

An Unusual Reaction of (β -Dimethylaminoethoxy)triethyltin with Phenyltin Trichloride. The First X-ray Structural Evidence of the Existence of Complexes $R_2SnXY \cdot R_2SnXY$ ($R = \text{Alkyl, Aryl}$; $X, Y = \text{Hal, OR, } X \neq Y$) Both as Unsymmetrical Adducts $[R_2SnX_2 \cdot R_2SnY_2]$ and Symmetrical Dimers $[R_2SnXY]_2$

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Keywords: Complexation / Tin / Dimerization / Stannanes / X-ray diffraction

The substituent exchange reaction of $PhSnCl_3$ with $[Et_3Sn(OCH_2CH_2NMe_2)]$ gives rise unexpectedly to the unsymmetrical adduct $[Ph_2SnCl_2 \cdot Ph_2Sn(OCH_2CH_2NMe_2)_2]$ (**2**). It has been unambiguously proved for the first time that compounds of the $RSnX_3$ type are able to undergo the hydrocarbon substituent redistribution reaction. The analogous tin complexes $[Et_2SnCl_2 \cdot Et_2Sn(OMe)_2]$ (**5**) and $[Bu_2Sn(OAc)_2 \cdot Bu_2Sn(OMe)_2]$ (**6**), which have ligands other than β -dimethyl-

aminoethoxy and could be considered as "organotin analogs of Grignard reagents" have symmetrical dimeric structures, i.e., can be formulated as $[Bu_2Sn(OMe)(OAc)]_2$ and $[Et_2Sn(OMe)Cl]_2$, respectively. Both types of structures, viz., unsymmetrical adduct (**2**) and symmetrical dimer (**5**, **6**), have been characterized by X-ray diffraction analysis.
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Introduction

Redistribution reactions are a convenient and widely used method for the synthesis of organometallic compounds.^[1] It has been shown previously that penta- and hexacoordinate organotin compounds such as $[Me_nSnAr_{4-n}]$ and $[Bu_2SnArCl]$, which contain electron-donating groups in the aryl ligands, are more active towards redistribution, and related (transmetallation), reactions than tetra-coordinate tin(IV) derivatives.^[2] Therefore, the redistribution reactions of hypercoordinate organotin compounds $[R_nSnX_{4-n}]$ containing electron-donating groups in the functional substituents X but not in the hydrocarbon substituents R, have been of significant interest. As a continuation of our investigations into the chemistry of (β -dimethylaminoethoxy)germanium and -tin derivatives,^[3] we report

here on the surprising results of the interaction between (β -dimethylaminoethoxy)triethyltin and -phenyltin trichloride.

Very recently, we have found that the reaction of $PhGeCl_3$ with $[Et_3Ge(OCH_2CH_2NMe_2)]$ affords $[PhGe(OCH_2CH_2NMe_2)_2Cl]$ in high yield.^[3f] However, the analogous reaction in the case of tin unexpectedly results in the unsymmetrical adduct $[Ph_2SnCl_2 \cdot Ph_2Sn(OCH_2CH_2NMe_2)_2]$ as the main reaction product.

Results and Discussion

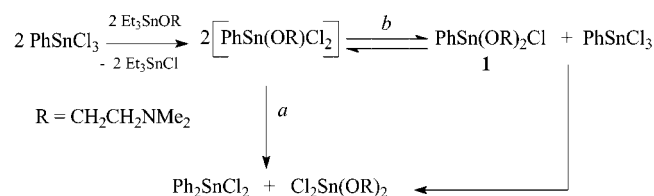
The reaction was carried out by the gradual addition of $[Et_3Sn(OCH_2CH_2NMe_2)]$ to a $PhSnCl_3$ solution in diethyl ether or tetrahydrofuran. In our opinion, it proceeds in three stages. In the first stage, diphenyldichloro- and dichlorodialkoxystannanes are formed. The formation of these products apparently proceeds by the initial formation of a $[PhSn(OCH_2CH_2NMe_2)Cl_2]$ intermediate, which can further disproportionate by two paths: either by the exchange of Ph and $OCH_2CH_2NMe_2$ substituents (path a) or by the exchange of Cl and $OCH_2CH_2NMe_2$ substituents (path b). Path a gives rise immediately to $[Ph_2SnCl_2]$ and $[Cl_2Sn(OCH_2CH_2NMe_2)_2]$, whereas path b first gives rise to $[PhSn(OCH_2CH_2NMe_2)_2Cl]$ (**1**) and $PhSnCl_3$, and a subsequent interchange of the Ph and Cl substituents affords $[Ph_2SnCl_2]$ and $[Cl_2Sn(OCH_2CH_2NMe_2)_2]$ (Scheme 1).

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Scheme 1. The first stage of the reaction of $[\text{PhSnCl}_3]$ with $[\text{Et}_3\text{Sn}(\text{OCH}_2\text{CH}_2\text{NMe}_2)]$.

