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Disproportionation reactions within the series of coordinated monoorganostannanes

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ABSTRACT

Interaction of monoorganotin trichlorides ($RSnCl_3$, R = Ph, Vin, All, Bn and *c*-Pr) with *O*-TMS-amides of 2-hydroxycarboxylic acids afforded a number of mononuclear and binuclear organotin complexes (**2a**–**j**). These organotin complexes disproportionate into diorganostannanes and inorganic coordination compounds containing two *O*,*O*-chelated ligands (**3a**–**c**). All the complexes were characterized by multinuclear NMR spectroscopy in solution and X-ray diffraction in crystalline state (**2a**, **2b**, **2j**, **3b**, **3c**). It was found that disproportionation reaction proceeded only for very well dissolved substances in concentrated solutions upon heating. The tendency for disproportionation depends on the nature of a substituent and decreases as follow: Vin ≈ Allyl > Bn > Ph ≈ *c*-Pr >> Alk. It is believed that the key step of the mechanism of disproportion reaction is a ligand exchange, which is possible only in the case of binuclear complexes acting as intermediate compounds.

1. Introduction

Comproportionation and disproportionation reactions are highly important for organometallic chemistry of non-transition main group metals. For example, the Kocheschkov reaction, which has been found in 1929 [1], so far is the best way to obtain a series of alkyl(aryl)halogenstannanes. It is well known that the ability of organotin compounds to enter into this reaction depends substantially on the nature of an organic group at the tin atom, and those having the substituents with sp^2 carbon atoms disproportionate much easier. Thus, the long-term heating in $POCl_3$ is needed to convert the mixture of Et_4Sn and $SnCl_4$ with 1:3 M ratio to $EtSnCl_3$ [2], Ph_4Sn reacts during 3–4 h at 150–180°C [1], and Vin_4Sn converts fully during 2 h at 70°C [3,4].

It seems that the disproportionation reaction does not play an important role in the synthetic organometallic chemistry and is mainly of the fundamental interest. To our knowledge, only few cases of disproportionation reactions of coordinated compounds of monoaryl tin (IV) have been reported [5–7], so the systematic studies of this type of reactions have never been performed.

In this paper, we show that the stability of monophenyl, -vinyl, -allyl, -benzyl and -cyclopropyl tin compounds depends on the nature of an organic substituent at the tin atom, and the disproportionation reaction leads to the formation of diorganostannanes and inorganic *O*,*O*-chelated complexes without a Sn–C bond.

2. Results and discussion

2.1. Synthesis

We have obtained the series of complexes of monophenyl, -vinyl, -allyl, -benzyl and -cyclopropyl tin compounds (**2a**–**i**) (Scheme 1) using the earlier developed approach, which is based on the interaction of alkyltin trichlorides with *O*-TMS-derivatives of amides of 2-hydroxycarboxylic acids [8].

The reaction proceeds in mild conditions – at room temperature during 2–4 h; the yields are 28–84%. The obtained compounds have been studied by multinuclear NMR spectroscopy (^{1}H, ^{13}C, ^{119}Sn) and X-ray diffraction (Figs. 1–5 and Table 1). It was shown that in solid state the complexes **2a**,**b** (Figs. 1 and 2) and the similar complexes described in Ref. [8] adopt dimeric structure. Four-membered metallacycles in **2a** and **2b** are planar, the Sn–O–Sn angles are 107.40(9) and 108.08(8)°, respectively. The ethyltin compound **2j** (Fig. 3) has been obtained in a similar way from the ligand **1e**. According to the XRD data, this compound is monomeric

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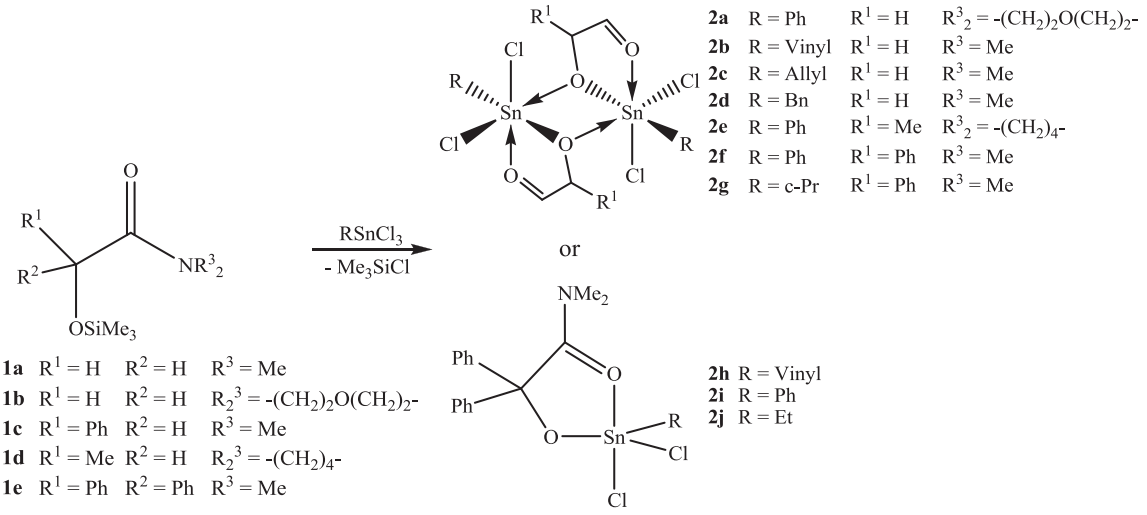


Scheme 1.

in crystal, and the tin atom has a distorted trigonal-bipyramidal surrounding. The deviation of the Sn1 atom from the plane of equatorial Cl2, O2 and C17 ones is 0.19050(7) Å towards the axial Cl1 atom. Thus, the structure of the ligand (first of all, its steric volume) has the critical effect on the structure of the tin complex (both monomeric and dimeric).

The compounds **2a**–**j** are white crystalline substances, non-soluble in nonpolar solvents (hexane, toluene) and moderately soluble in polar aprotic solvents (DMSO, acetonitrile). The worst solubility was observed for the compounds **2a**–e (derivatives of glycolic acid).

2.2. Disproportionation reaction

White crystalline compound **3b**, which is very poorly soluble even in hot DMSO, has been isolated by the attempt to recrystallize the compound **2f** from the minimal amount of boiling acetonitrile. The cyclopropyl and vinyl derivatives **2g** and **2h** behave in a similar way (Scheme 2).

According to XRD data, mutual disposition of Cl and O atoms in the complex **3b** can be described as *cis*. The similar configuration was observed in the case of previously reported complexes of Ge(IV) [9]. Unlike in the complex **3b**, the Cl and O atoms in **3c** adopt all-*trans* orientation. The configuration of *O*,*O*-chelated ligands herein is apparently governed by the steric effect of additional (as compared to **3b**) Ph substituents at five-member chelate cycles.

It has to be noted that the disproportionation reaction by the dilution does not proceed even upon long-time boiling: so the derivatives of glycolic acid poorly dissolved in acetonitrile, do not enter into this reaction.

