(26) | 2.197(11) |
| Sn–C(33) | 2.130(4) | Sn–C(1) | 2.166(8) | Sn–C(1) | 2.152(11) |
| Sn–C(31) | 2.144(5) | Sn–Br(1) | 2.520(5) | Sn–C(8) | 2.188(12) |
| C(31)–C(32) | 1.201(9) | C(1)–C(2) | 1.486(13) | C(8)–C(9) | 1.43(2) |
| C(33)–C(34) | 1.249(7) | | | C(9)–C(10) | 1.28(3) |
| Sn–C(31)–C(32) | 129.7(6) | Sn–C(1)–C(2) | 113.5(6) | Sn–C(1)–C(2) | 110.2(8) |
| Sn–C(33)–C(34) | 123.4(4) | | | Sn–C(8)–C(9) | 108.4(10) |



Scheme 2.

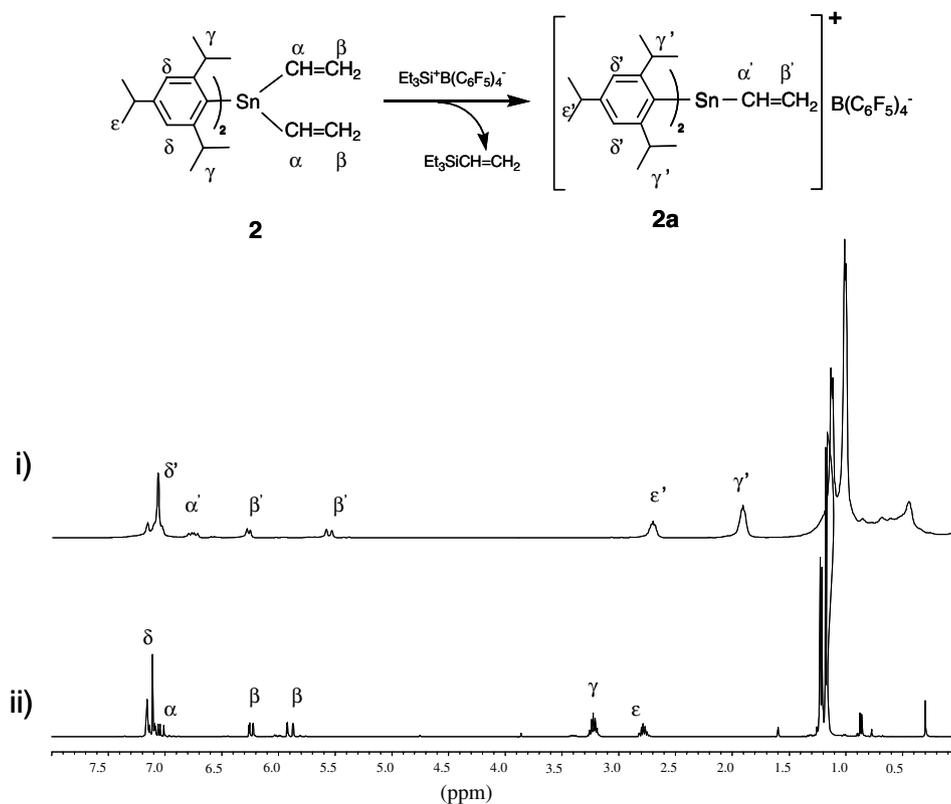


Fig. 4. ^1H NMR spectra (C_6D_6 , 25°C) of compounds **2** (ii) and **2a** (i).

normal σ -bound (η^1) benzyl [10b]. Interestingly, in the NMR spectra of cationic species **4a** we observed an upfield shift of the *ortho* benzyl hydrogens resonance (6.7 ppm), and a coupling constant $^1J_{\text{CH}}$ for the methylenic carbon value of 142 Hz. These spectroscopic features thus suggest that in the cationic species **4a** the benzyl ligand interacts, in some way, with the tin also through the π -aromatic system. Therefore, a $\eta^n(n > 1)$ coordination for the benzyl ligand can be hypothesized.