Scheme 1 was confirmed by an NMR spectroscopic study of the products of the reaction between the monochloroorganostannane **1**, which was prepared by an independent method involving reverse order of the reagent mixing (see below), and trichlorophenylstannane. In accordance with the multinuclear NMR spectroscopy data, the reaction mixture contains $[\text{Ph}_2\text{SnCl}_2]$ and $[\text{Cl}_2\text{Sn}(\text{OCH}_2\text{CH}_2\text{NMe}_2)_2]$. The latter was identified by comparison of its NMR spectral characteristics with those of the compound prepared by treatment of HgCl_2 with $[\text{Sn}(\text{OCH}_2\text{CH}_2\text{NMe}_2)_2]$.

A single-crystal X-ray diffraction analysis of **1** (Figure 1, Table 1) provided proof for the proposed structure and revealed that the tin atom is hexacoordinate with one carbon, one chlorine, two oxygen, and two nitrogen atoms, with an overall slightly distorted octahedral *cis-cis-trans* configuration, respectively.

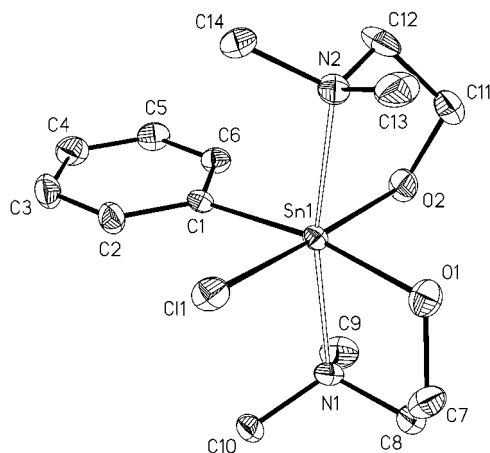


Figure 1. View of compound **1**. The hydrogen atoms have been omitted for clarity. Displacement ellipsoids are scaled to the 50% probability level. The coordination bonds are shown by open lines.

It is important to note that, in contrast to $[\text{PhGe}(\text{OCH}_2\text{CH}_2\text{NMe}_2)_2\text{Cl}]$, which tends to ionize in hydrogen-bond-donor solvents such as CHCl_3 to form the ionic pentacoordinate form $[\text{PhGe}(\text{OCH}_2\text{CH}_2\text{NMe}_2)_2][\text{Cl}]$ rather than the neutral hexacoordinate form,^[37] compound **1** exists only in the neutral hexacoordinate form.

The second stage is obviously the alkoxylation reaction of $[\text{Ph}_2\text{SnCl}_2]$, which yields $[\text{Ph}_2\text{Sn}(\text{OCH}_2\text{CH}_2\text{NMe}_2)_2]$, and the third stage is the complexation reaction between $[\text{Ph}_2\text{SnCl}_2]$ and $[\text{Ph}_2\text{Sn}(\text{OCH}_2\text{CH}_2\text{NMe}_2)_2]$, which yields the final poorly soluble complex **2**.

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

Sn(1)–O(1)	2.024(3)	Sn(1)–N(2)	2.306(3)
Sn(1)–O(2)	2.032(3)	Sn(1)–N(1)	2.340(3)
Sn(1)–C(1)	2.163(4)	Sn(1)–Cl(1)	2.5242(11)
O(1)–Sn(1)–O(2)	89.90(14)	C(1)–Sn(1)–N(1)	93.56(13)
O(1)–Sn(1)–C(1)	170.46(15)	N(2)–Sn(1)–N(1)	168.42(11)
O(2)–Sn(1)–C(1)	95.82(14)	O(1)–Sn(1)–Cl(1)	83.51(10)
O(1)–Sn(1)–N(2)	93.60(12)	O(2)–Sn(1)–Cl(1)	168.11(10)
O(2)–Sn(1)–N(2)	81.38(13)	C(1)–Sn(1)–Cl(1)	92.10(11)
C(1)–Sn(1)–N(2)	94.80(13)	N(2)–Sn(1)–Cl(1)	89.15(9)
O(1)–Sn(1)–N(1)	78.80(12)	N(1)–Sn(1)–Cl(1)	98.55(8)
O(2)–Sn(1)–N(1)	89.82(12)		

Proof of the structure of **2** came from a single-crystal X-ray diffraction analysis (Figure 2, Table 2), which revealed that **2** is the adduct $[\text{Ph}_2\text{SnCl}_2 \cdot \text{Ph}_2\text{Sn}(\text{OCH}_2\text{CH}_2\text{NMe}_2)_2]$ formed by the bridging oxygen atoms of the β-dimethylaminoethoxy ligands, with an unsymmetrical arrangement of the substituents at the tin atoms. It is located on a crystallographic C_2 axis that passes through the tin atoms. The tin atoms are hexacoordinate, with the phenyl groups in the *trans* configuration. The C–Sn–C angle at Sn1 [132.6(3)°] deviates substantially from the value of 180° (the phenyl rings are shifted towards the longer Sn←N coordination bonds), whereas that at Sn2 is essentially linear [177.3(3)°]. The basal plane of Sn1 is defined by an N_2O_2 donor set defined by two chelating β-dimethylaminoethoxy ligands with very long Sn←N bond lengths [2.766(4) Å]. Two chlorine and two oxygen atoms in the *cis* configuration make up the basal plane of Sn2. The bond angles in the equatorial planes vary from 70.8(1)° to 147.8(2)° for Sn1 and from 66.2(2)° to 105.44(7)° for Sn2. Thus, the geometry of Sn1 is best described as skew-trapezoidal bipyramidal, while that of Sn2 is best described as distorted octahedral.

