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Functionalised tetraarylstannanes $Sn[C_6H_4\text{-}R]_4$ ($R = -CH(CH_2O)_2$, $-CH{=}O$, $-COOH$, $-CH{=}N{-}NH{-}C_6H_3\text{-}2,4\text{-}(NO_2)_2$, $-CH_2OH$, $-CO{-}NH{-}CH_2{-}COO{-}CH_3$, $-CH[N(C_2H_4)_2O]_2$)

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Abstract

Reaction of tin tetrachloride with the appropriate Grignard reagent gave $Sn[C_6H_4{-}CH(OCH_2)_2]_4$ (**2**), which was transformed to $Sn[C_6H_4{-}CHO]_4$ (**3**) and its hydrazido and amino derivatives $Sn[C_6H_4{-}CH{=}N{-}NH{-}C_6H_3\text{-}2,4\text{-}(NO_2)_2]_4$ (**5**) and $Sn\{C_6H_4{-}CH[N(C_2H_4)_2O]_2\}_4$ (**8**). Oxidation of (**3**) produced $Sn[C_6H_4{-}COOH]_4$ (**4**) while reduction of (**3**) gave $Sn[C_6H_4{-}CH_2{-}OH]_4$ (**6**). From the acid **4**, an amino acid $Sn[C_6H_4{-}CO{-}NH{-}CH_2{-}CO{-}OCH_3]_4$ (**7**) could be obtained by reaction with the methyl ester of glycine. All compounds were isolated in pure form with yields of 40–64% and were characterised by spectroscopic means (heteronuclear NMR) or by X-ray structure determination (**3**).

Keywords: Organostannanes; Functionalisation; Branched species; Peptidic coupling with organotin compounds

1. Introduction

Organostannanes have attracted considerable attention in the last 50 years. Basic studies on their physical [1], spectroscopic (particularly mass spectrometry [2], NMR [3] and IR [4] spectroscopy) and catalytic properties [5] have been performed. Organic tin(IV) compounds also show a wide range of applications [6] as PVC-stabilizers, as oxidising agents for rubber, as catalysts for polymers and agricultural fungicides. The anti-tumoral effect of tin(IV) compounds is furthermore a very interesting application in medicine [7,8]. A necessary prerequisite for the use in medical application is the air- and water-stability of tin(IV) compounds [9]. Tetraorganotin derivatives of the general formula $Sn[C_6H_4{-}R]_4$ ($R =$ *para*-substituent) [10] are stable under such conditions and have therefore found our interest. Representatives of such tetraorganotin derivatives carrying different organic functionalities in *para*-position like $Sn[C_6H_4{-}CH(OCH_2)_2]_4$ (**2**) and $Sn[C_6H_4{-}CHO]_4$ (**3**) have already been described by Drefahl and Lorentz [11] and Hon et al. [12]. These compounds were so far only characterised by elemental analysis. In this paper, we report about modified syntheses of these compounds and their complete characterisation using modern spectroscopic methods, as multinuclear NMR, IR, mass spectrometry and X-ray diffraction. Furthermore, we report about the transformation or derivatisation of $Sn[C_6H_4{-}CHO]_4$ (**3**) into hydrazones, diamines or the corresponding alcohol (**6**) and acid (**4**). Finally, we describe the use of **4** to bind to amino acids, in view of a possible labelling of amino acids by use of ^{119}Sn NMR spectroscopy.