The formation of R_2SnCl_2 has been confirmed by ^{119}Sn NMR investigation of the reaction's product. Thus, after the heating of **2e**

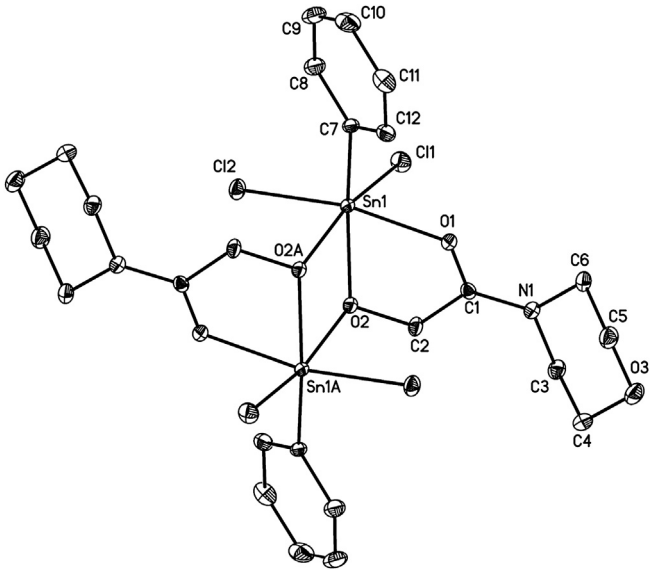


Fig. 1. Molecular structure of **2a** presented in thermal ellipsoids (probability 50%). Selected bonds and angles (Å and °): Sn1–O2 2.064(2), Sn1–C7 2.114(3), Sn1–O1 2.197(2), Sn1–O2A 2.286(2), Sn1–Cl1 2.3996(9), Sn1–Cl2 2.4143(9), O2–Sn1–C7 155.74(11), O2A–Sn1–Cl1 167.36(6), Sn1–O2–Sn1A 107.40(9). Atoms O2A and Sn1A obtained by symmetry operation $-x + 1/2, -y + 1/2, z$.

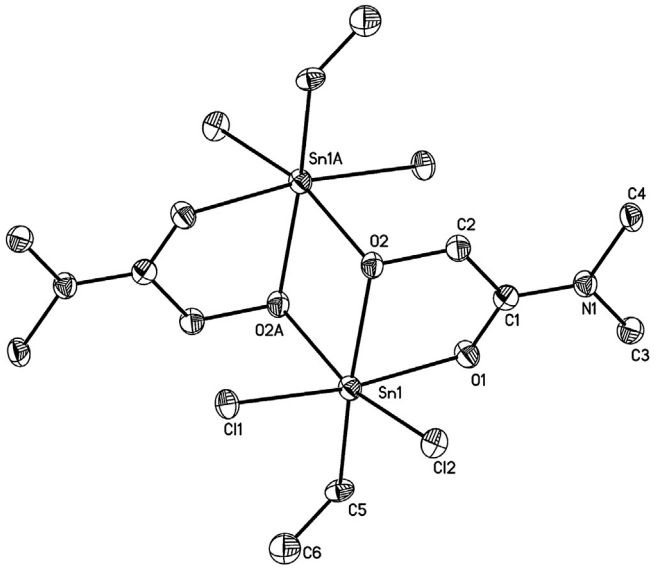


Fig. 2. Molecular structure of **2b** presented in thermal ellipsoids (probability 50%). Selected bonds and angles (Å and °): Sn1–O2 2.0967(18), Sn1–C5 2.129(3), Sn1–O1 2.1722(18), Sn1–O2A 2.2399(18), Sn1–Cl1 2.4279(7), Sn1–Cl2 2.4300(7), O2–Sn1A 2.2399(18), O1–Sn1–Cl1 168.00(5), O2A–Sn1–Cl2 164.00(5), Sn1–O2–Sn1A 108.08(8). Atoms O2A and Sn1A obtained by symmetry operation $-x + 1/2, -y + 1/2, z$.

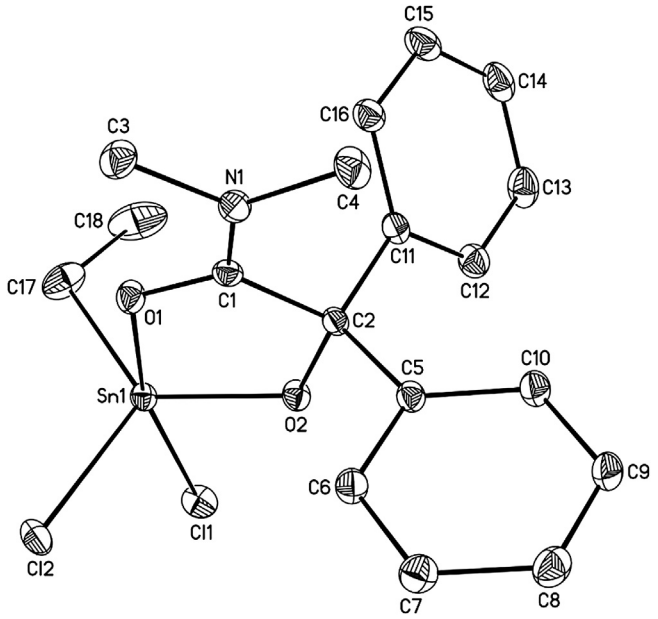


Fig. 3. Molecular structure of **2j** presented in thermal ellipsoids (probability 50%). Selected bonds and angles (Å and °): Sn1–O2 1.9867(7), Sn1–C17 2.1300(13), Sn1–O1 2.2110(8), Sn1–Cl2 2.3536(3), Sn1–Cl1 2.4093(3), O1–Sn1–Cl1 164.69(2), O2–Sn1–C17 129.12(5).

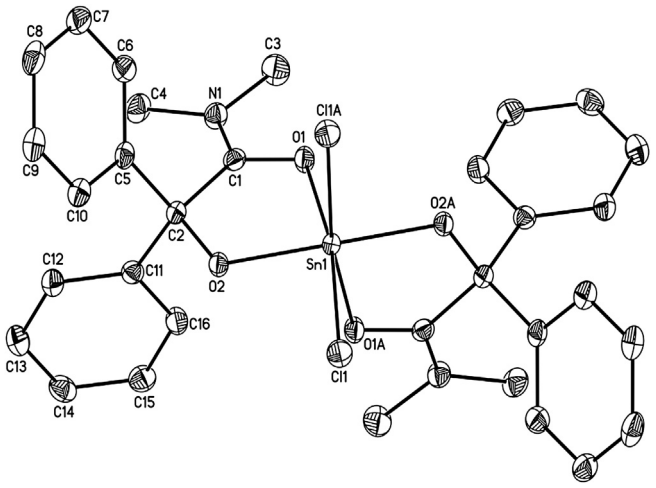


Fig. 5. Molecular structure of **3c** presented in thermal ellipsoids (probability 50%). Selected bonds and angles (Å and °): Sn1–O2 1.9996(11), Sn1–O2A 1.9996(11), Sn1–O1 2.1483(12), Sn1–O1A 2.1483(12), Sn1–Cl1A 2.3734(4), Sn1–Cl1 2.3734(4), O2–Sn1–O2A 161.27(7), O1A–Sn1–Cl1A 168.30(3), O1–Sn1–Cl1 168.30(3). Atoms O1A, O2A and Cl1A obtained by symmetry operation $-x+1, -y+1, -z$.

in CD_3CN at 70°C during 30 min the signals, which belong to the disproportionation product (**3a**) and Ph_2SnCl_2, do appear in the ^{119}Sn NMR spectrum.