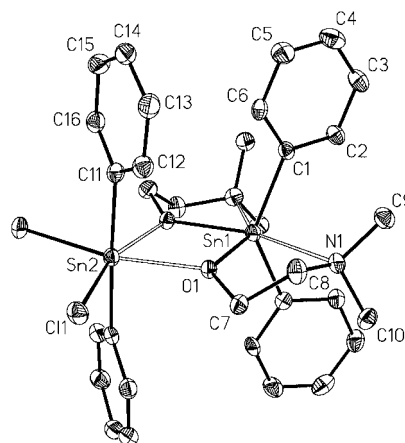


Figure 2. View of complex **2**. The hydrogen atoms have been omitted for clarity. Thermal ellipsoids are scaled to the 40% probability level. The coordination bonds are shown by open lines.

The covalent Sn–O [2.091(3) Å] and coordination Sn←O [2.242(3) Å] bond lengths in the four-membered Sn_2O_2 ring are significantly different and close to the corresponding

Table 2. Selected bond lengths [$\text{\AA}$] and angles [$^\circ$] for **2**.^[a]

Sn(1)–O(1)	2.091(3)	Sn(2)–C(11)	2.150(5)
Sn(1)–C(1)	2.112(5)	Sn(2)–O(1)	2.242(3)
Sn(1)–N(1)	2.766(4)	Sn(2)–Cl(1)	2.5178(14)
O(1)–Sn(1)–O(1) ⁱ	71.66(18)	C(11)–Sn(2)–O(1) ⁱ	89.13(16)
O(1)–Sn(1)–C(1)	113.44(17)	C(11)–Sn(2)–O(1)	88.62(17)
O(1)–Sn(1)–C(1) ⁱ	104.69(17)	O(1)–Sn(2)–O(1) ⁱ	66.15(17)
C(1)–Sn(1)–C(1) ⁱ	132.6(3)	C(11)–Sn(2)–Cl(1) ⁱ	91.36(15)
O(1)–Sn(1)–N(1)	70.77(14)	O(1)–Sn(2)–Cl(1) ⁱ	160.36(9)
O(1)–Sn(1)–N(1) ⁱ	141.13(13)	C(11)–Sn(2)–Cl(1)	90.27(14)
C(1)–Sn(1)–N(1)	81.65(16)	O(1)–Sn(2)–Cl(1)	94.21(9)
C(1)–Sn(1)–N(1) ⁱ	85.56(17)	Cl(1)–Sn(2)–Cl(1) ⁱ	105.44(7)
N(1)–Sn(1)–N(1) ⁱ	147.8(2)	Sn(1)–O(1)–Sn(2)	111.10(14)
C(11)–Sn(2)–C(11) ⁱ	177.3(3)		

[a] Symmetry transformations used to generate equivalent atoms: i: $-x, y, -z + 1/2$.

bond lengths in previously investigated mononuclear hexa-coordinate diphenyltin complexes.^[4] The Sn–C and Sn–Cl bond lengths are also similar to those found in other related dichloro- and diphenyltin compounds.^[4,5]

It is of interest that the result of the reaction of $[\text{PhSnCl}_3]$ with $[\text{Et}_3\text{Sn}(\text{OCH}_2\text{CH}_2\text{NMe}_2)]$ depends to a great extent on the order of reagent mixing. Upon the reverse order of mixing, i.e., when $[\text{PhSnCl}_3]$ is added to $[\text{Et}_3\text{Sn}(\text{OCH}_2\text{CH}_2\text{NMe}_2)]$ solution, di(alkoxy)chlorophenylstannane (**1**) is produced in high yield instead of **2**. Moreover, the use of an excess of $[\text{Et}_3\text{Sn}(\text{OCH}_2\text{CH}_2\text{NMe}_2)]$ does not allow the complete substitution of all three chlorine atoms in $[\text{PhSnCl}_3]$ with β -dimethylaminoethoxy groups. For the sake of comparison, we also carried out the same reaction for the alkyltin derivatives $[\text{MeSnCl}_3]$ and $[\text{EtSnI}_3]$. However, despite the utilization of similar reactions, in the case of the alkyltin derivatives, the reactions stopped after the first step, affording $[\text{MeSn}(\text{OCH}_2\text{CH}_2\text{NMe}_2)_2\text{Cl}]$ (**3**) and $[\text{EtSn}(\text{OCH}_2\text{CH}_2\text{NMe}_2)_2\text{I}]$ (**4**), respectively, in high yields. As for **1**, compounds **3** and **4** exist only in the neutral hexa-coordinate form.

It is very important to point out that unique phenyl group migration from $[\text{PhSnCl}_3]$ takes place in the reaction described here. Phenyl group migration has previously been observed only for the ionic complexes $[\text{PhSnHal}_4]^+$ or $[\text{PhSnHal}_5]^{2+}$, in which such migration is promoted by fluoride ion or tributylphosphane.^[6,7] Moreover, in these reports the final reaction products were not isolated from the reaction mixture and their structures were not determined unambiguously. In our case, however, only stannanes take part in the reaction and the structures of all key products have been determined by elemental analysis, multinuclear NMR spectroscopy, and X-ray diffraction. Thus, we have unambiguously proved for the first time that compounds of the type $R\text{SnX}_3$ are able to undergo a redistribution reaction of the hydrocarbon substituent. A more detailed verification of the supposed reaction scheme will be the subject of further investigations.