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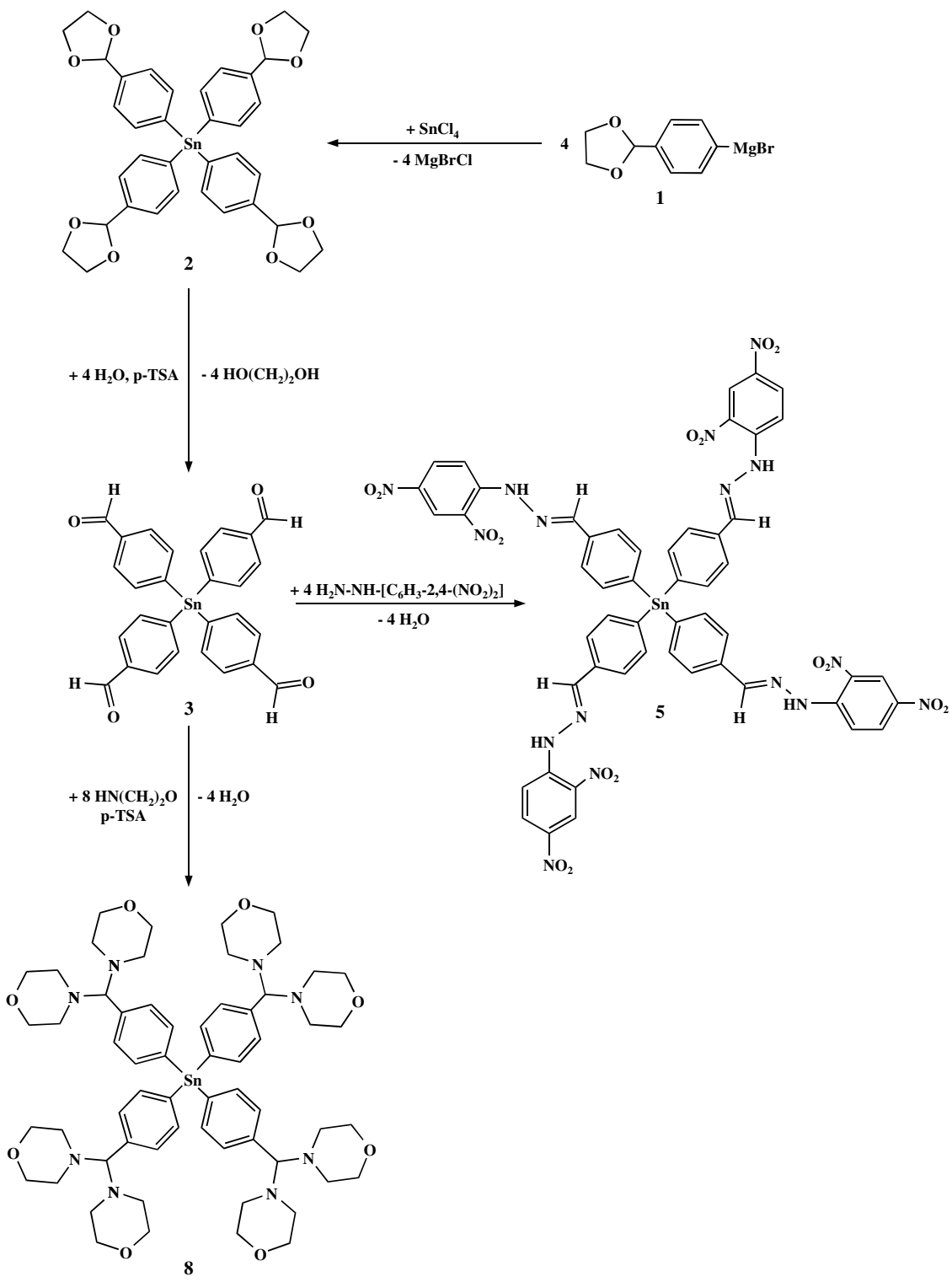
2. Results and discussion

The first step of our reaction sequences was the synthesis of $Sn[C_6H_4–CH(OCH_2)_2]_4$ (**2**) by the interaction of tin tetrachloride with the Grignard reagent of *p*-bromobenzaldehyde-ethyleneacetal [11,12] (Scheme 1). The crude product obtained after filtration from the inorganic salt and after evaporation of



Scheme 1.

the solvent was redissolved in CH_2Cl_2 and precipitated again by addition of ethanol. Repetition of this process for three times gave a pure, colorless powder of high purity.