Interaction of vinyltrichlorostannane, allyltrichlorostannane and benzyltrichlorostannane with *O*-TMS-amide **1**c leads at once to the disproportionation product **3b**. We did not succeed in isolating the intermediate complexes, similar to **2a**–**j**. In the case of the interaction of O-TMS-pyrrolydide of lactic acid (**1d**) and vinyltrichlorostannane it took about 5 h boiling in acetonitrile for the disproportionation reaction to occur (Scheme 3). Note that tin complexes containing alkyl groups (for example **2j**) do not enter into this reaction. Thus, the occurrence of disproportionation reaction depends mainly on the nature of a substituent at the tin

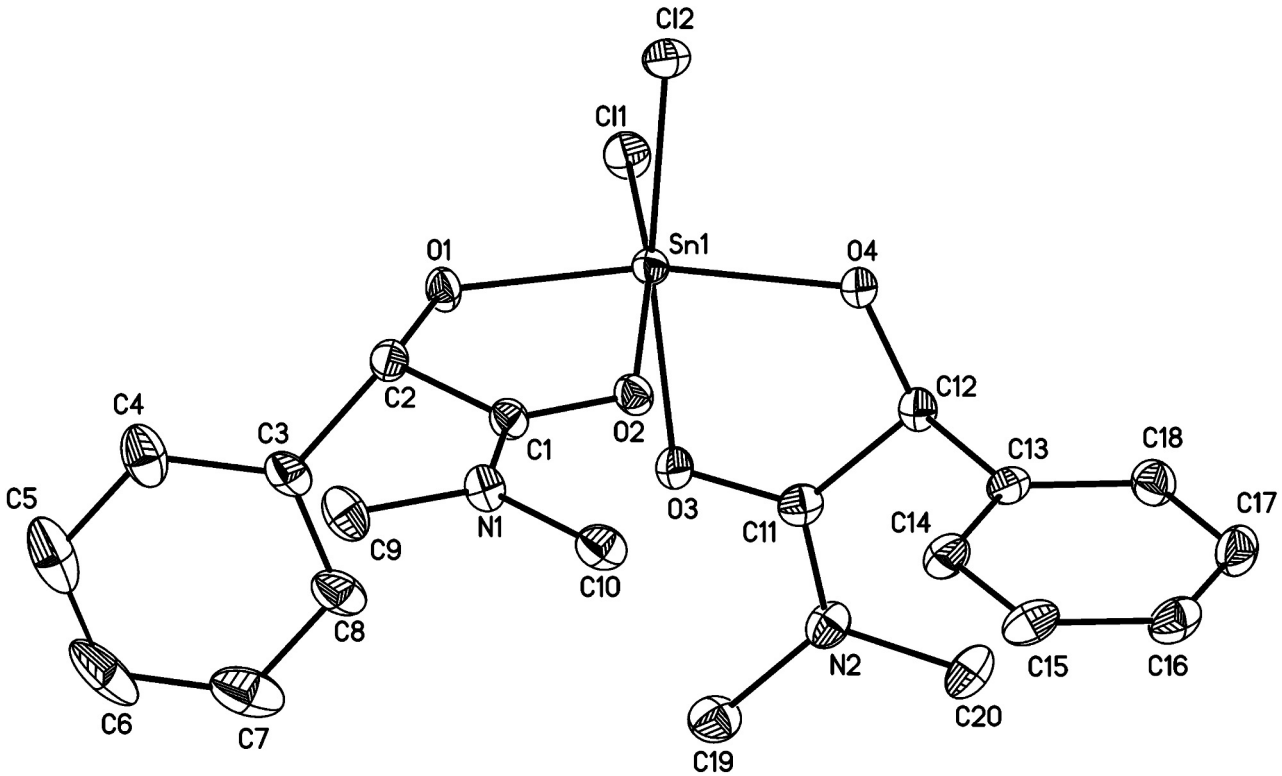


Fig. 4. Molecular structure of **3b** presented in thermal ellipsoids (probability 50%). Selected bonds and angles (Å and °): Sn1–Cl1 2.3934(8), Sn1–Cl1 2.3934(8), Sn1–Cl2 2.3770(8), Sn1–O1 1.988(2), Sn1–O2 2.125(2), Sn1–O3 2.155(2), Sn1–O4 1.997(2), O1–Sn1–O4 167.74(9), O2–Sn1–Cl1 167.00(6), O3–Sn1–Cl2 168.16(6).

Table 1
Experimental details and crystallographic data for **2a**–**b**, **2j**, **3b**–**c**.

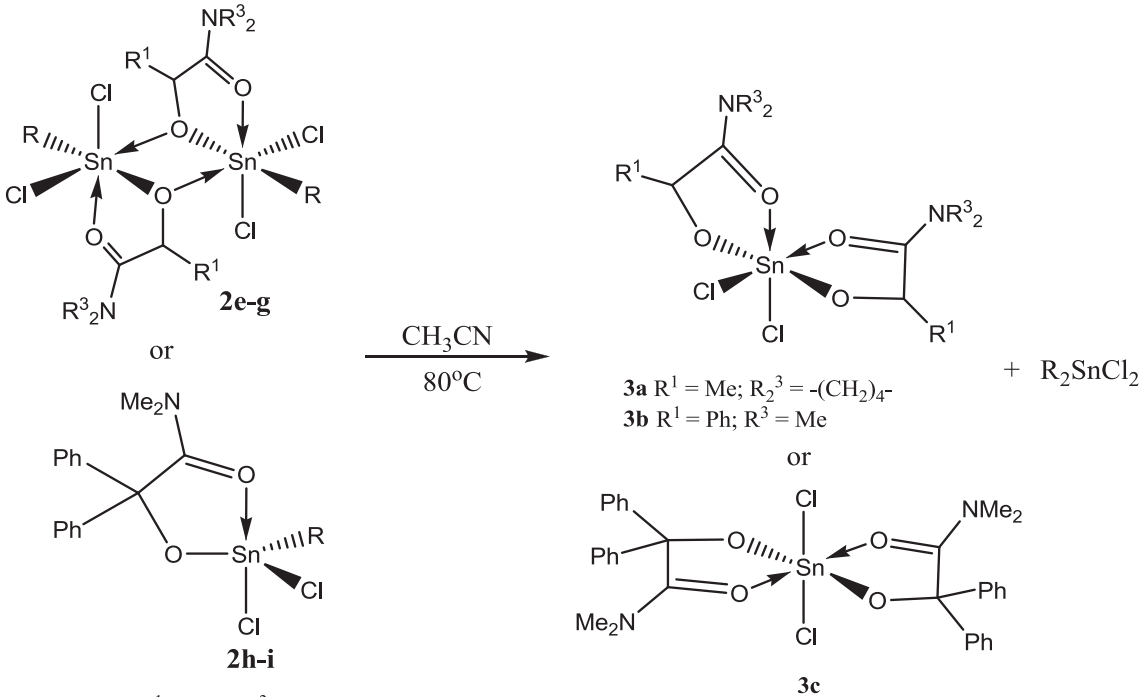
	2a	2b	2j	3b	3c
Molecular formula	$C_{24}H_{30}Cl_4N_2O_6Sn_2$	$C_{12}H_{22}Cl_4N_2O_4Sn_2$	$C_{18}H_{21}Cl_2NO_2Sn$	$C_{22}H_{27}Cl_2N_3O_4Sn$	$C_{36}H_{38}Cl_2N_4O_4Sn$
Formula weight	821.68	637.50	472.95	587.06	780.29
Space group	$P2_1/n$	$P2_1/c$	$P2_1$	$C2/c$	$Pccn$
a, Å	10.5427(15)	14.0612(9)	7.0286(3)	24.3229(17)	14.9737(6)
b, Å	9.9202(14)	14.4428(10)	16.3617(7)	11.3180(8)	15.3841(6)
c, Å	14.573(2)	10.6828(7)	9.0610(4)	18.8069(13)	15.5876(6)
β, °	109.043(3)	103.4560(10)	112.330(1)	108.646(1)	90
V, Å^3	1440.8(4)	2109.9(2)	963.87(7)	4905.5(6)	3590.7(2)
Z	2	4	2	8	4
μ, cm^{-1}	2.15		1.61	1.29	0.90
Crystal size (mm)	0.17 × 0.16 × 0.12	0.26 × 0.21 × 0.19	0.23 × 0.19 × 0.19	0.24 × 0.19 × 0.13	0.19 × 0.13 × 0.12
T_{min}, T_{max}	0.712, 0.783	0.520/0.601	0.708, 0.749	0.726, 0.862	0.847, 0.899
Observed reflections [$I > 2\sigma(I)$]	3459	6467	5858	5190	4134
R_{int}	0.0000	0.0414	0.019	0.079	0.047
θ_{max}, °	30.55	30.59	30.61	29.97	30.52
$R_1[F^2 > 2\sigma(F^2)]$	0.039	0.0253	0.012	0.043	0.026
$wR(F^2)$	0.073	0.0569	0.032	0.078	0.065
GOF	1.03	1.017	1.00	1.04	1.01
Reflections collected	4411	27,745	21,969	29,991	34,086
Independent reflections	4411	5075	5919	7091	5493
Parameters	172	221	220	294	216
ρ_{max}/ρ_{min} (e Å^{-3})	1.07, −0.98	0.89, −0.89	0.25, −0.61	0.67, −1.42	0.45, −0.42
Flack parameter	–		−0.003(7)	–	–

