Gradient-Enhanced 2D Multinuclear NMR and X-ray Diffraction Studies of Reaction Products of Dimethyltin(IV) Salicylaldoximate with Chiral Alcohols

Abdelkrim Meddour[a][+], Abdeslam Bouhdid[b], Marcel Gielen[b], Monique Biesemans[a,b], Frédéric Mercier[a,b], Edward R. T. Tiekink[c], and Rudolph Willem*[a,b]

High Resolution NMR Centre (HNMR)[a] and Laboratory of General and Organic Chemistry (AOSC)[b],
Free University of Brussels (VUB),
Pleinlaan 2, B-1050 Brussels, Belgium
Fax: (internat.) + 32-2/629-3281
E-mail: rwillem@vub.ac.be

Department of Chemistry, The University of Adelaide[c],
Australia 5005

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The complex {[$(CH_3)_2Sn]_2$[$(CH_3)_2SnO$](OCH_3)(HONZO)(ONZO)} (**3**) [ONZOH is the oximate residue, *o*-(–ON=CH–C_6H_4–OH), HONZO the corresponding phenolate residue, *o*-(HON=CH–C_6H_4–O–), and ONZO the dibasic species *o*-(–ON=CH–C_6H_4–O–), all derived from salicylaldoxime, *o*-(HON=CH–C_6H_4–OH)] reacts with an excess of racemic (*d*,*l*)-2-methyl-1-butanol to afford the μ_2-substitution product **5a** {[$(CH_3)_2Sn]_2$[$(CH_3)_2SnO$][$OCH_2CH(CH_3)CH_2CH_3$](HONZO)(ONZO)]}. Crystallographic characterisation of the trinuclear microcluster **5a** shows the presence of the monobasic HONZO ligand in a tridentate μ_2-O,N mode and of the dibasic ONZO ligand in a tridentate O,N,O mode. This coordination mode leads to one seven-coordinate and two five-coordinate tin centers that are linked by a μ_3-oxo function. The coordination geometries are distorted pentagonal bipyramidal and trigonal bipyramidal, respectively. The two low-coordinate tin atoms are linked by the alkoxide ion. The corresponding chiral (*S*)-2-methyl-1-butanol reacts analogously to yield **5b**. By contrast, reaction of **3** with chiral secondary alcohols (2-butanol or 1-phenyl-1-ethanol), in various molar ratios, failed to provide the corresponding μ_2-alkoxy complex. Instead, pure crystals of {[$(CH_3)_2Sn]_2$[$(CH_3)_2SnO$](OH)(HONZO)(ONZO)} (**2a**) were isolated.

Introduction

Reaction of salicylaldoxime, *o*-(HON=CH−C_6H_4−OH), and diorganotin(IV) oxide, R_2SnO (R = Me, *n*-Bu), yields small clusters represented as [$(R_2Sn)_2(R_2SnO)$(ONZOH)(HONZO)(ONZO)] (**1b**: R = *n*-Bu; **2b**: R = Me), where ONZOH is the oximate residue *o*-(−ON=CH−C_6H_4−OH), HONZO is the phenolate *o*-(HON=CH−C_6H_4−O−), and ONZO is the dibasic species *o*-(−ON=CH−C_6H_4−O−), associated with salicylaldoxime[1]. Their general structure is displayed in Figure 1[1].

Attempts to crystallize crude **1b** or **2b** with hydroxylated solvents usually lead to substitution compounds like the μ_2-hydroxy-bridged compound **1a** (R = *n*-Bu)[1a], or a μ_2-alkoxy-bridged compound (R = Me)[1b], as e.g. **3**, the μ_2-bridged ONZOH unit being eliminated as salicylaldoxime (HONZOH).

Such compounds undergo facile reversible μ_2-nucleophilic substitutions with protonated nucleophiles, according to Scheme 1[2][3].

X-ray data on several such compounds reveal that ligand A is planar, with Sn(1), Sn(2) and Sn(3) being coplanar. By contrast, ligand B is dramatically twisted since the atom N18 is 0.3 Å away from the mean plane of the aromatic ring with which it is associated[1a][1b][2]. As a consequence, these derivatives have a chiral skeleton in the solid state.