The ^{119}Sn chemical shift for the species **4a** measured in C_6D_6 solvent, in the presence of few drops of ClC_6D_5 , appeared at higher field (535 ppm) in comparison with the signal measured in neat benzene. For that reason the effect of the ClC_6D_5 concentration on the ^{119}Sn chemical shift was studied: in the presence of ClC_6D_5 in 1:1 and 65:1 molar ratio with tin the signal appears respectively at 585 ppm and at 524 ppm. Therefore, the addition of a stronger coordinating solvent than aromatic hydrocarbons to the positively charged center leads to the upfield shift of the tin resonance. It is well established that an increase in coordination number of the tin atom from four to five, six or seven produces the upfield shift of $\delta(^{119}\text{Sn})$ [5]. It is also known from the literature that chlorobenzene could coordinate unsaturated species, and recently Jordan reported the crystal structure of various Zr(IV) cations displaying the chlorobenzene η^1 -coordinated via chlorine [12].

Compound **3** was reacted with AgSbF_6 in ClC_6D_5 solvent. The reaction proceeded with formation of the cationic species **3a** and precipitation of AgBr . The reaction

was fast and selective. The upper layer was analyzed by ^1H , ^{13}C , and ^{119}Sn NMR spectroscopy (Fig. 6). Interestingly, though the cation in the species **3a** had identical formula to the cation in species **4a**, their NMR spectra showed significant differences. In order to evaluate the presence of some $\eta^n(n > 1)$ coordination of the benzyl group to the metal, we analyzed the NMR spectra. We found a $^1J_{\text{CH}}$ value for the CH_2 group of 136 Hz, which is higher than usual value for sp^3 carbons (125 Hz), but is too close to that one observed in tetrabenzyltin (133 Hz), usually taken as a model for a normal σ -bound (η^1) benzyl groups [10b]. Moreover, the ^1H NMR signal of the *ortho* hydrogen atoms appeared around 7.0–7.3 ppm (overlapped with the signals of others aromatic hydrogens), in the expected range for usual (η^1) benzyl ligand. Therefore, we have not any evidence of $\eta^n(n > 1)$ coordination of the benzyl group to tin in the cationic species **3a**. The ^{19}F NMR analysis also excluded any interaction with the anion SbF_6^- : a single resonance at 118.7 ppm was in fact observed. It is worth noting that in the species **4a** also the anion does not interact with the cation. The ^{119}Sn NMR spectrum displays a single resonance at 257 ppm, at higher field in comparison to the resonance observed with **4a**, clear indication of the presence of a different species. As discussed above, the large upfield shift of $\delta(^{119}\text{Sn})$ is likely due to the coordinating solvent. It is worth nothing that for the existence of cationic species **3a** the use of ClC_6D_5 as solvent seems to be essential: in fact in CDCl_3 or CD_2Cl_2 as solvent the reaction led quickly to decomposition products. It is reasonable