Removing the protecting acetal group in **2** was achieved by hydrolysis in the polar solvent THF using *p*-TSA as catalyst [13]. After extraction of **3** with CH_2Cl_2 and a subsequent work up the corresponding stannane $Sn[C_6H_4–CH{=}O]_4$ (**3**) [11], containing four aldehydic functions, was obtained as a yellow solid. In comparison to the original literature [11], these two modified procedures lead to higher yields (60%) and avoid the time-consuming purification of **2** and **3** by chromatography over aluminium oxide and subsequent repeated recrystallisation. The reaction from **2** to **3** can easily be followed by ^1H and ^{13}C NMR. The formation of the aldehyde groups is accompanied by a change of the hybridisation on the corresponding carbon atom from sp^3 to sp^2 that has a dramatic effect in the two spectra. Whereas the hydrogen resonances of the acetal moiety in the starting compound **2** appear at 4.10 ppm, the hydrogen at the new aldehydic function is shifted to 10.09 ppm. Parallel changes can be observed in ^{13}C NMR for the carbon atom attached in the *para*-position of the ring by a shift of the signal at 65.3 to 192.3 ppm.

Colourless crystals of $Sn[C_6H_4–CHO]_4$ (**3**), suitable for the X-ray diffraction study could be obtained by recrystallisation from dichloromethane. The intensity measurements were performed on a Stoe Image Plate (IPDS) at 293 K. The structure was solved by direct methods and refined by the full-matrix least-squares method on *F*. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were kept fixed in calculated positions. Programs used were SHELX-93 and SHELX-97 [14]. Unfortunately, the refinement of the X-ray structure of compound **3** could not be performed satisfactorily, because only tiny crystals of **3** were available. Here, we only give a graphic representation of **3** with some mean bond lengths and angles (Fig. 1) [15].

In order to test the accessibility of the CO groups (absorption at 1701 cm^{-1} of the CO valence stretching vibration) in **3** for further bonding, the molecule was reacted with four equivalents of 2,4-dinitrophenylhydrazine to give the hydrazone [13,16,17] $Sn[C_6H_4–CH{=}N–NH–C_6H_3\text{-}2,4\text{-}(NO_2)_2]_4$ (**5**) as an orange powder whereas in the reaction of **3** with the primary amine morpholine each C=O function reacted with two morpholine molecules [13,17] to form $Sn\{C_6H_4–CH[N(C_2H_4)_2O]_2\}_4$ (**8**) which separated as a pale brown powder. In both reactions, the released water was removed continuously with a water separator (Scheme 1).

Following classical routes the oxidation [13,17], respectively, reduction [13,17] of the aldehydic function in

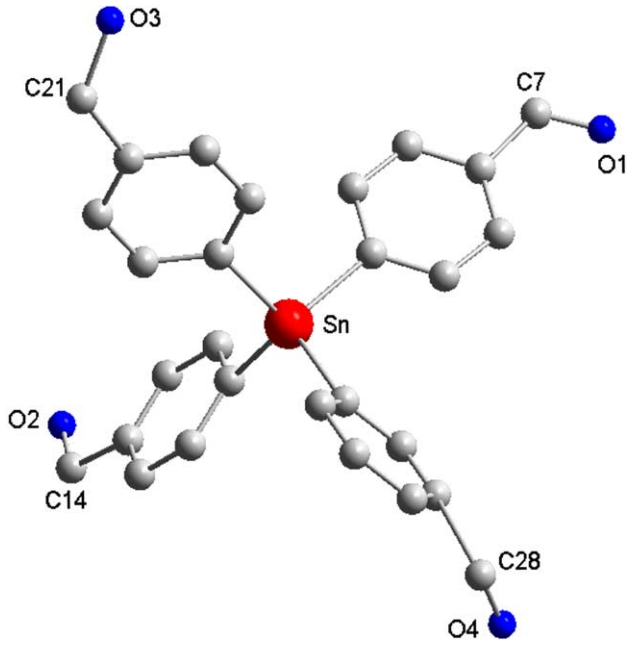
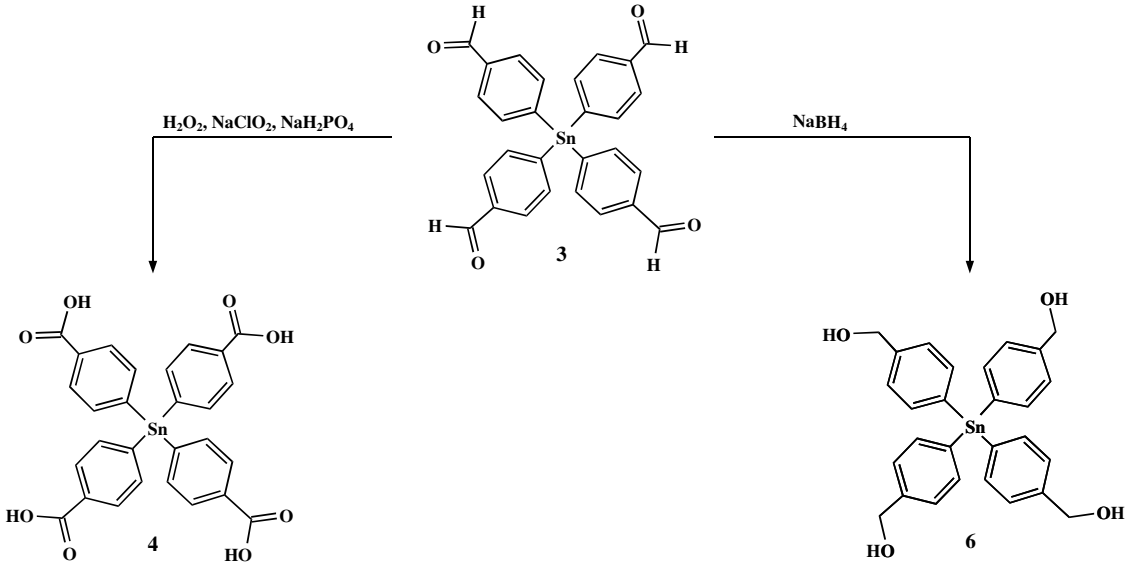