Complex **2** is the first compound of the type $R_2\text{SnX}_2 \cdot R_2\text{SnY}_2$ whose structure has been determined by X-ray diffraction. Previously, Kocheshkov and co-workers

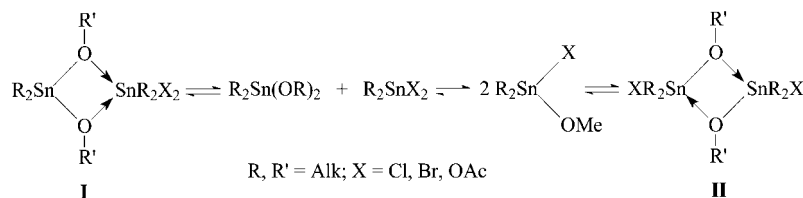
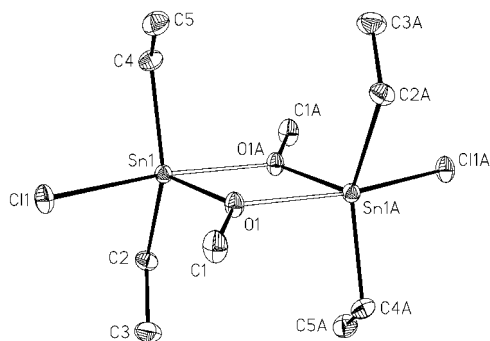
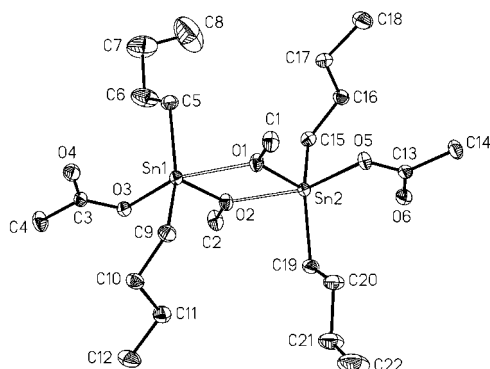
have reported the existence of unsymmetrical adducts in solution by studying the interaction of $[\text{R}_2\text{Sn}(\text{OMe})_2]$ with $[\text{R}_2\text{SnCl}_2]$ or $[\text{R}_2\text{Sn}(\text{OAc})_2]$ ($R = \text{alkyl}$) by calorimetric, dielectric, dielectrometric, and cryoscopic methods.^[8] However, as was shown later by Davies and co-workers, the structure of these complexes in solution is additionally complicated by the occurrence of the equilibria presented in Scheme 2. These authors suggested that complexes of the type $R_2\text{SnXY} \cdot R_2\text{SnXY}$ could be considered to be “organotin analogs of Grignard reagents”.^[9] However, no unambiguous evidence of the structure of the complexes $R_2\text{SnXY} \cdot R_2\text{SnXY}$ was available until now. It should be noted that in the paper cited above, the authors gave preference to the symmetrical structure of type **II** for these complexes.

Taking into account the possible application of these reactions to the solution of different synthetic and applied problems,^[10] we have decided to fill this gap. To this end, we carried out the reactions of diethyltin dichloride with dimethoxydiethyltin and dibutyltin diacetate with dimethoxydibutyltin. The products obtained were studied by X-ray diffraction analysis. It turned out that they consist of symmetrical dimers $[\text{Et}_2\text{Sn}(\text{Cl})(\text{OMe})_2]_2$ (**5**) and $[\text{Bu}_2\text{Sn}(\text{OAc})(\text{OMe})_2]_2$ (**6**) (Figures 3 and 4 and Tables 3 and 4), respectively, with Sn atoms linked by bridging methoxy groups in the crystal. The coordination geometry around the metal atoms is a strongly distorted trigonal bipyramid with the two C atoms and the covalently bonded O atom of the bridging methoxy group in the equatorial plane. The coordinated O atom of the bridging methoxy group and Cl or OAc substituents for **5** and **6**, respectively, occupy the axial positions. The distortion from the ideal trigonal-bipyramidal geometry is especially apparent in the C–Sn–C and O–Sn–O angles. The tin atoms in these compounds can also be regarded as [4+1]-coordinate, i.e. they represent model compounds along the transformation path tetrahedron $\leftrightarrow$ trigonal bipyramid.

Note that the disposition of the substituents implies the presence of an intrinsic inversion center in both **5** and **6**. However, in the crystal, the crystallographically imposed inversion center is retained only in the case of **5**. In the crystal structure of **6**, two out of the four butyl groups adopt different conformations and are slightly disordered (Figure 4); the inversion center is lost because of this.

Similar to **2**, the covalent Sn–O and coordination Sn–O bond lengths in the four-membered Sn_2O_2 rings of **5** and **6** are substantially different [2.054(2) and 2.246(2) $\text{\AA}$ for **5** and 2.054(2) and 2.277(2) and 2.058(2) and 2.271(2) $\text{\AA}$ for **6**, respectively]. However, in contrast to **2**, these bonds occupy mutually opposite rather than neighboring positions in the Sn_2O_2 rings.