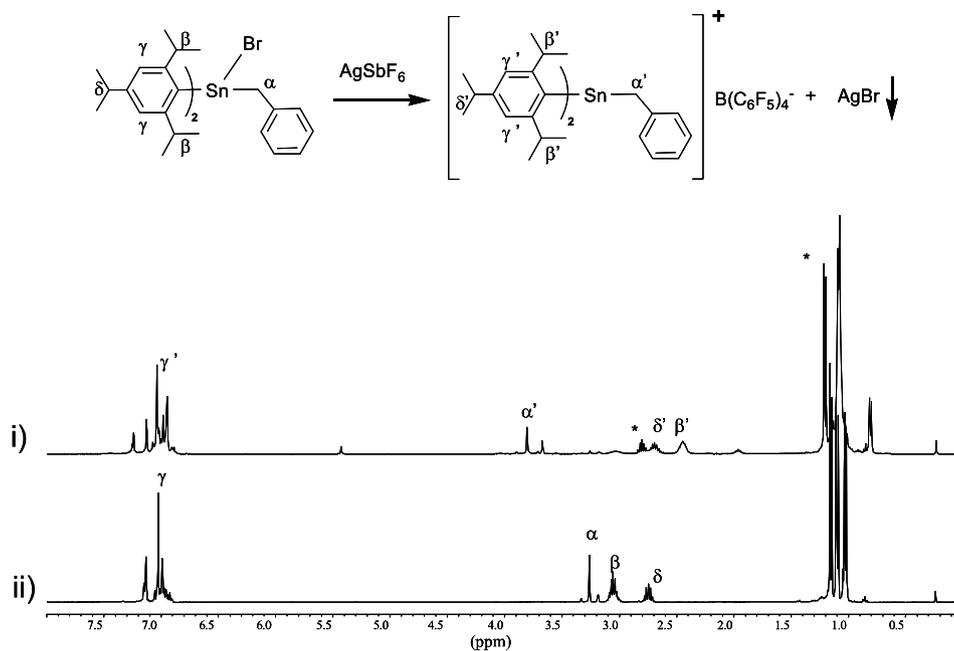


Fig. 6. ^1H NMR spectra (C_6D_6 , 25 °C) of compounds **3** (ii) and **3a** (i). (*) Refers to the “free” ligand (1,3,5 triisopropylbenzene) impurities.

3. Conclusions

New Tin(IV) compounds of general formula Tip_2SnR_2 (Tip = 2,4,6-triisopropylbenzene; R = alkyl, halogen) have been synthesized and fully characterized by ^1H , ^{13}C , ^{119}Sn NMR, mass spectroscopy and elemental analysis. Characterization by single-crystal X-ray diffraction analysis has been obtained for compounds **2**, **3** and **4**, showing the metal in a distorted tetrahedral geometry. The reactivity with ionizing agents was studied by NMR spectroscopy. Compounds **2** and **4** underwent alkyl abstraction by $[(\text{CH}_3\text{CH}_2)_3\text{Si}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ affording stable cationic species (**2a**, **4a**), while a cationic species (**3a**) was generated from compound **3** using AgSbF_6 as ionizing agent. Interestingly, for the cationic species **4a** a π -interaction of the benzyl group with the metal centre was recognized by solution NMR studies.

The cationic species (**2a**, **3a**) exhibited moderate activity as initiator in the cationic polymerization of 1,4-butadiene and good activity in the ring opening polymerization (ROP) of propylene oxide and ϵ -caprolactone.

4. Experimental section

4.1. General procedure

Manipulation of sensitive materials were carried out under nitrogen using Schlenk or glove box techniques. Toluene and THF were refluxed over sodium/benzophenone and distilled under nitrogen prior to use. Diethyl ether was distilled from LiAlH_4 , chlorobenzene was dried over CaH_2 and distilled prior to use. CDCl_3 , CD_2Cl_2 and C_6D_6 were distilled from CaH_2 , C_6D_6 was distilled from triisobutylaluminium, and all were stored over molecular

seives in a glove box. Reagents were purchased from Aldrich and used as received. ϵ -Caprolactone and propylene oxide were distilled in vacuum from CaH_2 prior to use. The carbenium salt $[\text{C}(\text{C}_6\text{H}_5)_3]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ was purchased from Boulder and used as received. Butadiene and ethylene were purchased from SON; butadiene was purified by distillation from triisopropylaluminium prior to use. NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer (^1H , 400 MHz; ^{13}C , 100 MHz; ^{119}Sn , 149 MHz; ^{19}F , 376 MHz). The ^{119}Sn NMR spectra were measured relative to $\text{Sn}(\text{CH}_3)_4$. EI MS data were obtained with a Finnigan Thermoquest GCQ Plus 200 spectrometer using a direct insertion probe. Elemental analysis were recorded on Thermo Finnigan Flash EA 1112 series C,H,N,S Analyzer.

4.2. Synthesis of bis[2,4,6-triisopropylphenyl]dimethyltin(IV) (**1**)

To a stirred solution of $\text{Cl}_2\text{Sn}(\text{CH}_3)_2$ (504 mg, 2.3 mmol) in dry toluene (30 ml) at 0 °C was added dropwise a THF solution of tri-isopropylphenylmagnesiumbromide (11.1 ml, 5.0 mmol). The mixture was allowed to reflux for 16 h, then cooled at room temperature, and quenched with H_2O and 10% aqueous HBr. The organic portion was washed with H_2O (2×20 ml), NaHCO_3 (2×20 ml) and H_2O again (2×20 ml). The organic solution was dried over MgSO_4 , the solvent was removed to give a light yellow oil. The crude product was dissolved with methyl alcohol and the solution was stored at -20 °C. A white solid deposited overnight (730 mg, 60%). ^1H NMR (CDCl_3 , 293 K): δ = 0.61 (6 H, s, $^2J^{117}\text{Sn}-^1\text{H}$ = 51 Hz, $^2J^{117}\text{Sn}-^1\text{H}$ = 53 Hz, $\text{Sn}-\text{CH}_3$), 1.03 (24H, d, $J^1\text{H}-^1\text{H}$ = 6.8 Hz, *o*- $\text{CH}(\text{CH}_3)_2$), 1.19 (12H, d, $J^1\text{H}-^1\text{H}$ = 6.9 Hz, *p*- $\text{CH}(\text{CH}_3)_2$), 2.81 (2H,