Fig. 1. Molecular structure of $Sn[C_6H_4–CHO]_4$ (**3**) (carbon atoms are light). Mean bond lengths (Å) and angles (°): Sn–C: 2.149 (9), C–O: 1.34(2), C–Sn–C: 109.4(5), C–C–O: 116.0(9).

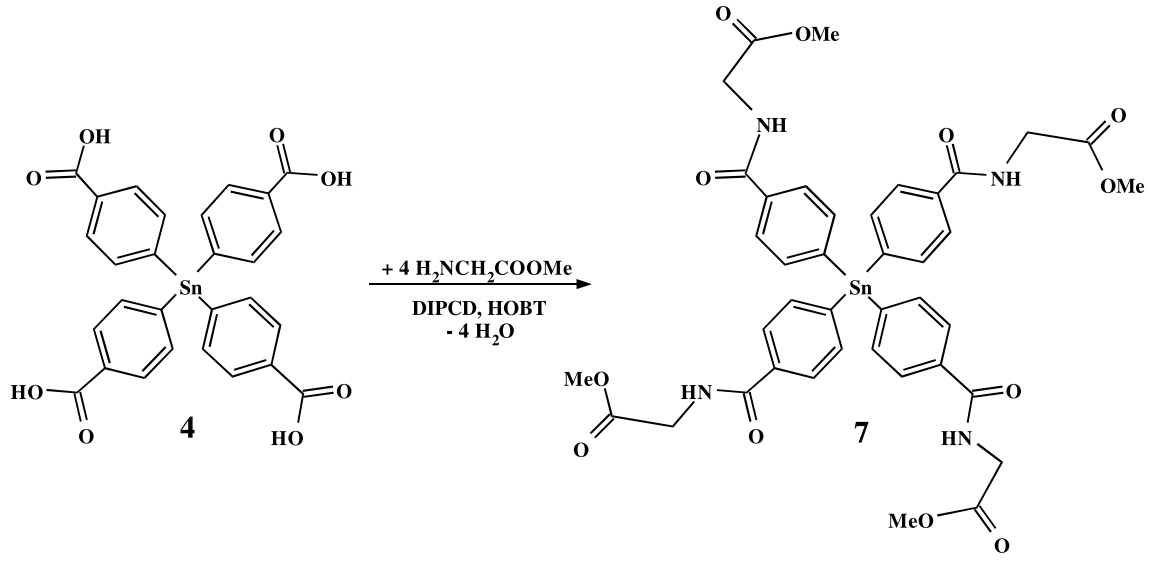
$Sn[C_6H_4–CHO]_4$ (**3**) gave the water soluble $Sn[C_6H_4–COOH]_4$ (**4**) and $Sn[C_6H_4–CH_2–OH]_4$ (**6**) in acceptable yields (see Scheme 2) without scission of the tin–carbon bond. The products **4** and **6** were obtained as pure compounds as may be deduced by inspection of the spectroscopic and analytical data.