According to the DFT calculations (see Supporting Information), there are no complexes of type **I** on the potential energy surfaces corresponding to the interactions of $[\text{Et}_2\text{SnCl}_2]$ with $[\text{Et}_2\text{Sn}(\text{OMe})_2]$ and $[\text{Bu}_2\text{Sn}(\text{OAc})_2]$ with $[\text{Bu}_2\text{Sn}(\text{OMe})_2]$. The rearrangement of X and OMe substituents to yield monomeric $[\text{R}_2\text{Sn}(\text{OMe})\text{X}]$ is exothermic ($\Delta H^0 = -1.5 \text{ kcal mol}^{-1}$ for $R = \text{Et}$, $X = \text{Cl}$ and

Scheme 2. The equilibria of “organotin analogs of Grignard reagents” in solution.^[9]Figure 3. View of complex **5**. The hydrogen atoms have been omitted for clarity. Displacement ellipsoids are scaled to the 50% probability level. The coordination bonds are shown by open lines.Figure 4. View of complex **6**. The hydrogen atoms have been omitted for clarity. Displacement ellipsoids are scaled to the 50% probability level. The coordination bonds are shown by open lines.Table 3. Selected bond lengths [Å] and angles [°] for **5**.^[a]

Sn(1)–O(1)	2.0539(19)	Sn(1)–O(1) ⁱⁱ	2.2464(19)
Sn(1)–C(4)	2.125(3)	Sn(1)–Cl(1)	2.5101(8)
Sn(1)–C(2)	2.126(3)		
O(1)–Sn(1)–C(4)	106.93(9)	O(1)–Sn(1)–Cl(1)	91.85(6)
O(1)–Sn(1)–C(2)	108.53(10)	C(4)–Sn(1)–Cl(1)	93.26(8)
C(4)–Sn(1)–C(2)	143.82(11)	C(2)–Sn(1)–Cl(1)	92.56(8)
O(1)–Sn(1)–O(1) ⁱⁱ	69.94(9)	Cl(1)–Sn(1)–O(1) ⁱⁱ	161.79(5)
C(4)–Sn(1)–O(1) ⁱⁱ	91.89(10)	Sn(1)–O(1)–Sn(1) ⁱⁱ	110.06(9)
C(2)–Sn(1)–O(1) ⁱⁱ	93.56(9)		

[a] Symmetry transformations used to generate equivalent atoms: ii: $-x, -y + 1, -z$.

$-3.0 \text{ kcal mol}^{-1}$ for $R = \text{Bu}$, $X = \text{OAc}$). Their further dimerization leads to complexes of type **II** ($\Delta H^0 = -16.2$ and $-14.2 \text{ kcal mol}^{-1}$, respectively).

Table 4. Selected bond lengths [Å] and angles [°] for **6**.

Sn(1)–O(2)	2.0538(18)	Sn(2)–O(1)	2.0577(18)
Sn(1)–C(5)	2.121(3)	Sn(2)–C(19)	2.129(3)
Sn(1)–C(9)	2.137(3)	Sn(2)–C(15)	2.133(3)
Sn(1)–O(3)	2.160(2)	Sn(2)–O(5)	2.1558(19)
Sn(1)–O(1)	2.2769(19)	Sn(2)–O(2)	2.2714(19)
O(2)–Sn(1)–C(5)	102.24(10)	O(1)–Sn(2)–C(15)	108.79(10)
O(2)–Sn(1)–C(9)	109.69(10)	C(19)–Sn(2)–C(15)	143.19(11)
C(5)–Sn(1)–C(9)	144.82(11)	O(1)–Sn(2)–O(5)	84.57(7)
O(2)–Sn(1)–O(3)	84.87(8)	C(19)–Sn(2)–O(5)	99.91(9)
C(5)–Sn(1)–O(3)	100.27(9)	C(15)–Sn(2)–O(5)	98.12(10)
C(9)–Sn(1)–O(3)	96.97(10)	O(1)–Sn(2)–O(2)	69.74(7)
O(2)–Sn(1)–O(1)	69.70(7)	C(19)–Sn(2)–O(2)	88.72(10)
C(5)–Sn(1)–O(1)	89.50(9)	C(15)–Sn(2)–O(2)	88.74(10)
C(9)–Sn(1)–O(1)	88.04(10)	O(5)–Sn(2)–O(2)	154.24(7)
O(3)–Sn(1)–O(1)	154.22(7)	Sn(2)–O(1)–Sn(1)	110.09(8)
O(1)–Sn(2)–C(19)	104.65(10)	Sn(1)–O(2)–Sn(2)	110.44(8)

Conclusions

The isolation of complexes **2**, **5**, and **6** provides evidence for the existence of complexes $R_2\text{SnXY} \cdot R_2\text{SnXY}$ ($R = \text{Alk}$, Ar ; $X, Y = \text{Hal, OR}$, $X \neq Y$) both as unsymmetrical adducts $[R_2\text{SnX}_2 \cdot R_2\text{SnY}_2]$ and symmetrical dimers $[R_2\text{SnXY}]_2$. Moreover, it has been unambiguously proved for the first time that compounds of the type $[R\text{SnX}_3]$ are able to undergo a hydrocarbon substituent redistribution reaction. The similarity of the redistribution reactions of hypercoordinate organotin compounds containing electron-donating groups both in the hydrocarbon R and in the functional X substituents indicates that the chemical properties of these compounds are determined primarily by the coordination mode of the tin atom rather than by the types of ligands. We believe that our findings open-up alluring prospects for the investigation of different transmetallation processes.