m, *p*-CH(CH₃)₂, 2.96 (4H, m, *o*-CH(CH₃)₂), 6.90 (4H, s, ⁴J¹¹⁹Sn–¹H = 17.4 Hz, ArH). ¹³C NMR (CDCl₃, 293 K): δ = –0.5 (Sn–CH₃), 24.1 (*p*-CH(CH₃)₂), 24.8 (*o*-CH(CH₃)₂), 34.4 (*p*-CH(CH₃)₂), 37.1 (*o*-CH(CH₃)₂), 121.2 (ArCH), 140.5, 149.2, 154.8 (Ar–C). ¹¹⁹Sn (CD₂Cl₂, 293 K): δ = –113.7. EI MS *m/z* = 555 [M]⁺. Anal. Calc. for C₃₂H₅₂Sn (555.47): C, 69.19; H, 9.44. Found: C, 66.37; H, 9.12%.

4.3. Synthesis of bis[2,4,6-triisopropylphenyl]divinyl tin(IV) (2)

This compound was prepared as above but using Cl₂Sn(CH=CH₂)₂ (0.900 g, 3.75 mmol) in 60 ml of toluene and 17 ml of tri-isopropylphenylmagnesiumbromide solution in THF (0.50 M, 8.5 mmol). (Yield 1.89 g, 87%). White crystals for X-ray crystal structure determination were grown from methyl alcohol at –20 °C. ¹H NMR (C₆D₆, 293 K): δ = 1.17 (24H, d, ¹J¹H–¹H = 6.8 Hz, *o*-CH(CH₃)₂), 1.22 (12H, d, ¹J¹H–¹H = 6.9 Hz, *p*-CH(CH₃)₂), 2.81 (2H, m, *p*-CH(CH₃)₂), 3.20 (4H, m, *o*-CH(CH₃)₂), 5.91 (2H, dd, ¹J¹H–¹H = 2.9, 20.1 Hz, ³J¹¹⁹Sn–¹H = 46 Hz, CH=CH₂), 6.25 (2H, dd, ¹J¹H–¹H = 2.9, 13.5 Hz, ³J¹¹⁹Sn–¹H = 90 Hz, CH=CH₂), 7.0 (2H, m, CH=CH₂), 7.10 (4H, s, ⁴J¹¹⁹Sn–¹H = 18.8 Hz, ArH). ¹³C NMR (C₆D₆, 293 K): δ = 24.6 (*p*-CH(CH₃)₂), 24.8 (*o*-CH(CH₃)₂), 35.0 (*p*-CH(CH₃)₂), 38.1 (*o*-CH(CH₃)₂), 122.0 (ArCH), 134.1 (CH=CH₂), 142.7 (CH=CH₂), 139.3, 150.4, 155.8 (Ar–C). ¹¹⁹Sn (C₆D₆, 293 K): δ = –169.0. EI MS *m/z* = 579 [M]⁺. Anal. Calc. for C₃₄H₅₂Sn (579.49): C, 70.47; H, 9.04. Found: C, 69.81; H, 8.93%.