In order to assess whether this skeleton chirality could be detected in solution, we prepared dimethyltin salicylaldoximate derivatives containing a ligand with a chiral center bridging the Sn(2) and Sn(3) tin atoms. Provided the chirality of the cluster skeleton would be maintained in solution, it should indeed be observable through the formation of the diastereoisomers necessarily obtained[4].

This paper presents solid-state and solution characterization by X-ray diffraction and 1D- and 2D-NMR spectroscopy, mainly gradient assisted[5] ^1H-^{13}C HMQC[6a] and HMBC[6b][6c] and ^1H-^{119}Sn HMQC[7], of compounds derived from the reaction of **3** with chiral alcohols. The first tris(dimethyltin) disalicylaldoximate with a chiral μ_2-bridged alkoxy ligand is reported.

Results and Discussion

Synthesis

Reaction of **3** with an excess of racemic (*d*,*l*)-2-methyl-1-butanol provides, after recrystallization from dichlorometh-

[+] Present address: Laboratoire de Chimie Structurale Organique, Université de Paris-Sud, Bât. 410, ICMO, CNRS URA no. 1384, F-91405 Orsay Cedex, France.

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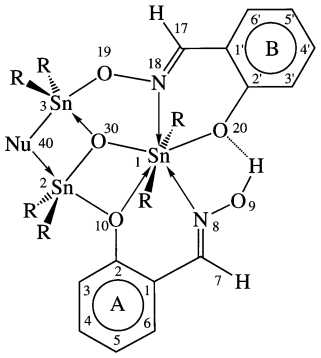
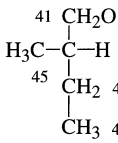
Figure 1. General structure, with atom labelling, of compounds from several condensation reactions between di-*n*-butyl or dimethyltin(IV) oxide and salicylaldoxime (HONZOH); HOZNO represents the salicylaldoximate residue bound to O40 by the oxygen atom of its oximate moiety[1][2][3]; Nu stands for a nucleophile μ_2-bridging the five-coordinate tin atoms Sn2 and Sn3



	Nu	R
1a	HO	n-Bu
1b	HOZNO	n-Bu
2a	HO	Me
2b	HOZNO	Me
3	MeO	Me
4	F	Me
5		Me

Scheme 1

$$[(R_2Sn)_2(R_2SnO)(Nu)(HONZO)(ONZO)] + Nu'\text{-}H \rightleftharpoons [(R_2Sn)_2(R_2SnO)(Nu')(HONZO)(ONZO)] + Nu\text{-}H$$

ane/hexane (1:1), pure crystals of μ_2-(*d,l*)-2-methylbutoxydimethyltin salicylaldoximate (**5a**) (Figure 1). Similarly, crystals of μ_2-(*S*)-2-methylbutoxydimethyltin salicylaldoximate (**5b**) were obtained starting from (*S*)-(−)-2-methyl-1-butanol.

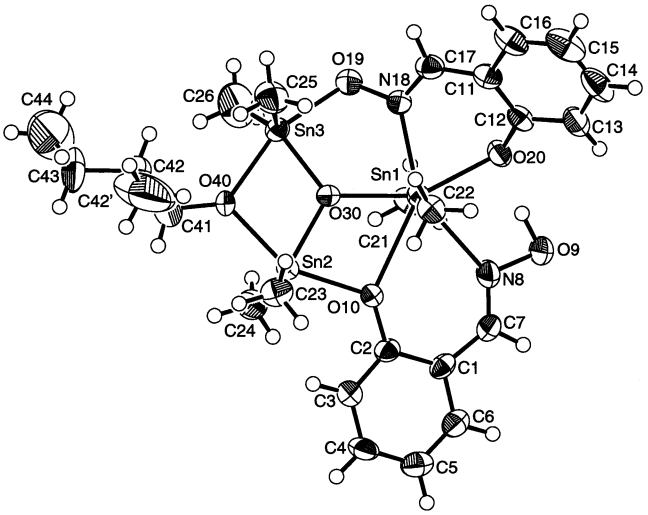
By contrast, reaction of **3** with chiral secondary alcohols (2-butanol or 1-phenyl-1-ethanol), in various molar ratios, failed to provide the corresponding crystalline μ_2-alkoxy complex. Instead, pure crystals of **2a** were isolated; the compound **2a** was observed so far only as a transient[1b][2][3], where the μ_2-methoxy moiety of **3** is substituted for a μ_2-hydroxy one.