Experimental Section

General Procedures: All manipulations 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. $[\text{PhSnCl}_3]$,^[11] $[\text{MeSnCl}_3]$,^[11] $[\text{EtSnI}_3]$,^[11] $[\text{Et}_3\text{Sn}(\text{OCH}_2\text{CH}_2\text{-NMe}_2)]$,^[3a] $[\text{Et}_2\text{Sn}(\text{Cl})(\text{OMe})_2]$ (**5**),^[8] and $[\text{Bu}_2\text{Sn}(\text{OAc})(\text{OMe})_2]$ (**6**)^[8] were synthesized as described earlier. NMR spectra were recorded with a Bruker AM-360 NMR spectrometer at 360.134 MHz (^1H) and 90.555 MHz (^{13}C) for samples in CDCl_3 or CD_2Cl_2 . Chemical shifts are relative to SiMe_4 for H , C or indirectly refer-

enced to TMS via the solvent signals. The accuracy of the coupling constants is ± 0.1 Hz, and the accuracy of chemical shift measurements is ± 0.01 ppm for ^1H and ± 0.05 ppm for ^{13}C . Melting points were measured in sealed capillaries with a SANYO Gallenkamp PLC melting point apparatus without any additional corrections. Elemental analyses were performed on a Carlo Erba EA1108 CHNS-O elemental analyzer.

[PhSn(OCH₂CH₂NMe₂)₂Cl] (1): A solution of [PhSnCl₃] (3.78 g, 12.50 mmol) in thf (20 mL) was added to an intensely stirred solution of [Et₃Sn(OCH₂CH₂NMe₂)₂] (11.85 g, 40.35 mmol) in 70 mL of thf. The solution was stirred for 2 h. The solvent was then removed under vacuum to about one sixth of the initial volume and 70 mL of hexane was added. A white crystalline precipitate was obtained, filtered, and washed three times with hexane (in 30 mL portions) and dried in vacuo. The yield was 3.05 g (60%). M.p. 129–131 °C. C₁₄H₂₅ClN₂O₂Sn (407.50): calcd. C 41.26, H 6.18, N 6.87; found C 40.98, H 6.55, N 6.40. ^1H NMR ([D₈]thf): δ = 2.29 (br. s, 12 H, Me₂N), 2.62–2.68, 2.76–2.86 (two br. m, 4 H, NCH₂), 3.81–3.86, 3.93–3.99 (two br. m, 4 H, OCH₂), 7.10–7.40 (m, 3 H, Ph), 8.12–8.40 (br. s, $^3J_{\text{Sn,H}}$ = 99.0 Hz, 2 H, Ph) ppm. ^{13}C NMR ([D₈]thf): δ = 46.12 (br., Me₂N), 58.59 (NCH₂), 63.47 (OCH₂), 128.60 ($^3J_{\text{Sn,C}}$ = 112/108 Hz, C_m), 129.52 ($^4J_{\text{Sn,C}}$ = 21.6 Hz, C_p), 138.04 (br., $^2J_{\text{Sn,C}}$ = 61.7 Hz, C_o), 148.99 (C_i) ppm.

[Ph₂SnCl₂·Ph₂Sn(OCH₂CH₂NMe₂)₂] (2): A solution of [Et₃Sn(OCH₂CH₂NMe₂)₂] (7.82 g, 26.63 mmol) in thf (30 mL) was added slowly to a stirred solution of [PhSnCl₃] (4.08 g, 13.50 mmol) in Et₂O (50 mL) or thf (50 mL) at room temperature. A large amount of white precipitate appeared immediately. After stirring the mixture for 2 h and storing it overnight the white precipitate was filtered, washed with benzene, and dried in vacuo. The yield of white

solid was 1.33 g (49.7% scaled to the amount of [PhSnCl₃]). M.p. 168.7–169 °C. C₃₂H₄₀Cl₂N₂O₂Sn₂ (792.94): calcd. C 48.47, H 5.08, N 3.53; found C 48.30, H 5.30, N 3.55. ^1H NMR (CD₂Cl₂): δ = 2.36 (br. s, 12 H, NMe₂), 2.73–2.78 (br. m, 4 H, NCH₂), 3.91–3.96 (br. m, 4 H, OCH₂), 7.87–7.91, 7.10–7.50 (two m, 20 H, Ph) ppm. ^{13}C NMR (CD₂Cl₂): δ = 45.45 (br., NMe₂), 45.60, 45.92 (NMe₂), 60.43, 61.06 (NCH₂), 62.48 (br., OCH₂), 128.87, 129.10 (C_m), 129.03, 129.40 (C_p), 130.11, 130.51 (C_o), 136.03, 136.20 (C_i) ppm.