4.4. Synthesis of benzylbromobis[2,4,6-triisopropylphenyl] tin(IV) (3)

To a stirred solution of SnBr₄ (2.0 g, 4.5 mmol) in dry THF (80 ml) was added dropwise a THF solution of triisopropylphenylmagnesium bromide (25 ml, 10.8 mmol) at 0 °C. The mixture was allowed to reflux for 16 h. The reaction was then cooled 0 °C and a THF solution of benzylmagnesium bromide (12 ml, 10.8 mmol) was added. The mixture was allowed to reflux for 5 h and then cooled to room temperature and stirred overnight. The reaction was quenched with H₂O and 10% aqueous HBr. The organic portion was washed with H₂O (2 × 20 ml), NaHCO₃ (2 × 20 ml) and H₂O again (2 × 20 ml). The organic solution was dried over Na₂SO₄, the solvent was removed to give a light yellow oil. The crude product was dissolved in hexane and the solution was stored at –20 °C. A white solid deposited overnight (2.3 g, 73%). Suitable crystals for X-ray crystal structure determination were grown from hexane at –20 °C. ¹H NMR (C₆D₅Cl, 293 K): δ = 1.16 (12H, d, ¹J¹H–¹H = 6.5 Hz, CH(CH₃)₂), 1.24 (12H, d, ¹J¹H–¹H = 6.6 Hz, CH(CH₃)₂), 1.30 (12H, d, ¹J¹H–¹H = 6.9 Hz, CH(CH₃)₂), 2.89 (2H, m, *p*-CH(CH₃)₂), 3.19 (4H, m, *o*-CH(CH₃)₂), 3.39 (2H, s, ²J¹¹⁹Sn–¹H = 58.7 Hz, CH₂Ph), 7.03–7.28 (9H, m, Ph +

ArH). ¹³C NMR (C₆D₅Cl, 293 K): δ = 24.0 (*o*-CH(CH₃)₂), 24.9 (*p*-CH(CH₃)₂), 34.5 (*p*-CH(CH₃)₂), 34.7 (CH₂Ph), 38.1 (*o*-CH(CH₃)₂), 122.0 (ArCH), 126–155 (Ph–C + Ar–C). ¹¹⁹Sn (C₆D₅Cl, 293 K): δ = –56.1. EI MS *m/z* = 605 [M–CH₂(C₆H₅)]⁺. Anal. Calc. for C₃₇H₅₃BrSn (696.43): C, 63.81; H, 7.67. Found: C, 63.59; H, 7.31%.

4.5. Synthesis of allylbromobis[2,4,6-triisopropylphenyl] tin(IV) (4)

To a stirred solution of benzylbromobis[2,4,6-triisopropylphenyl] tin(IV) (3) (760 mg, 1.1 mmol) in dry toluene (60 ml) at 0 °C was added dropwise a THF solution of allylmagnesiumbromide (8 ml, 6.4 mmol). The solution was refluxed for 2 days. The reaction was then quenched with H₂O and 10% aqueous HBr. The organic portion was washed with H₂O (2 × 50 ml), NaHCO₃ (2 × 50 ml) and H₂O again (2 × 50 ml). The organic solution was dried over MgSO₄, the solvent was removed to give a light yellow oil. The product was crystallized from methanol/hexane 5:1 (509 mg, 70%). Suitable crystals for X-ray crystal structure determination were grown from methanol/hexane at –20 °C. ¹H NMR (C₆D₆, 293 K): δ = 1.03 (12H, d, ¹J¹H–¹H = 6.6 Hz, CH(CH₃)₂), 1.15 (12H, d, ¹J¹H–¹H = 6.8 Hz, CH(CH₃)₂), 1.19 (12H, d, ¹J¹H–¹H = 6.9 Hz, CH(CH₃)₂), 2.37 (2H, d, ¹J¹H–¹H = 8.4 Hz, ²J¹¹⁹Sn–¹H = 66.0 Hz, CH₂CH₂=CH), 2.75 (2H, m, *p*-CH(CH₃)₂), 2.87 (4H, m, *o*-CH(CH₃)₂), 3.0 (2H, s, ²J¹¹⁹Sn–¹H = 56.4 Hz, CH₂Ph), 4.83 (1H, dd, ¹J¹H–¹H = 2.0, 16.9 Hz, CH₂CH=CH₂), 5.03 (1H, dd, ¹J¹H–¹H = 1.9, 16.9 Hz, CH₂CH=CH₂), 5.96 (1H, m, CH₂CH=CH₂), 7.05 (4H, s, ⁴J¹¹⁹Sn–¹H = 18.4 Hz, ArH), 6.8–7.0 (5H, m, Ph). ¹³C NMR (C₆D₆, 293 K): δ = 23.5 (CH₂CH=CH₂), 24.5, 24.8, 25.3 (CH(CH₃)₂), 25.8 (CH₂Ph), 34.9 (*p*-CH(CH₃)₂), 38.5 (*o*-CH(CH₃)₂), 112.7 (CH₂CH=CH₂), 122.0 (ArCH), 124.6 (CH₂CH=CH₂), 137.8 (Ph–C), 141.0, 142.1, 150.3, 155.4 (Ar–C). ¹¹⁹Sn (C₆D₆, 293 K): δ = –120.6. EI MS *m/z* = 617 [M–CH₂CH=CH₂]⁺. Anal. Calc. for C₄₀H₅₈Sn (657.6): C, 73.06; H, 8.89. Found: C, 72.45; H, 8.23%.