NMR analysis of the crude product obtained by reaction of **3** with secondary alcohols revealed the presence of the desired μ_2-(*sec*)-alkoxy compound in small fractions, depending on the starting alcohol, in addition to **3** and **2b**. Monitoring the reaction of **3** with (*d,l*)-2-butanol by ^{1}H, ^{13}C and ^{119}Sn NMR reveals an equilibrium mixture with the μ_2-1-methylpropoxy compound as a minor species, even when the secondary alcohol is used in large excess. This result implies that a μ_2-alkoxy moiety bridging Sn(2) and Sn(3) is more stable when it originates from a primary alcohol than from a secondary one, probably due to steric hindrance of the latter.

X-ray Diffraction Analysis of Compound 5a

The molecular structure of **5a** resembles closely those found for related systems[1][2][3] and hence, only a brief description of **5a** is given (Figure 2).

Figure 2. Molecular structure and crystallographic numbering scheme employed for **5a**



There are two distinct coordination geometries about the tin atoms in the trinuclear structure. The Sn(1) atom is seven-coordinate, existing in a distorted pentagonal bipyramidal geometry with the methyl substituents occupying axial positions, C−Sn−C is 167.4(3)°. The equatorial plane is defined by the phenoxide O(10) and O(20) atoms, the oxime N(8) and N(18) atoms and an oxo O(30) atom. In this description, the Sn(1) atom lies 0.0012(4) Å out of the plane in the direction of the C(21) atom. The remaining tin atom geometries are based on trigonal bipyramidal geometries defined by the oxo O(30) atom, the alkoxide O(40) atom, two methyl substituents and for Sn(2) the phenoxide O(10) atom and for Sn(3) the oxime O(19) atom. The Sn(2) atom lies 0.0932(4) Å above the $C_2O(30)$ trigonal plane in the direction of the O(10) atom and the deviation of the Sn(3) atom from the $C_2O(30)$ plane is 0.0324(4) Å, in the direction of the O(19) atom. The geometric parameters describing **5a** (Table 1) are in essential agreement with those found in the analogous T = Me, Et, *n*Pr and *i*Pr structures[1b]. Notable features in the structure include the presence of the tri-coordinate O(30) atom, the symmetric alkoxide bridge [Sn(2)−O(40) is 2.164(4) Å and Sn(3)−O(40) is 2.174(4) Å], and an intramolecular hydrogen bond formed between the O(9)*H* and O(20) atoms such that O(9)*H*···O(20) is 1.59 Å and O(9)−H···O(20) is 166°. The crystal structure of **5a** is comprised of equal amounts of the *R* and *S* forms of the chiral alcohol, i.e. is racemic.

An investigation of the structure of the chiral *S* form of the compound, i.e. **5b**, was also undertaken[8]. The crystal