atom and correlates with the ability of this group to leave in the reactions with an electrophile.

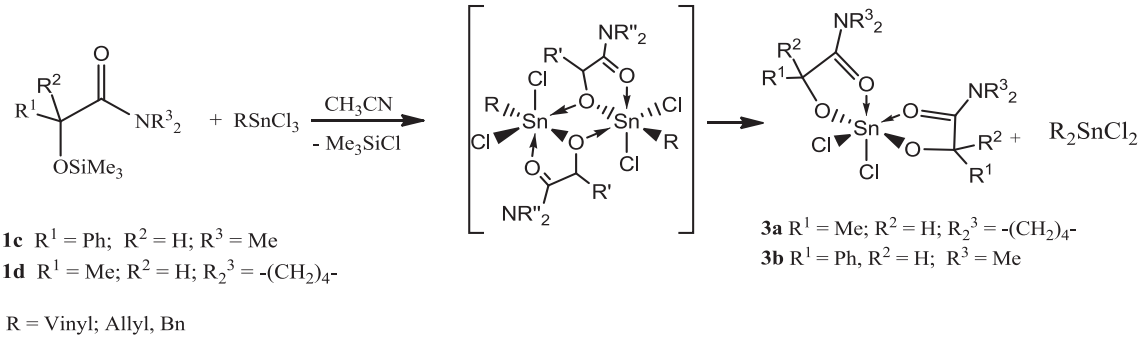
We suggest the following mechanism of the disproportionation reactions (Scheme 4). As it was mentioned earlier, these reactions proceed only for very well dissolved substances, in concentrated solutions and by heating. The key step is the ligand exchange, which can proceed only in the case of association.

3. Conclusions

Thus, new coordination compounds of monoorganotin (**2a**–**j**) were obtained; they were studied both in solutions and in solid state. It has been shown that the coordination compounds of monoorganotin, depending on the substituent at the tin atom, had the tendency for the disproportionation reaction, giving



Scheme 2.



Scheme 3.

diorganostannanes and inorganic coordination compounds as its products. The driving force for this reaction is the stronger coordination in inorganic derivatives of tin, what coincides well with the idea that the Lewis acidity increases with the diminishing of the number of organic substituents. The tendency for disproportionation depends on the nature of a substituent and changes as follows: Vin ≈ Allyl > Bn > Ph ≈ *c*-Pr >> Alk.

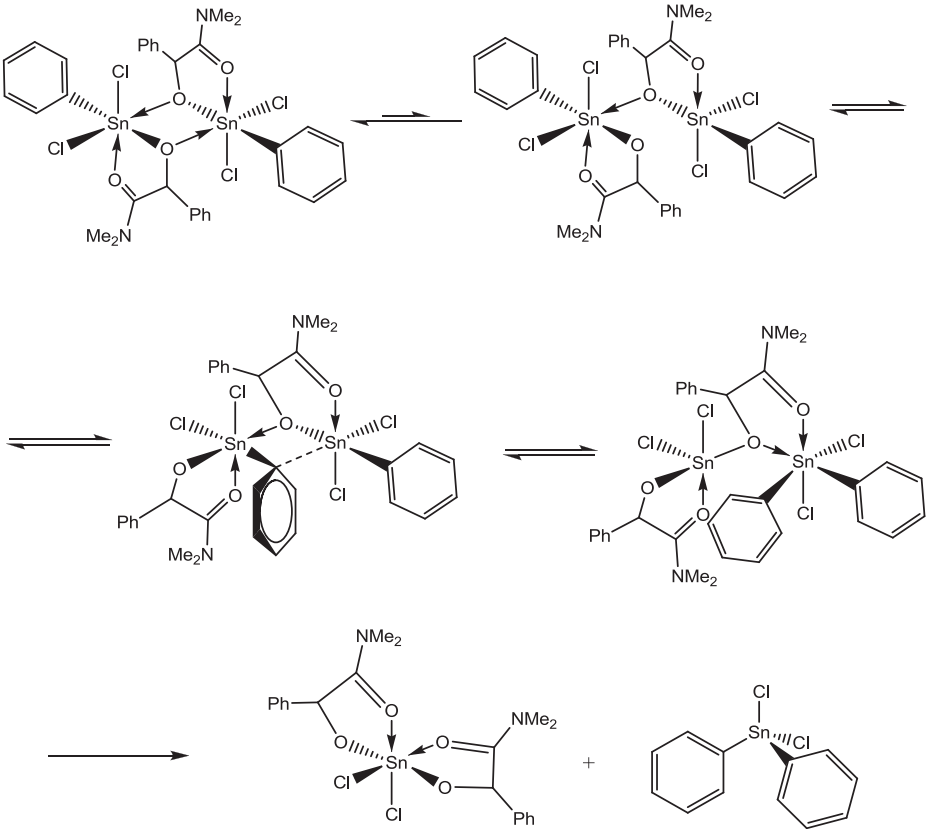
3.1. Experimental

The IR spectra were recorded using a 200 Thermo Nicolet apparatus. The ^{1}H, ^{13}C and ^{119}Sn NMR spectra were recorded at 25 °C using a Bruker Avance 400 NMR spectrometer (400.1, 100.6 and 106.2 MHz, respectively). The chemical shifts were measured using tetramethylsilane (^{1}H, ^{13}C) or tetramethyltin (^{119}Sn) as the internal references. All solvents were purified using standard procedures and redistilled prior to use. Syntheses of the compounds **2a**–**j** were carried out in the argon atmosphere using standard Schlenk technique.

The initial *O*-TMS derivatives of amides **1a** [8], **1b** [9], **1c** [8] and trichlorostannanes $PhSnCl_3$ [1], $VinSnCl_3$ [3,4], $AllSnCl_3$ [10] were synthesized by described procedures.