4.6. Generation of {bis[2,4,6-triisopropylphenyl]vinyl tin(IV)}⁺[B(C₆F₅)₄][–] (2a)

The reaction was carried out in a glove box in a 5 mm NMR tube. To a solution of carbenium salt [C(C₆H₅)₃]⁺[B(C₆F₅)₄][–] (160 mg, 0.17 mmol) in 0.5 ml of dry C₆D₆ was added triethylsilane (25 mg, 0.22 mmol). Addition produced two layers. The top colorless phase, containing organic subproduct, was taken off with a syringe and a brown oil (lower phase) remained in the NMR tube. A solution of compound 2 (110 mg, 0.19 mmol) in 0.5 ml dry C₆D₆ was added to create two layer again. The upper phase was removed and the oil phase, at bottom, was characterized by NMR. ¹H NMR (C₆D₆, 293 K): δ = 1.0 (24H, d, ¹J¹H–¹H = 6.9 Hz, *o*-CH(CH₃)₂), 1.13 (12H, d, ¹J¹H–¹H = 6.8 Hz, *p*-CH(CH₃)₂), 1.90 (4H, m, *o*-CH(CH₃)₂), 2.70 (2H, m, *p*-CH(CH₃)₂), 5.5 (1H, dd,

$J^1\text{H}-^1\text{H} = 19.6$ Hz, $\text{CH}=\text{CH}_2$), 6.3 (1H, dd, $J^1\text{H}-^1\text{H} = 11.8$ Hz, $\text{CH}=\text{CH}_2$), 6.7 (1H, m, $\text{CH}=\text{CH}_2$), 7.0 (4H, s, ArH). ^{13}C NMR (C_6D_6 , 293 K): $\delta = 23.2$ ($p\text{-CH}(\text{CH}_3)_2$), 24.1 ($o\text{-CH}(\text{CH}_3)_2$), 34.6 ($p\text{-CH}(\text{CH}_3)_2$), 44.1 ($o\text{-CH}(\text{CH}_3)_2$), 124.4 (ArCH), 144.7 ($\text{CH}=\text{CH}_2$), 145.5 ($\text{CH}=\text{CH}_2$), 134–158 (Ar-C). ^{119}Sn (C_6D_6 , 293 K): $\delta = 591.7$.

4.7. Generation of {benzylbis[2,4,6-triisopropylphenyl]tin(IV)}⁺[SbF₆]⁻ (**3a**)

Compound **3** (19 mg, 27 μmol) was dissolved in dry ClC_6D_5 (0.5 ml) and AgSbF_6 (9 mg, 27 μmol) was added. A white solid (AgCl) precipitated. The solution was analysed by NMR spectroscopy. ^1H NMR ($\text{C}_6\text{D}_5\text{Cl}$, 293 K): $\delta = 1.23$ (36H, d, $J^1\text{H}-^1\text{H} = 7.5$ Hz, $\text{CH}(\text{CH}_3)_2$), 2.58 (4H, m, $o\text{-CH}(\text{CH}_3)_2$), 2.83 (2H, m, $p\text{-CH}(\text{CH}_3)_2$), 3.94 (2H, s, $^2J^{119}\text{Sn}-^1\text{H} = 73.6$ Hz, CH_2Ph), 7.0–7.3 (9H, m, Ph + ArH). ^{13}C NMR ($\text{C}_6\text{D}_5\text{Cl}$, 293 K): $\delta = 23.7$ ($\text{CH}(\text{CH}_3)_2$), 34.5 ($p\text{-CH}(\text{CH}_3)_2$), 37.9 (CH_2Ph), 40.8 ($o\text{-CH}(\text{CH}_3)_2$), 123.4 (ArCH), 140–154 (Ph-C + Ar-C). ^{19}F ($\text{C}_6\text{D}_5\text{Cl}$, 293 K): $\delta = -118.7$. ^{119}Sn ($\text{C}_6\text{D}_5\text{Cl}$, 293 K): $\delta = 257.4$.