As a test reaction for binding acid amides the oxidation product $Sn[C_6H_4–COOH]_4$ (**4**) was reacted with the methylester of glycine [18] to yield $Sn[C_6H_4–CO–NH–CH_2–CO–OCH_3]_4$ (**7**). The reaction was carried out in THF as a solvent using 1-hydroxybenzotriazole (HOBT) and diisopropyldiimide (DICPD) as coupling reagents (Scheme 3). These auxiliary substances are frequently used to activate the carboxylic groups of the reactant without deprotection of glycine [13,17]. The target compound **7** could be isolated in an overall yield of 50% and could be fully characterised by ^1H, ^{13}C, ^{119}Sn NMR, IR and mass spectroscopic means.

The ^{119}Sn NMR spectra have been obtained of all compounds **2**–**8**. The narrow chemical shift differences (**2**: $\delta = -126.5$ ppm; **3**: $\delta = -133.2$ ppm; **4**: $\delta = -142.0$ ppm, **5**: $\delta = -125.0$ ppm; **6**: $\delta = -128.3$ ppm; **7**: $\delta = -131.4$, **8**: $\delta = -141.9$ ppm) reflect the similar environment of the tin atoms in the molecules. Only minor effects can be noticed from the substituents in the *para*-positions of the phenyl groups. As expected the ^{119}Sn NMR spectroscopy may therefore be used in the labelling of amino acids when a binding to the acid has been performed.



Scheme 2.



Scheme 3.

3. Conclusion

The stepwise syntheses of several new organotin compounds having four identical reactive organic functionalities were reported in this work. The stability of the Sn–C bonds towards oxygen and water has proved to be sufficient to synthesize the presented organotin derivatives **2**–**8**. Compounds **4** and **6** are water soluble and may be used in biological environments. We were successful to bind the glycine methylester to **4**, showing the potential of these molecules as docking agents: we also could demonstrate the ^{119}Sn NMR spectroscopy as a labelling tool in the detection of amino acids.

4. Experimental details

4.1. General

IR spectroscopy was performed on a Bio-Rad Win-IR FTIR Spectrometer. ^{1}H, ^{13}C and ^{119}Sn NMR spectra were obtained on a Bruker AC 200 spectrometer (^{1}H at 200.1 MHz, ^{13}C at 50.3 MHz and ^{119}Sn at 74.63 MHz). CP/MAS-spectra were recorded on a Bruker MSL 200S. Mass spectroscopy was performed on a TSQ Quantum from Thermo Finnigan. C, H, N elemental analyses were obtained from a LECO (CHN-900) instrument.

$SnCl_4$ was distilled and stored under dry nitrogen before use. Diisopropyldiimide (DIPCD) and

1-hydroxybenzotriazole (HOTB) were purchased and used without further purification.

4.2. $Sn[C_6H_4–CH(OCH_2)_2]_4$ (2)