3.1.1. Synthesis of $PhCH_2SnBu_3$

To magnesium turnings (9.72 g, 0.40 mol) in THF (30 mL) benzyl chloride (5 mL) was added. After initiation of the reaction the solution of benzyl chloride (23.32 g, 0.20 mol) and Bu_3SnCl (32.55 g, 0.10 mol) in THF (60 mL) was added dropwise. The reaction mixture was refluxed for 4 h, cooled to 10 °C and quenched by 1 M solution of HCl. The residue magnesium was filtered off, the organic layer was separated, the aqueous layer extracted by ether (3 × 50 mL). The combined organic fractions were washed with water and dried



Scheme 4.

over Na_2SO_4. After concentration under reduced pressure the residue was fractionated in vacuo to give benzyltributyltin (33.16 g, 87%) as a colorless liquid, b.p. 148–155° (0.1 mm Hg). Lit. [11]. b.p. 192–194 °C (24 mm Hg).

^{1}H NMR ($CDCl_3$, 400.1 MHz): δ = 7.22–7.16, 7.04–6.97 (m, 5H, Ph), 2.34 (s, $^2J(^{119}Sn, ^1H)$ = 56.3 Hz, 2H, PhC**H**$_2$), 1.55–1.38, 1.34–1.25 and 0.92–0.83 ppm (m, 27H, Bu).

^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 143.66 ($^2J(^{119}Sn, ^{13}C)$ = 35.1 Hz, *ipso*-C_6H_5), 128.22 ($^3J(^{119}Sn, ^{13}C)$ = 11.7 Hz, *meta*-C_6H_5), 126.94 ($J(^{119}Sn, ^{13}C)$ = 20.5 Hz, *ortho*-C_6H_5), 122.82 ($J(^{119}Sn, ^{13}C)$ = 13.2 Hz, *para*-C_6H_5), 29.08 ($^3J(^{119}Sn, ^{13}C)$ = 20.5 Hz, $SnCH_2CH_2\mathbf{C}H_2CH_3$), 27.38 ($^2J(^{119}Sn, ^{13}C)$ = 54.2 Hz, $SnCH_2\mathbf{C}H_2CH_2CH_3$), 18.22 ($^1J(^{119}Sn, ^{13}C)$ = 240.1 Hz, Ph**C**H_2Sn), 13.71 ($SnCH_2CH_2CH_2\mathbf{C}H_3$), 9.35 ppm ($^1J(^{119}Sn, ^{13}C)$ = 318.4 Hz, Sn**C**$H_2CH_2CH_2CH_3$).

^{119}Sn NMR ($CDCl_3$, 106.2 MHz): δ = −9.9 ppm.

3.1.2. Synthesis of $PhCH_2SnCl_3$

At −30°C $PhCH_2SnBu_3$ (11.43 g, 30.0 mmol) was slowly added dropwise to $SnCl_4$ (3.50 mL, 7.82 g, 30.0 mmol) in argon atmosphere and the mixture was allowed to warm to room temperature and stirred for 30 min. The resulting thick mass was dissolved in CH_3CN (25 mL) and extracted with pentane (6 × 25 mL) to remove Bu_3SnCl. After concentration at reduced pressure followed by distillation in vacuo $PhCH_2SnCl_3$ (6.61 g, 70%) was obtained, b.p. 105–108°C (0.5 mm Hg) of 91% purity by NMR (Bu_3SnCl impurity). Lit. [12]. b.p. 94–96°C (0.1 mm Hg). The substance is pure enough and in subsequent experiments may be used without additional purification.

^{1}H NMR (C_6D_6, 400.1 MHz): δ = 6.99–6.86, 6.81–6.70 (m, 5H, Ph), 2.51 ppm ($^2J(^{119}Sn, ^1H)$ = 108.6 Hz, s, 2H, PhC**H**$_2$).

^{13}C NMR (C_6D_6, 100.6 MHz): δ = 131.14, 129.39 ($^3J(^{119}Sn, ^{13}C)$ = 43.2 Hz, *ortho*-C_6H_5), 128.92 ($^2J(^{119}Sn, ^{13}C)$ = 71.7 Hz, *ipso*-C_6H_5), 127.81 (Ph), 37.07 ppm ($^1J(^{119}Sn, ^{13}C)$ = 607.4 Hz, Ph**C**H_2Sn).

^{119}Sn NMR (C_6D_6, 106.2 MHz): δ = −32.3 ppm.

3.1.3. Synthesis of **1e**

To a solution of *N*,*N*-dimethylamide of diphenylglycolic acid [13] (7.66 g, 0.030 mol) in THF (30 mL) sodium hydride (1.32 g of 60% dispersion in mineral oil, 0.033 mol) was added portionwise, and the reaction mixture was stirred for 30 min. Then Me_3SiCl (4.93 g, 0.030 mol) was added and the mixture was refluxed for 3 h. The precipitate was separated by centrifugation, the solvent was removed in vacuo to give **1e** (8.14 g, 83%) as a viscous oil.

^{1}H NMR ($CDCl_3$, 400.1 MHz): δ = 7.42–7.26 (m, 10H, Ph), 3.00 (s, 3H, NCH_3), 2.90 (s, 3H, NCH_3), −0.04 ppm (s, 9H, Me_3Si).

^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 172.26 (C=O), 143.28, 127.66, 127.50, 127.14 (Ph), 85.05 (O**C**Ph_2), 38.43, 37.52 (NCH_3), 1.30 ppm (Me_3Si).

3.1.4. Synthesis of **2a**

The mixture of **1b** (1.11 g, 5.1 mmol) and $PhSnCl_3$ (1.54 g, 5.1 mmol) in CH_3CN (10 mL) was stirred at room temperature for 2 h. The precipitate was filtered off, washed with ether and dried in vacuo (0.1 mm Hg) to give **2a** (1.75 g, 84%) as a white powder, m.p. > 250 °C.

IR spectrum (KBr): 1609, 1479, 1438, 1423, 1265, 1114, 1063, 1029 cm^{-1}.

^{1}H NMR (DMSO-d_6, 400.1 MHz): δ = 7.75–7.71 ($^3J(^{119}Sn, ^1H)$ = 132.7 Hz, m, 2H, Ph), 7.39–7.27 (m, 3H, Ph), 4.58 ($^3J(^{119}Sn, ^1H)$ = 92.7 Hz, s, 2H, $SnOCH_2$), 3.68–3.63, 3.52–3.48 ppm (m, 8H, $NC\mathbf{H}_2C\mathbf{H}_2O$).

^{13}C NMR (DMSO-d_6, 100.6 MHz): δ = 176.88 (C=O), 151.72, 133.86 ($^3J(^{119}Sn, ^{13}C)$ = 72.3 Hz, *ortho*-C_6H_5), 128.58, 127.84 ($^2J(^{119}Sn, ^{13}C)$ = 129.3 Hz, *ipso*-C_6H_5) (Ph), 65.79 and 65.71 ($NCH_2\mathbf{C}H_2O$), 60.02 ($^2J(^{119}Sn, ^{13}C)$ = 45.0 Hz, $SnOCH_2$), 44.12 and 43.87 ppm ($N\mathbf{C}H_2CH_2O$).

^{119}Sn NMR (DMSO-d_6, 106.2 MHz): δ = −436.9 ppm.

Found (%) C 35.38, H 4.06, N 3.60. $C_{12}H_{15}NO_3SnCl_2$. Calcd. (%) C 35.08, H 3.68, N 3.41.

Single crystals, suitable for X-ray analysis were obtained by recrystallization of the sample of substance from acetonitrile.

3.1.5. Synthesis of **2b**

The procedure was analogous to synthesis of **2a**. Compound **2b** (1.10 g, 55%) was obtained from $VinSnCl_3$ (1.59 g, 6.3 mmol) and **1a** (1.11 g, 6.3 mmol); m.p. 203–204 °C.

IR spectrum (KBr): 1637, 1414, 1249, 1229, 1047 cm^{-1}.