4.8. Generation of {benzylbis[2,4,6-triisopropylphenyl]tin(IV)}⁺[B(C₆F₅)₄]⁻ (**4a**)

The cationic species **4a** was generated as described for species **2a** but using 124 mg of $[\text{C}(\text{C}_6\text{H}_5)_3]^+ [\text{B}(\text{C}_6\text{F}_5)_4]^-$ (0.13 mmol), 24 mg of triethylsilane (0.17 mmol) and 99 mg of allylbenzylbis[2,4,6-triisopropylphenyl]tin (0.15 mmol) in C_6D_6 dry. ^1H NMR (mixture of 0.5 ml C_6D_6 and 1 ml ClC_6D_5 , 293 K): $\delta = 0.93$ (24H, d, $J^1\text{H}-^1\text{H} = 6.3$ Hz, $o\text{-CH}(\text{CH}_3)_2$), 1.10 (12H, d, $J^1\text{H}-^1\text{H} = 6.9$ Hz, $p\text{-CH}(\text{CH}_3)_2$), 1.88 (4H, m, $o\text{-CH}(\text{CH}_3)_2$), 2.70 (2H, m, $p\text{-CH}(\text{CH}_3)_2$), 3.4 (2H, s, $^2J^{119}\text{Sn}-^1\text{H} = 56.2$, CH_2Ph), 6.7 (2H, d, $J^1\text{H}-^1\text{H} = 7.7$ Hz, $o\text{-Ph}$), 7.04 (4H, s, ArH), 6.9–7.03 (3H, m, Ph). ^{13}C NMR (C_6D_6 , 293 K): $\delta = 23.7$, 24.5 ($\text{CH}(\text{CH}_3)_2$), 35.1 ($p\text{-CH}(\text{CH}_3)_2$), 42.9 (CH_2Ph), 46.1 ($o\text{-CH}(\text{CH}_3)_2$), 124.8 (ArCH), 136–157 (Ar-C). ^{119}Sn NMR (C_6D_6 , 293 K): $\delta = 599.9$; ^{119}Sn NMR (mixture of 0.5 ml C_6D_6 and 15 μl ClC_6D_5 , 293 K): $\delta = 585.3$; ^{119}Sn NMR (mixture of 0.5 ml C_6D_6 and 1 ml ClC_6D_5 , 293 K): $\delta = 524.9$.

5. Polymerization tests

5.1. Propylene oxide

A typical polymerization test was carried out at 25 °C using 60 μmol of neutral compound (**2** or **3**) and 60 μmol of suitable ionizing agent (AgSbF_6 , $\text{Et}_3\text{Si}^+\text{B}(\text{C}_6\text{F}_5)_4^-$) in 15 ml of toluene dry. Propylene oxide (5 ml) was added. After 5 min, the solvent was removed in vacuo to give an oily product (Yield = 2.6 g). ^1H NMR (CDCl_3 , 25 °C) $\delta = 1.04$ (d, 3H, CH_3), 3.30–3.68 (br m, 3H, $\text{OCH}(\text{CH}_3)$ and OCH_2).

5.2. ϵ -Caprolactone

A typical polymerization test was carried out as above but using 1.5 ml of ϵ -caprolactone. After 1 day the polymerization was quenched in heptane. The polymer was filtered, dried in vacuo and characterized by NMR spectroscopy (Yield = 1.13 g). ^1H NMR (CDCl_3 , 25 °C) $\delta = 1.37$ (m, 2H, $-\text{CH}_2-$), 1.65 (m, 4H, $-\text{CH}_2-$), 2.29 (t, 2H, $-\text{CH}_2\text{C}(\text{O})\text{O}-$), 4.08 (t, 2H, $-\text{CH}_2\text{OC}(\text{O})-$).