A solution of 17.00 g (74.7 mmol) of *p*-bromobenzaldehyde-ethyleneacetal in 80 mL THF was slowly added over a period of 30 min to 1.93 g (79.4 mmol) of Mg turnings. In order to start the reaction a crystal of I_2 was added. The dropwise addition was continued in that way that the solution continued to reflux. To complete the reaction, the mixture was still heated to 70 °C for 20 min. After cooling down to room temperature, insoluble parts like unreacted magnesium, were filtered off. In the next step, a solution of 1.15 g (4.40 mmol) of freshly distilled tin tetrachloride in 8 mL benzene was added dropwise. The reaction mixture was refluxed for 8 h, whereas the desired product **2** precipitated. By treating the reaction mixture with a saturated solution of NH_4Cl at 0 °C the precipitate dissolved and two layers were obtained. The organic layer was separated and washed with water. The water layer was treated with $CHCl_3$. The combined organic layers were washed again with water resulting in a clear yellow solution, which was dried over anhydrous $CaCl_2$. Removal of the solvent provided a brown oil, which dissolved in less CH_2Cl_2. After addition of 200 mL of dry ethanol a suspension was formed. Under reduced pressure the CH_2Cl_2 was removed (**2** is soluble in CH_2Cl_2!). Compound **2** was filtered off and dried in vacuum (10^{-2} Torr). Impurities were in the filtrate. To raise the purity of **2** the solid was washed again with dry ethanol, filtered and dried under reduced pressure. The 4.2 g (60%) of **2** was obtained as a white powder. M.p. 268°. ^{1}H NMR ($CDCl_3$): δ (ppm) 4.10 (m, 16H, O–C*H*$_2$), 5.79 (s, 4H, Ar–C*H*<), 7.52 (m, 16H, Ar–*H*). ^{13}C NMR ($CDCl_3$): δ (ppm) 65.3 (s, O–*C*H$_2$), 103.6 (s, Ar–*C*H<), 126.5 (s, *C*H$_{Ar}$), 127.3 (s, *C*$_{q\text{-}Ar}$), 137.2 (s, *C*H$_{Ar}$), 138.9 (s, *C*$_{q\text{-}Ar}$). ^{119}Sn NMR ($CDCl_3$) δ (ppm) −126.5 (s). IR (KBr disk): 812 cm^{-1} (Ar ring), 1365 cm^{-1} (C–O–C), 1472 cm^{-1} (CH_2), 2965 cm^{-1} (CH alkane). Anal. Calc. for $C_{36}H_{36}O_8Sn$: C, 60.44; H, 5.07. Found: C, 60.44; H, 5.17%. CI-MS ($CHCl_3$): *m*/*z* Calc. for $C_{36}H_{36}O_8{}^{120}Sn$: 716.14 $(M)^+$. Found: 717.21 $(M+H)^+$ (correct isotopic set of signals and intensities).

4.3. $Sn[C_6H_4–CHO]_4$ (3)

To a solution of 2.0 g (2.80 mmol) of compound **2** in 90 mL THF were added 30 mL H_2O and 0.2 g (0.90 mmol) *p*-toluenesulfonic acid. The reaction mixture was refluxed for 8 h under nitrogen. Compound **3** was extracted with dichloromethane (5×20 mL) and washed two times with 20 mL of water. The organic phase was separated and dried over anhydrous $CaCl_2$. Removal of the solvent under reduced pressure (10^{-2} Torr) provided compound **3** as a yellow powder (1.0 g, 65%). M.p. 180°. ^{1}H NMR ($CDCl_3$): δ (ppm) 7.85 (m, 16H, Ar–H), 10.09 (s, 4H, CHO). ^{13}C NMR ($CDCl_3$): δ (ppm) 129.6 (s, CH_{Ar}), 137.1 (s, $C_{q\text{-}Ar}$), 137.3 (s, CH_{Ar}), 144.5 (s, $C_{q\text{-}Ar}$), 192.3 (s, CHO). ^{119}Sn NMR ($CDCl_3$) δ (ppm) −133.2 (s). IR (KBr disk): 802 cm^{-1} (Ar), 1701 cm^{-1} (CHO), 2926 cm^{-1} (alk). Anal. Calc. for $C_{28}H_{20}O_4Sn$: C, 62.37; H, 3.74. Found: C, 62.44; H, 3.83%. CI-MS ($CHCl_3$): *m*/*z* Calc. for $C_{28}H_{20}O_4{}^{120}Sn$: 540.03 $(M)^+$. Found: 541.11 $(M+H)^+$ (correct isotopic set of signals and intensities).

4.4. $Sn[C_6H_4–COOH]_4$ (4)