^{1}H NMR (DMSO-d_6, 400.1 MHz): δ = 6.50–5.82 (m, 3H, Vin); 4.43 ($^3J(^{119}Sn, ^1H)$ = 93.2 Hz, s, 2H, $SnOCH_2$), 3.03 (s, 3H, NCH_3), 3.00 ppm (s, 3H, NCH_3).

^{13}C NMR (DMSO-d_6, 100.6 MHz): δ = 177.67 (C=O), 149.62, 130.35 (Vin), 59.93 ($^2J(^{119}Sn, ^{13}C)$ = 44.2 Hz, $SnOCH_2$), 36.70 and 35.01 ppm (NCH_3).

^{119}Sn NMR (DMSO-d_6, 106.2 MHz): δ = −437.4 ppm.

Found (%) C 22.53, H 3.52, N 4.22. $C_6H_{11}NO_2SnCl_2$. Calcd. (%) C 22.61, H 3.48, N 4.39.

Single crystals, suitable for X-ray analysis were obtained by recrystallization of the sample of substance from acetonitrile.

3.1.6. Synthesis of **2c**

The procedure was analogous to synthesis of **2a**. Compound **2c** (0.53 g, 34%) was obtained from $AllSnCl_3$ (1.25 g, 4.7 mmol) and **1a** (0.83 g, 4.7 mmol); m.p. 192–193 °C.

IR spectrum (KBr): 1639; 1409; 1046 cm^{-1}.

^{1}H NMR (DMSO-d_6, 400.1 MHz): δ = 6.00–5.83 (m, 1H, C**H**=CH_2); 5.00–4.74 (m, 2H, CH=C**H**$_2$); 4.42 ($^3J(^{119}Sn, ^1H)$ = 88.2 Hz, s, 2H, $SnOCH_2$), 3.04 (s, 3H, NCH_3), 2.99 (s, 3H, NCH_3), 2.35 ppm (d, ^3J(H,H) = 8.4 Hz, $^2J(^{119}Sn, ^1H)$ = 183.0 Hz, 2H, $SnCH_2$).

^{13}C NMR (DMSO-d_6, 100.6 MHz): δ = 177.72 (C=O), 135.11 ($^2J(^{119}Sn, ^{13}C)$ = 130.1 Hz, **C**H=CH_2), 113.94 ($^3J(^{119}Sn, ^{13}C)$ = 167.0 Hz, CH=**C**H_2), 60.12 ($^2J(^{119}Sn, ^{13}C)$ = 41.8 Hz, $SnOCH_2$), 41.96 (br., $SnCH_2$), 36.63 and 34.97 ppm (NCH_3).

^{119}Sn NMR (DMSO-d_6, 106.2 MHz): δ = −408.5 ppm.

Found (%) C 24.99, H 3.86, N 4.23. $C_7H_{13}NO_2SnCl_2$. Calcd. (%) C 25.26, H 3.94, N 4.21.

3.1.7. Synthesis of **2d**

The procedure was analogous to synthesis of **2a**. Compound **2d** (1.16 g, 51%) was obtained from $PhCH_2SnCl_3$ (1.88 g, 5.9 mmol) and **1a** (1.04 g, 5.9 mmol); m.p. 201–202 °C.

^{1}H NMR (DMSO-d_6, 400.1 MHz): δ = 7.18–7.02 (m, 5H, Ph); 4.40 ($^3J(^{119}Sn, ^1H)$ = 88.4 Hz, s, 2H, OCH_2), 2.96 (br. s., 6H, NCH_3), 2.89 ppm ($^2J(^{119}Sn, ^1H)$ = 174.8 Hz, s, 2H, $SnCH_2$).

^{13}C NMR (DMSO-d_6, 100.6 MHz): δ = 177.66 (C=O), 139.19, 129.12 ($^2J(^{119}Sn, ^{13}C)$ = 70.3 Hz, *ipso*-C_6H_5), 127.44 ($^3J(^{119}Sn, ^{13}C)$ = 42.5 Hz, *ortho*-C_6H_5), 124.24 (Ph), 60.16 (OCH_2), 44.24 (br., $SnCH_2$), 36.50 and 34.87 ppm (NCH_3).

^{119}Sn NMR (DMSO-d_6, 106.2 MHz): δ = −416.0 ppm.

Found (%) C 34.64, H 4.01, N 3.80. $C_{11}H_{15}NO_2SnCl_2$. Calcd. (%) C 34.51, H 3.95, N 3.66.

3.1.8. Synthesis of **2e**

The procedure was analogous to synthesis of **2a**. Compound **2e** (0.61 g, 48%) was obtained from $PhSnCl_3$ (0.94 g, 3.1 mmol) and **1d** (0.67 g, 3.1 mmol); m.p. 204–205°C.

IR spectrum (KBr): 1614, 1477, 1452, 1432, 1336, 1049 cm^{-1}.

^{1}H NMR (DMSO-d_6, 400.1 MHz): δ = 7.74 (d, ^3J(H,H) = 6.5 Hz, $^3J(^{119}Sn, ^1H)$ = 132.0 Hz, 2H, o-Ph), 7.40–7.25 (m, 3H, Ph); 4.75 (q, ^3J(H,H) = 6.5 Hz, $^3J(^{119}Sn, ^1H)$ = 125.3 Hz; 1H, OCH), 3.74 (m, 1H, NCH_2), 3.54–3.43 (m, 3H, NCH_2), 2.02–1.80 (m, 4H, $NCH_2C\mathbf{H}_2$), 1.41 ppm (d, ^3J(H,H) = 6.5 Hz, 3H, CH_3).

^{13}C NMR (DMSO-d_6, 100.6 MHz): δ = 178.61 (C═O), 152.66, 133.87 ($^{3}J(^{119}Sn, ^{13}C)$ = 70.8 Hz, *ortho*-C_6H_5), 128.36, 127.71 ($^{2}J(^{119}Sn, ^{13}C)$ = 131.9 Hz, *ipso*-C_6H_5) (Ph), 65.99 ($^{2}J(^{119}Sn, ^{13}C)$ = 44.7 Hz, OCH), 47.87, 46.78 (NCH_2), 25.40, 23.21 ($NCH_2\mathbf{C}H_2$), 20.59 ppm (CH_3).

^{119}Sn NMR (DMSO-d_6, 106.2 MHz): δ = −448.3 ppm.

Found (%) C 38.21, H 4.12, N 3.39. $C_{13}H_{17}NO_2SnCl_2$. Calcd. (%) C 38.17, H 4.16, N 3.43.

3.1.9. Synthesis of **2f**

The procedure was analogous to synthesis of **2a**. Compound **2f** (0.92 g, 77%) was obtained from $PhSnCl_3$ (0.83 g, 2.7 mmol) and **1c** (0.68 g, 2.7 mmol); m.p. 204–205°C.

IR spectrum: 1635, 1492, 1479, 1430, 1407, 1070, 1020 cm^{-1}.

^{1}H NMR (DMSO-d_6, 400.1 MHz): δ = 7.79 (d, ^{3}J(H,H) = 6.9 Hz, $^{2}J(^{119}Sn, ^{1}H)$ = 132.6 Hz, 2H, o-Ph), 7.43–7.28 (m, 8H, Ph), 5.62 ($^{3}J(^{119}Sn, ^{1}H)$ = 60.4 Hz, s, 1H, OCH), 3.11 (s, 3H, NCH_3), 2.76 ppm (s, 3H, NCH_3).