Reaction of [PhSn(OCH₂CH₂NMe₂)₂Cl] (1) With [PhSnCl₃] (NMR Experiment): A solution of **1** (0.52 g, 1.3 mmol) and [PhSnCl₃] (0.39 g, 1.3 mmol) in thf (10 mL) was mixed in a vacuum of 10^{-3} Torr. The mixture was stored for 1 h at about 20 °C, then thf was removed by evacuation and CD₂Cl₂ (1 mL) was introduced. The solution was transferred to a 5-mm NMR tube and sealed. According to the ^1H and ^{13}C NMR spectra, the solution contained [Cl₂Sn(OCH₂CH₂NMe₂)₂] and [Ph₂SnCl₂] as the main products. Ph₂SnCl₂: ^1H NMR (CD₂Cl₂): δ = 7.60–7.67 (m, 3 H, Ph), 7.81–7.84 (m, $^3J_{\text{Sn,H}}$ = 81.2 Hz, 2 H, Ph) ppm. ^{13}C NMR (CD₂Cl₂): δ = 130.32 (3J = 85.1 Hz, C_m), 132.48 (4J = 18.4 Hz, C_p), 135.57 (2J = 63.6 Hz, C_o), 137.50 (C_i) ppm.

[Cl₂Sn(OCH₂CH₂NMe₂)₂]: A solution of [Sn(OCH₂CH₂NMe₂)₂] (1.76 g, 5.96 mmol) in thf (15 mL) was quickly added to an intensely stirred solution of HgCl₂ (1.62 g, 5.96 mmol) in thf (20 mL). A large amount of heavy dark-grey precipitate appeared immediately. The mixture was stirred for 30 min and stored overnight. After filtration, the solvent was removed under vacuum to about one sixth of the initial volume. After addition of hexane (50 mL) a white crystalline precipitate was obtained. This was filtered under argon, washed with hexane, and dried in vacuo. The yield was 2.12 g (97%). M.p. 205 °C (with decomp.). C₈H₂₀Cl₂N₂O₂Sn

Table 5. Crystallographic data for **1**, **2**, **5**, and **6**.

	1	2	5	6
Empirical formula	C ₁₄ H ₂₅ ClN ₂ O ₂ Sn	C ₃₂ H ₄₀ Cl ₂ N ₂ O ₂ Sn ₂	C ₁₀ H ₂₆ Cl ₂ O ₂ Sn ₂	C ₂₂ H ₄₈ O ₆ Sn ₂
<i>FW</i>	407.50	792.94	486.59	645.98
<i>T</i> [K]	120	120	100	100
Crystal size [mm]	0.2 × 0.2 × 0.1	0.2 × 0.2 × 0.2	0.3 × 0.2 × 0.2	0.3 × 0.2 × 0.2
Crystal system	monoclinic	monoclinic	orthorhombic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>Pbca</i>	<i>P</i> 2 ₁
<i>a</i> [Å]	11.496(2)	18.208(3)	8.5007(16)	8.2721(4)
<i>b</i> [Å]	8.7351(17)	10.1149(11)	13.843(3)	20.433(2)
<i>c</i> [Å]	16.660(3)	19.274(3)	14.118(3)	8.3571(5)
α [°]	90	90	90	90
β [°]	90.947(6)	116.799(5)	90	100.660(5)
γ [°]	90	90	90	90
<i>V</i> [Å ³]	1672.7(5)	3168.4(8)	1661.4(6)	1388.17(17)
<i>Z</i>	4	4	4	2
<i>D_c</i> [g cm ⁻³]	1.618	1.662	1.945	1.545
<i>F</i> (000)	824	1584	944	656
μ [mm ⁻¹]	1.690	1.777	3.316	1.829
$2\theta_{\text{max}}$ [°]	56	54	56	56
Index range	−15 ≤ <i>h</i> ≤ 15 −11 ≤ <i>k</i> ≤ 11 −19 ≤ <i>l</i> ≤ 22	−23 ≤ <i>h</i> ≤ 23 −12 ≤ <i>k</i> ≤ 12 −24 ≤ <i>l</i> ≤ 24	−11 ≤ <i>h</i> ≤ 11 −18 ≤ <i>k</i> ≤ 18 −18 ≤ <i>l</i> ≤ 18	−10 ≤ <i>h</i> ≤ 10 −27 ≤ <i>k</i> ≤ 26 −11 ≤ <i>l</i> ≤ 11
No. of reflections collected	13779	14829	15113	13583
No. of unique reflections	3972	3453	1984	6565
No. of reflections with <i>I</i> > 2σ(<i>I</i>)	3010	2434	1927	6515
Data/restraints/parameters	3972/6/181	3453/0/182	1984/0/73	6565/10/272
<i>R</i> 1; <i>wR</i> 2 [<i>I</i> > 2σ(<i>I</i>)]	0.0401; 0.0986	0.0496; 0.1121	0.0248; 0.0548	0.0210; 0.0537
<i>R</i> 1; <i>wR</i> 2 (all data)	0.0570; 0.1100	0.0712; 0.1206	0.0260; 0.0555	0.0213; 0.0538
GOF on <i>F</i> ²	1.009	1.038	1.018	1.022
<i>T</i> _{min} ; <i>T</i> _{max}	0.676; 0.878	0.660; 0.730	0.390; 0.500	0.590; 0.690