To a solution of 0.400 g (0.74 mmol) of **3** in 10 mL THF was added a solution of 0.023 g (0.18 mmol) NaH_2PO_4 in 300 μL of water and 300 μL of an aqueous solution of H_2O_2 (35% concentration). After stirring for 5 min, 0.470 g (1.3 mmol) $NaClO_2$ in 5 mL H_2O were added over a period of 30 min. The mixture was stirred overnight at room temperature. After evaporation of THF, the residue was diluted with 15 mL water and extracted with CH_2Cl_2 (3×25 mL). The organic layer was stored over anhydrous $MgSO_4$, concentrated and dried in vacuo resulting a white solid **4** (0.295 g, 65%). M.p. dec. >200°. ^{1}H NMR (d^6-DMSO): δ (ppm) 7.80 (m, 4H, Ar–H), 13.01 (s, 1H, COOH). ^{13}C NMR (d^6-DMSO): δ (ppm) 130.5 (s, CH_{Ar}), 133.4 (s, $C_{q\text{-}Ar}$), 138.4 (s, CH_{Ar}), 144.6 (s, $C_{q\text{-}Ar}$), 168.6 (s, COOH). ^{119}Sn NMR (d^6-DMSO) δ (ppm) −142.0 (s). IR (KBr disk): 832 cm^{-1} (Ar ring), 1690 cm^{-1} (C=O), 3025 cm^{-1} (OH). Anal. Calc. for $C_{28}H_{20}O_8Sn$: C, 55.76; H, 3.34. Found: C, 55.13; H, 3.88%. CI-MS (DMSO): (*m*/*z*) Calc. for $C_{28}H_{20}O_8{}^{120}Sn$: 604.01. Found: 639.01 $(M+H_2S+H)^+$ (correct isotopic set of signals and intensities).

4.5. $Sn[C_6H_4–CH{=}N–NH–C_6H_3\text{-}2,4\text{-}(NO_2)_2]_4 \cdot 2C_7H_8$ (5)

A solution of 0.5 g (0.93 mmol) **3**, 0.74 g 2,4-dinitrophenylhydrazine and 40 mL dry toluene was refluxed for 20 h. In order to shift the equilibrium to the side of the products a water separator was used. The formed precipitate was filtered off and washed with 20 mL dry toluene. After drying under reduced pressure (10^{-3} Torr) compound **8** was obtained as an orange powder. M.p. 245° dec. ^{1}H NMR (DMSO): δ (ppm) 2.29 (s, CH_3 (toluene)), 7.20 (m, ArH (toluene)), 7.50–8.00 (m, Ar–H), 8.20 (m, Ar–H), 8.71 (s, CH=N), 8.83 (m, Ar–H). ^{13}C NMR (DMSO): δ (ppm) 21.2 (s, CH_3 (toluene)), 116.9 (s, C_{Ar} (hydrazine ligand)), 123.2 (s, C_{Ar} (hydrazine ligand)), 125.5 (s, C_{Ar} (toluene)), 127.6 (s, C_{Ar} (hydrazine ligand)), 128.4 (s, C_{Ar} (toluene)), 129.0 (s, C_{Ar} (toluene)), 129.8 s, (C_{Ar} (hydrazine ligand)), 130.0 (s, C_{Ar}), 135.0 (s, C_{Ar} (hydrazine ligand)), 137.2 (s, C_{Ar} (toluene)), 137.4 (s, C_{Ar}), 137.6 (s, C_{Ar}), 140.8 (s, CH=N), 144.6 (s, C_{Ar}), 149.3 (s, C_{Ar} (hydrazine ligand)). ^{119}Sn (CP-MAS): δ (ppm) −125.0. IR (KBr

disk): 833 cm^{-1} (Ar ring), 1619 cm^{-1} (C=N), 3105 cm^{-1} (C_{Ar}=C_{Ar}), 3288 cm^{-1} (NH). Anal. Calc. for $C_{52}H_{36}N_{16}O_{16}Sn \cdot 2C_7H_8$: C, 54.90; H, 3.63; N, 15.22. Found: C, 55.18; H, 3.58; N, 14.95%.

4.6. $Sn[C_6H_4–CH_2–OH]_4$ (6)

To a solution of 0.100 g (0.18 mmol) **3** was added 10 mL THF. After 5 min stirring, 0.028 g (0.74 mmol) $NaBH_4$ was added over a period of 10 min at 0 °C. After one hour of further stirring, 1 mL of a solution of 0.1 N NaOH was added at room temperature. The reaction mixture was extracted with 10 mL CH_2Cl_2 and the combined organic layers were dried over anhydrous Na_2SO_4. Removal of the solvent provided the compound **6** (0.395 g, 40%) as a white powder. M.p. dec. >200°. ^1H NMR (d^6-DMSO): δ (ppm) 4.56 (m, 8H, CH_2), 7.52 (m, 16H, Ar–H). ^{13}C NMR (d^6-DMSO): δ (ppm) 64.5 (s, CH_2), 128.7 (s, CH_{Ar}), 137.1 (s, $C_{q\text{-}Ar}$), 137.8 (s, CH_{Ar}), 145.4 (s, $C_{q\text{-}Ar}$). ^{119}Sn NMR (d^6-DMSO) δ (ppm) −128.3 (s). IR (KBr disk): 802 cm^{-1} (Ar ring), 1464 cm^{-1} (CH_2), 2841 cm^{-1} (CH_2), 3272 cm^{-1} (OH).