^{13}C NMR (DMSO-d_6, 100.6 MHz): δ = 178.55 (C═O), 140.49, 133.81 ($^{3}J(^{119}Sn, ^{13}C)$ = 69.8 Hz, *ortho*-C_6H_5), 128.63, 128.55, 128.36, 127.89 (Ph), 72.54 (OCH), 37.65 and 37.32 ppm (NCH_3).

^{119}Sn NMR (DMSO-d_6, 106.2 MHz): δ = −445.3 (br.), −454.1 ppm.

Found (%) C 43.25, H 4.05, N 3.41. $C_{16}H_{17}NO_2SnCl_2$. Calcd. (%) C 43.18, H 3.82, N 3.15.

3.1.10. Synthesis of **2g**

The mixture of c-$PrSnCl_3$ (1.44 g, 5.4 mmol) in CH_3CN (5 mL) and **1c** (1.36 g, 5.4 mmol) in CH_3CN (5 mL) was stirred at room temperature for 2 h, then the solvent was evaporated at reduced pressure to 1/2 of initial volume and left for 12 h at 4°C. The precipitate was filtered, washed by ether and dried in vacuo (0.1 mm Hg) to give **2g** (0.62 g, 28%) as white powder; m.p. 105–106 °C.

IR spectrum (KBr): 1618, 1480, 1452, 1430, 1245, 1186, 1065, 1028 cm^{-1}.

^{1}H NMR (DMSO-d_6, 400.1 MHz): δ = 7.36–7.28 (m, 5H, Ph), 5.50 ($^{3}J(^{119}Sn, ^{1}H)$ = 58.6 Hz, s, 1H, OCH), 3.07 (s, 3H, NCH_3), 2.72 (s, 3H, NCH_3), 0.99-0.48 ppm (m, 5H, *c*-Pr).

^{13}C NMR (DMSO-d_6, 100.6 MHz): δ = 178.51 (C═O), 140.55, 128.54, 128.29, 127.76 (Ph), 72.46 (OCH), 37.46, 37.19 (NCH_3), 21.79 (SnCH), 3.52 ppm ($^{2}J(^{119}Sn, ^{13}C)$ = 40.2 Hz, $SnCH\mathbf{C}H_2$).

^{119}Sn NMR (DMSO-d_6, 106.2 MHz): δ = −389.2 ppm.

Found (%) C 38.33, H 4.33, N 3.52. $C_{13}H_{17}NO_2SnCl_2$. Calcd. (%) C 38.19, H 4.19, N 3.43.

3.1.11. Synthesis of **2h**

The mixture of $VinSnCl_3$ (1.00 g, 4.0 mmol) and **1e** in CH_3CN (15 mL) was stirred at room temperature for 4 h. Then the solvent was evaporated at reduced pressure to 1/5 of initial volume, ether (10 mL) was added and the mixture was stored overnight at 4 °C. The precipitate was filtered, washed by ether and dried in vacuo (0.1 mm Hg) to give **2h** (0.61 g, 32%) as white powder; m.p. 148–149 °C.

IR spectrum (KBr): 1610, 1043 cm^{-1}.

^{1}H NMR (DMSO-d_6, 400.1 MHz): δ = 7.42–7.27 (m, 10H, Ph), 6.55–5.87 (m, 3H, $C\mathbf{H}═C\mathbf{H}_2$), 3.21 (s, 3H, NCH_3) and 2.49 ppm (s, 3H, NCH_3).

^{13}C NMR (DMSO-d_6, 100.6 MHz): δ = 178.17 (C═O), 150.81, 143.52 (Vin), 129.95, 128.44, 128.00, 127.53 (Ph), 81.77 ($SnO\mathbf{C}Ph_2$), 40.28 and 39.05 ppm (NCH_3).

^{119}Sn NMR (DMSO-d_6, 106.2 MHz): δ = −435.4 (minor), −463.7 ppm (major).

Found (%) C 45.67, H 4.11, N 2.89. $C_{18}H_{19}NO_2SnCl_2$. Calcd. (%) C 45.90, H 4.07, N 2.97.

3.1.12. Synthesis of **2i**

The procedure was analogous to synthesis of **2h**. Compound **2i** (3.02 g, 70%) was obtained from $PhSnCl_3$ (2.51 g, 8.3 mmol) and **1e** (2.72 g, 8.3 mmol); m.p. 211–212 °C.

IR spectrum (KBr): 1605, 1475, 1432, 1411, 1043, 1028 cm^{-1}.

^{1}H NMR (DMSO-d_6, 400.1 MHz): δ = 7.78 (d, ^{3}J(H,H) = 6.9 Hz, $^{3}J(^{119}Sn, ^{1}H)$ = 131.1 Hz, 2H, SnPh), 7.47–7.18 (m, 18H, Ph), 3.28 (s, 3H, NCH_3) and 2.55 ppm (s, 3H, NCH_3).

^{13}C NMR (DMSO-d_6, 100.6 MHz): δ = 178.27 (C═O), 152.89, 133.58 ($J(^{119}Sn, ^{13}C)$ = 74.7 Hz), 128.48, 128.04, 128.87, 127.57 (Ph), 81.97 ($SnO\mathbf{C}Ph_2$), 40.38 and 39.24 ppm (NCH_3).

^{119}Sn NMR (DMSO-d_6, 106.2 MHz): δ = −434.7 (minor), −463.7 ppm (major).

Found (%) C 50.61, H 4.20, N 3.36. $C_{22}H_{21}NO_2SnCl_2$. Calcd. (%) C 50.71, H 4.06, N 2.69.

3.1.13. Synthesis of **2j**

The mixture of $EtSnCl_3$ (0.79 g, 3.1 mmol) and **1e** (1.02 g, 3.1 mmol) in toluene (10 mL) was stirred at room temperature for 2 h. The precipitate was filtered off, washed with hexanes and dried in vacuo (0.1 mm Hg) to give **2j** (0.89 g, 61%) as white powder; m.p. 160–161 °C.

IR spectrum (KBr): 1614, 1483, 1448, 1429, 1408, 1042, 1028 cm^{-1}.

^{1}H NMR (DMSO-d_6, 400.1 MHz): δ = 7.42–7.27 (m, 10H, Ph), 3.21 (s, 3H, NCH_3), 2.49 (s, 3H, NCH_3), 1.54 (q, ^{3}J(H,H) = 7.8 Hz, $^{2}J(^{119}Sn, ^{1}H)$ = 140.5 Hz; 2H, $SnCH_2$), 1.27 ppm (t, ^{3}J(H,H) = 7.8 Hz, 3H, $SnCH_2C\mathbf{H}_3$).

^{13}C NMR (DMSO-d_6, 100.6 MHz): δ = 178.34 (C═O), 143.57, 128.49, 128.01, 127.52 (Ph), 81.93 ($SnO\mathbf{C}Ph_2$), 40.18, 38.95 (NCH_3), 31.03 ($SnCH_2$), 10.27 ppm ($^{2}J(^{119}Sn, ^{13}C)$ = 73.9 Hz, $SnCH_2\mathbf{C}H_3$).

^{119}Sn NMR (DMSO-d_6, 106.2 MHz): δ = −375.6 (minor), −404.2 ppm (major).

Found (%) C 45.93, H 4.61, N 2.90. $C_{18}H_{21}NO_2SnCl_2$. Calcd (%) C 45.71, H 4.48, N 2.96.

Single crystals, suitable for X-ray investigations were received by recrystallization of the sample of substance from acetonitrile.

3.1.14. Disproportionation of **2f**, synthesis of **3b**

The sample (180 mg, 0.4 mmol) of **2f** was dissolved in minimal volume of boiling CH_3CN (~1 mL), the solution was stored overnight at room temperature. The precipitate was separated by decantation, washed by CH_3CN and dried in vacuo (0.1 mm Hg) to give **3b** (60 mg, 54%); m.p. >250 °C.