(365.87): calcd. C 26.26, H 5.51, N 7.66; found C 26.05, H 5.41, N 7.40. ^1H NMR (CD_2Cl_2): δ = 2.73, 2.74 (two s, 12 H, Me); 2.83–2.86 (m, 4 H, CH_2N), 3.80–3.85 (m, 4 H, CH_2O) ppm. ^{13}C NMR (CD_2Cl_2): δ = 46.78, 46.87 (two s, Me_2N), 58.03 ($^3J_{\text{Sn,C}}$ = 24.5 Hz, CH_2N), 63.02 ($^2J_{\text{Sn,C}}$ = 57.5 Hz, CH_2O) ppm.

[MeSn(OCH₂CH₂NMe₂)₂Cl] (3): A solution of $[\text{Et}_3\text{Sn}(\text{OCH}_2\text{CH}_2\text{NMe}_2)]$ (6.65 g, 23.33 mmol) in Et_2O (20 mL) was added dropwise to a stirred solution of $[\text{MeSnCl}_3]$ (2.80 g, 11.66 mmol) in Et_2O (30 mL). After two hours of stirring an abundant white precipitate had formed. This was filtered, washed with hexane, and dried in vacuo. The yield was 2.49 g (61.8%). M.p. 139–140 °C. $\text{C}_9\text{H}_{23}\text{ClN}_2\text{O}_2\text{Sn}$ (345.45): calcd. C 31.29, H 6.71, N 8.11; found C 31.05, H 6.80, N 7.97. ^1H NMR (CD_2Cl_2): δ = 0.71 (br. s, $^2J_{\text{Sn,H}}$ = 99.0/103.6 Hz, 3 H, MeSn), 2.57 (br. s, 12 H, Me_2N), 2.70 (br., 4 H, CH_2N), 3.78 (br. m, 4 H, CH_2O) ppm. ^{13}C NMR (CD_2Cl_2): δ = 10.80 (MeSn), 46.27 (Me_2N), 58.74 (br., CH_2N), 63.61 (br., CH_2O) ppm.

[EtSn(OCH₂CH₂NMe₂)₂] (4): A solution of $[\text{Et}_3\text{Sn}(\text{OCH}_2\text{CH}_2\text{NMe}_2)]$ (4.47 g, 15.21 mmol) in thf (25 mL) was added dropwise to a stirred solution of EtSnI_3 (4.04 g, 7.64 mmol) in Et_2O (30 mL). The mixture was stirred for 2 h and stored overnight. The solvent was removed in vacuo to about one sixth of the initial volume, then 50 mL of hexane was added to give a white crystalline precipitate. This was filtered under argon, washed with hexane, and dried in vacuo. The yield was 1.90 g (56%). M.p. 108–109 °C. $\text{C}_{10}\text{H}_{25}\text{IN}_2\text{O}_2\text{Sn}$ (450.93): calcd. C 26.64, H 5.59, N 6.21; found C 26.35, H 5.78, N 6.15. ^1H NMR (CD_2Cl_2): δ = 1.20 (m, 3 H, $\text{CH}_3\text{CH}_2\text{Sn}$), 1.73 (m, 2 H, $\text{CH}_3\text{CH}_2\text{Sn}$), 2.63 (br. s, 12 H, Me_2N), 2.72 (br., 4 H, CH_2N), 3.80 (br. m, 4 H, CH_2O) ppm. ^{13}C NMR (CD_2Cl_2): δ = 10.49 (br., $\text{CH}_3\text{CH}_2\text{Sn}$), 13.39 ($^2J_{\text{Sn,C}}$ = 64.4 Hz, $\text{CH}_3\text{CH}_2\text{Sn}$), 46.82 (br., Me_2N), 58.66 (CH_2N), 63.32 (CH_2O) ppm.

X-ray Crystal Structure Determination: Data were collected on a Bruker three-circle diffractometer equipped with a SMART 1000 CCD detector and corrected for absorption using the SADABS program.^[12] Data reduction was performed with the SMART^[13] and SAINTPlus^[14] programs (see Table 5 for details). The structures were solved by direct methods and refined by full-matrix least-squares on F^2 with anisotropic thermal parameters for non-hydrogen atoms. The value of the Flack parameter for complex **6**, 0.363(18), indicates that the absolute structure in this case cannot be determined unambiguously due to the specific centrosymmetric arrangement of the heavy tin atoms as well as most of the substituents (see above). All calculations were carried out using the SHELXTL program (PC Version 5.10).^[15]

CCDC-607745 through -607748 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.

Supporting Information (see also the footnote on the first page of this article): Details of the quantum-chemical calculations.

Acknowledgments

This work was supported financially by the Russian Foundation for Basic Research (projects nos. 04-03-32662 and 04-03-32549) and the Russian Academy of Sciences within the frame of the subprogram “Theoretical and experimental study of chemical bonding and

mechanisms of chemical reactions and processes”. We thank Dr. M. G. Kuznetsova for performing the multinuclear NMR measurements.

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Received: June 6, 2006

Published Online: September 13, 2006