5.3. Butadiene

A polymerization test was carried out at 25 °C using 100 μmol of compound (**2**) and 100 μmol of $\text{Et}_3\text{Si}^+\text{B}(\text{C}_6\text{F}_5)_4^-$ in 30 ml of toluene. The monomer was distilled from $\text{Al}(i\text{-Pr})_3$ at -78 °C. After 90 h the polymerization was stopped with acidified methanol solution. The solution was treated with water and hexane (3×50 ml). The organic phase was dried on Na_2SO_4 and the solvent removed by rotary evaporation. (Yield = 2.17 g).

A polymerization test in the presence of compound (**3**) (100 μmol) and AgSbF_6 (100 μmol) was carried out analogously in 30 ml of dry chlorobenzene. After 90 h the polymerization was stopped with acidified methanol. The polymer was filtered and dried in vacuo (Yield = 0.290 g). The products were characterized by NMR spectroscopy. ^{13}C NMR (CDCl_3 , 25 °C) $\delta = 32.9$, 130.2 (1,4 *trans* units) 30.3, 38.4, 43.7, 114.4, 142.9 (minor resonances, 1,2 isolated units).

6. X-ray crystallography

Suitable crystals were selected and mounted in Lindemann capillaries under inert atmosphere. Diffraction data were measured at room temperature with a Rigaku AFC7S diffractometer using graphite monochromated $\text{Mo K}\alpha$ radiation ($\lambda = 0.71069$ Å). Data reduction was performed with the crystallographic package CrystalStructure [14]. The structures were solved by direct methods using the program SIR92 [15] and refined by means of full-matrix least-squares based on F^2 using the program SHELXL97 [16]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were positioned geometrically and included in structure factors calculations but not refined. Restraints were applied to $\text{CH}-\text{CH}_3$ distances of isopropyl groups. Crystal data and refinement details are reported in Table 2. Crystal structures are drawn by means of the program ORTEP32 [17].

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC-287930 (compound **2**), CCDC-287931 (compound **3**) and CCDC-287929 (compound **4**). Copies of data may be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 2EZ, UK [Fax: +44(1223)336-03; e-mail: deposit@ccdc.cam.ac.uk].

Table 2
Crystal data and structure refinement details for compounds 2–4

| | 2 | 3 | 4 |
|---|-----------------------------------|-------------------------------------|-----------------------------------|
| Formula | SnC ₃₄ H ₅₂ | SnBrC ₃₇ H ₅₃ | SnC ₄₀ H ₅₈ |
| Formula weight | 579.47 | 696.40 | 657.55 |
| Crystal system | Triclinic | Monoclinic | Monoclinic |
| Space group | <i>P</i> $\bar{1}$ | <i>P</i> 2 ₁ / <i>c</i> | <i>C</i> 2/ <i>c</i> |
| <i>a</i> (Å) | 9.606(4) | 12.023(3) | 37.490(15) |
| <i>b</i> (Å) | 12.126(4) | 10.264(2) | 11.136(4) |
| <i>c</i> (Å) | 16.853(3) | 29.716(6) | 18.267(6) |
| α (°) | 103.07(2) | | |
| β (°) | 96.62(2) | 93.387(19) | 98.99(3) |
| γ (°) | 112.53(3) | | |
| <i>V</i> (Å ³) | 1721.4(10) | 3660.8(14) | 7533(5) |
| <i>Z</i> | 2 | 4 | 8 |
| <i>D</i> _{calc} (g cm ⁻³) | 1.118 | 1.264 | 1.160 |
| μ (Mo K α) (mm ⁻¹) | 0.76 | 1.81 | 0.70 |
| <i>F</i> (000) | 612 | 1440 | 2784 |
| Independent reflections measured | 10053 | 3403 | 6631 |
| Parameters/restraints | 316/66 | 352/29 | 370/66 |
| <i>R</i> ₁ [<i>F</i> _o > 4 σ (<i>F</i> _o)] | 0.0452 (5771) | 0.0461 (2569) | 0.0635 (3559) |
| <i>wR</i> ₂ (all reflections) | 0.1305 | 0.1303 | 0.2664 |
| Goodness-of-fit | 2.473 | 0.897 | 1.057 |
| $\Delta\rho$ min/ $\Delta\rho$ max (e Å ⁻³) | -0.68/0.71 | -1.39/0.75 | -1.31/1.27 |

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2005.12.011.

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