IR spectrum (KBr): 2933, 2835, 1622, 1481, 1454, 1436, 1406, 1259, 1186, 1093, 1072 cm^{-1}.

^{1}H NMR (DMSO-d_6, 400.1 MHz): δ = 7.46–7.31 (m, 5H, Ph), 5.74 (s, 1H, OCH); 3.06 (s, 3H, NCH_3) and 2.76 ppm (s, 3H, NCH_3).

The ^{13}C and ^{119}Sn NMR spectra were not obtained due to very low solubility of compound **3b** in common organic solvents (CD_3CN, $CDCl_3$, DMSO-d_6).

Found (%) C 43.91, H 4.53, N 5.29. $C_{20}H_{24}N_2O_4SnCl_2$. Calcd (%) C 43.99, H 4.43, N 5.13.

3.1.15. Disproportionation of **2g**, synthesis of **3b**

The procedure was analogous to **2f**, according to spectroscopic data (^{1}H NMR, IR) the product was identical to **3b**.

3.1.16. Disproportionation of **2h**, synthesis of **3c**

The sample (250 mg, 0.3 mmol) of **2h** was dissolved in minimal volume of boiling CH_3CN (~1 mL), the solution was stored overnight at 4 °C. The precipitate was separated by decantation, washed by CH_3CN and dried in vacuo (0.1 mm Hg) to give **3c** (90 mg, 83%); m.p. >250 °C.

^{1}H NMR (DMSO-d_6, 400.1 MHz): $\delta = 7.50–7.21$ (m, 10H, Ph), 2.83 (s, 3H, NCH_3) and 2.53 ppm (s, 3H, NCH_3).

^{13}C NMR (DMSO-d_6, 100.6 MHz): δ = 177.17 (C═O), 144.53, 142.73, 142.03, 128.21, 128.12, 128.06, 127.94, 127.73, 127.64, 127.52, 126.75, 126.67 (Ph), 81.80, 81.58 (SnO**C**Ph_2); 40.32 and 38.06 ppm (NCH_3).

^{119}Sn NMR (DMSO-d_6, 106.2 MHz): $\delta = -495.9$ ppm.

Found (%) C 55.08, H 4.84, N 4.08. $C_{32}H_{32}N_2O_4SnCl_2$. Calcd (%) C 55.05, H 4.62, N 4.01.

3.1.17. Synthesis of **3a**

The mixture of $VinSnCl_3$ (1.29 g, 5.1 mmol) and **1d** (1.10 g, 5.1 mmol) in CH_3CN (10 mL) was refluxed for 5 h. The solvent was evaporated at reduced pressure to 1/3 of initial volume and ether (20 mL) was added. The oily product was separated by decantation, washed by ether and dried in vacuo. Then it was heated to boiling in THF (20 mL), the precipitate was filtered off, washed by ether and dried in vacuo (0.1 mm Hg) to give **3a** (630 mg, 52%) as a white powder; m.p. >250 °C.

IR spectrum (KBr): 2933, 2835, 1622, 1481, 1454, 1436, 1406, 1259, 1186, 1093, 1072 cm^{-1}.

^{1}H NMR (DMSO-d_6, 400.1 MHz): $\delta = 4.75$ (q, ^3J(H,H) = 6.4 Hz, ^3J(^{119}Sn, ^{1}H) = 151.4 Hz, 1H, OCH), 3.82–3.34 (m, 4H, NCH_2); 2.02–1.73 (m, 4H, $NCH_2C\mathbf{H}_2$); 1.31 ppm (d, ^3J(H,H) = 6.4 Hz, 3H, $CHC\mathbf{H}_3$).

^{13}C NMR (DMSO-d_6, 100.6 MHz): δ = 177.37 (C═O), 65.45 and 65.22 (OCH), 47.91, 46.67 (NCH_2), 25.16, 23.12 ($NCH_2\mathbf{C}H_2$), 20.64 and 20.35 ppm ($CH\mathbf{C}H_3$).

^{119}Sn NMR (DMSO-d_6, 106.2 MHz): $\delta = -473.7, -479.8$ ppm.

Found (%) C 35.40, H 5.19, N 5.19. $C_{14}H_{24}N_2O_4SnCl_2$. Calcd (%) C 35.48, H 5.10, N 5.91.

3.1.18. Interaction of $AllSnCl_3$ with **1c**, synthesis of **3b**

The mixture of $AllSnCl_3$ (1.27 g, 4.8 mmol) and **1c** (1.20 g, 4.8 mmol) in CH_3CN (10 mL) was stirred at room temperature for 2 h. The precipitate was filtered off, washed by CH_3CN and dried in vacuo (0.1 mm Hg). The product (0.88 g, 67%) was identified by NMR as **3b**.

3.1.19. Interaction of $VinSnCl_3$ with **1c**, synthesis of **3b**

The mixture of $VinSnCl_3$ (1.31 g, 5.2 mmol) and **1c** (1.31 g, 5.2 mmol) in CH_3CN (10 mL) was stirred at room temperature for 3 h. The precipitate was filtered off, washed by CH_3CN and dried in vacuo (0.1 mm Hg). The product (0.87 g, 62%) was identified by NMR as **3b**.

3.1.20. Interaction of $PhCH_2SnCl_3$ with **1c**, synthesis of **3b**

The mixture of $PhCH_2SnCl_3$ (0.98 g, 3.1 mmol) and **1c** (0.78 g, 3.1 mmol) in CH_3CN (10 mL) was stirred at room temperature for 5 h. The solvent was evaporated at reduced pressure to 1/3 of initial volume. Then ether (20 mL) was added, the precipitate was separated by decantation washed by ether and dried in vacuo. The residue was heated to boil in CH_3CN (20 mL) and stored overnight at room temperature. The precipitate was filtered, washed by CH_3CN and dried in vacuo to give **3b** (0.40 g, 48%).

3.1.21. Disproportionation of **2e** (NMR experiment)

The sample of **2e** (50 mg) was dissolved in CD_3CN (0.5 mL) at 70°C and kept at this temperature for 30 min. The mixture was analyzed by ^{119}Sn NMR.

^{119}Sn NMR (CD_3CN, 106.2 MHz): $\delta = -123.7$ (Ph_2SnCl_2), −440.1 (initial **2e**), −473.6 and −478.6 ppm ($L^{O,O}{}_2SnCl_2$ (**3a**)).

3.1.22. Disproportionation of **2i** (NMR experiment)

The sample of **2i** (50 mg) was dissolved in CD_3CN (0.5 mL) at 70°C and kept at this temperature for 30 min. The mixture was analyzed by ^{119}Sn NMR.

^{119}Sn NMR (CD_3CN, 106.2 MHz): $\delta = -123.7$ (Ph_2SnCl_2), −293.3 (initial **2i**), −493.8 ppm ($L^{O,O}{}_2SnCl_2$ (**3c**)).

3.2. X-ray diffraction study

X-ray diffraction measurements for **2a**–**b**, **2j**, **3b**–**c** were carried out with a Bruker APEX II diffractometer. Structures were solved by direct methods and non-hydrogen atoms were refined in full-matrix anisotropic approximation. The hydrogen atoms were located from differential Fourier synthesis of the electron density and refined using rigid body model. All calculations were carried out using the SHELXTL 5.1 program package [14] and OLEX2 program [15]. Experimental details and crystallographic data are presented in Table 1.

Appendix A. Supplementary material

CCDC 930157–930160 and 930613 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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