4.7. $Sn[C_6H_4–CONH–CH_2–COOCH_3]_4$ (7)

In 10 mL THF, 0.500 g (0.829 mmol) of **4** was dissolved and 0.416 g (3.32 mmol) of $H_2N–CH_2–OOCH_3$, 505 μL (3.75 mmol) of Et_3N and 0.067 g (0.497 mmol) HOBT were added to this mixture at 0 °C. The solution was maintained at pH 5. Then 5.568 μL (3.75 mmol) DIPCD was added. This mixture was stirred at 0 °C for 30 min and warmed up to room temperature overnight. The crude material was purified by filtration and by vacuum drying. Compound **7** (0.350 g, 50%) was obtained as white powder. ^1H NMR ($CDCl_3$): δ (ppm) 3.52 (s, CH_2), 3.70 (s, O–CH_3), 7.38–7.74 (m, Ar–H). ^{13}C NMR ($CDCl_3$): δ (ppm) 41.5 (s, CH_2), 52.0 (s, O–CH_3), 127.0 (s, CH_{Ar}), 134.4 (s, $C_{q\text{-}Ar}$), 136.7 (s, CH_{Ar}), 140.8 (s, $C_{q\text{-}Ar}$), 167.5 (s, C=O), 170.3 (s, C=O). ^{119}Sn NMR ($CDCl_3$): δ (ppm) −131.4 (s). IR (KBr disk): 802 cm^{-1} (Ar ring), 1259 cm^{-1} (C–O ester), 1380 cm^{-1} (CH_2, CH_3), 1533, 1647 and 3349 cm^{-1} (CO–NH), 1755 cm^{-1} (C=O ester), 2876 cm^{-1} (OCH_3), 2971 cm^{-1} (CH_2 and CH_3). CI-MS ($CHCl_3$): m/z Calc. for $C_{40}H_{40}O_{12}N_4{}^{120}Sn + H$: 889.17. Found: 889.40 $(M + H)^+$ (correct isotopic set of signals and intensities).

4.8. $Sn\{C_6H_4–H[N(CH_2)_2O]_2\}_4 \cdot 1.5C_7H_8$ (8)

A solution of 0.450 g (0.84 mmol) **3**, 1.160 g (13.35 mmol) morpholine and 0.100 g *p*TSA in 25 mL toluene was refluxed for 12 h. The released water was removed with a water separator. The formed precipitate was filtered off, washed with 20 mL dry toluene and dried in vacuum (10^{-3} Torr) at room temperature. Compound **5** (0.62 g, 64%) was obtained as a pale brown powder. M.p. 180° dec. ^1H NMR ($CDCl_3$, without toluene): δ (ppm) 2.49 (m, CH_2), 3.00 (s, Ar–CH–N), 3.71 (m, CH_2), 7.20–7.70 (m, Ar–H). ^{13}C NMR ($CDCl_3$, without toluene): δ (ppm) 49.5 (s, CH_2), 67.5 (s, CH_2), 88.9 (s, CH), 125.7 (s, CH_{Ar}), 129.2 (s, CH_{Ar}), 136.5 (s, CH_{Ar}), 137.7 (s, CH_{Ar}). ^{119}Sn ($CDCl_3$): δ (ppm) −141.9. IR (KBr disk): 876 cm^{-1} (Ar ring), 1116 cm^{-1} (C–O–C), 1453 cm^{-1} (CH_2), 2811–2957 cm^{-1} (CH_{Ar}; CH_2), 3443 cm^{-1} (C–N). Anal. Calc. for $C_{60}H_{84}N_8O_4Sn \cdot 1.5C_7H_8$: C, 65.02; H, 7.43; N, 8.60. Found: C, 64.91; H, 7.47; N 8.57%.

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