Table 1. Selected bond lengths [Å] and angles [°] for **5a**

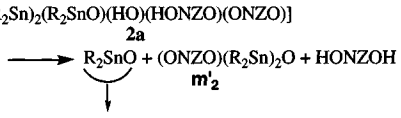
Sn(1)−O(10)	2.634(4)	Sn(1)−O(20)	2.193(4)
Sn(1)−O(30)	2.171(4)	Sn(1)−N(8)	2.543(6)
Sn(1)−N(18)	2.291(5)	Sn(1)−C(21)	2.091(7)
Sn(1)−C(22)	2.103(7)	Sn(2)−O(10)	2.149(4)
Sn(2)−O(30)	2.001(4)	Sn(2)−O(40)	2.164(4)
Sn(2)−C(23)	2.104(7)	Sn(2)−C(24)	2.102(7)
Sn(3)−O(19)	2.115(5)	Sn(3)−O(30)	1.999(4)
Sn(3)−O(40)	2.174(4)	Sn(3)−C(25)	2.097(8)
Sn(3)−C(26)	2.077(9)	O(9)−N(8)	1.425(7)
O(10)−C(2)	1.349(7)	O(19)−N(18)	1.368(7)
O(20)−C(12)	1.333(7)	N(8)−C(7)	1.284(8)
N(18)−C(17)	1.276(8)		
O(10)−Sn(1)−O(20)	142.5(1)	O(10)−Sn(1)−O(30)	65.2(1)
O(10)−Sn(1)−N(8)	67.6(2)	O(10)−Sn(1)−N(18)	142.2(2)
O(10)−Sn(1)−C(21)	88.4(2)	O(10)−Sn(1)−C(22)	81.8(2)
O(20)−Sn(1)−O(30)	152.3(1)	O(20)−Sn(1)−N(8)	75.1(2)
O(20)−Sn(1)−N(18)	75.1(2)	O(20)−Sn(1)−C(21)	89.9(2)
O(20)−Sn(1)−C(22)	93.2(2)	O(30)−Sn(1)−N(8)	132.4(2)
O(30)−Sn(1)−N(18)	77.4(2)	O(30)−Sn(1)−C(21)	90.7(2)
O(30)−Sn(1)−C(22)	92.2(2)	N(8)−Sn(1)−N(18)	150.2(2)
N(8)−Sn(1)−C(21)	82.0(2)	N(8)−Sn(1)−C(22)	87.0(2)
N(18)−Sn(1)−C(21)	97.7(2)	N(18)−Sn(1)−C(22)	94.8(2)
C(21)−Sn(1)−C(22)	167.4(3)	O(10)−Sn(2)−O(30)	78.2(2)
O(10)−Sn(2)−O(40)	151.7(2)	O(10)−Sn(2)−C(23)	100.1(2)
O(10)−Sn(2)−C(24)	97.4(2)	O(30)−Sn(2)−O(40)	73.6(2)
O(30)−Sn(2)−C(23)	115.0(2)	O(30)−Sn(2)−C(24)	116.5(3)
O(40)−Sn(2)−C(23)	93.1(2)	O(40)−Sn(2)−C(24)	93.8(2)
C(23)−Sn(2)−C(24)	127.9(3)	O(19)−Sn(3)−O(30)	85.3(2)
O(19)−Sn(3)−O(40)	158.2(2)	O(19)−Sn(3)−C(25)	95.3(3)
O(19)−Sn(3)−C(26)	91.4(3)	O(30)−Sn(3)−O(40)	73.4(2)
O(30)−Sn(3)−C(25)	111.1(3)	O(30)−Sn(3)−C(26)	119.0(4)
O(40)−Sn(3)−C(25)	96.6(3)	O(40)−Sn(3)−C(26)	94.9(3)
C(25)−Sn(3)−C(26)	129.8(4)	Sn(1)−O(10)−Sn(2)	97.1(1)
Sn(1)−O(10)−C(2)	138.7(4)	Sn(2)−O(10)−C(2)	124.2(4)
Sn(3)−O(19)−N(18)	116.1(4)	Sn(1)−O(20)−C(12)	122.2(4)
Sn(1)−O(30)−Sn(2)	119.3(2)	Sn(1)−O(30)−Sn(3)	128.0(2)
Sn(2)−O(30)−Sn(3)	112.7(2)	Sn(2)−O(40)−Sn(3)	100.3(2)
Sn(1)−N(8)−O(9)	109.8(4)	Sn(1)−N(8)−C(7)	139.1(5)
Sn(1)−N(18)−O(19)	119.6(4)	Sn(1)−N(18)−C(17)	125.0(5)

structure obtained for a crystal chosen from the recrystallisation of **5b** shows the presence of both the *S* form as well as a small amount of the *R* form. The asymmetric unit contains two pseudo-centrosymmetrically related molecules. One site contains 100% of the *S* form, while the other site contains 58.6% of the *R* form, giving a 1.414(22):0.586 ratio of the two forms in the crystal investigated. A number of crystals were examined and similar results were obtained each time, including under conditions of low temperature (200 K). Presumably, the centrosymmetric structure packing ($P2_1/c$) is thermodynamically favoured implying that the better grown crystals have a higher percentage of the minor component[8]. The geometric features determined for **5b** are as described for the racemic species.

Solution-State Structure

Dissolving dimethyltin salicylaldoximates usually gives rise to minor species involved in a complex equilibrium, among which **2b** and the dimethyl analogue of m_2[1a]. In benzene solution, **5** remains the major species. By contrast, when **2a** is dissolved in C_6D_6, it remains only as a minor species, the transient signals of m_2 dominating the ^{119}Sn NMR spectrum. This is accompanied by an important precipitation in the NMR tube. This observation is accounted for by the reaction of Scheme 2.

Scheme 2

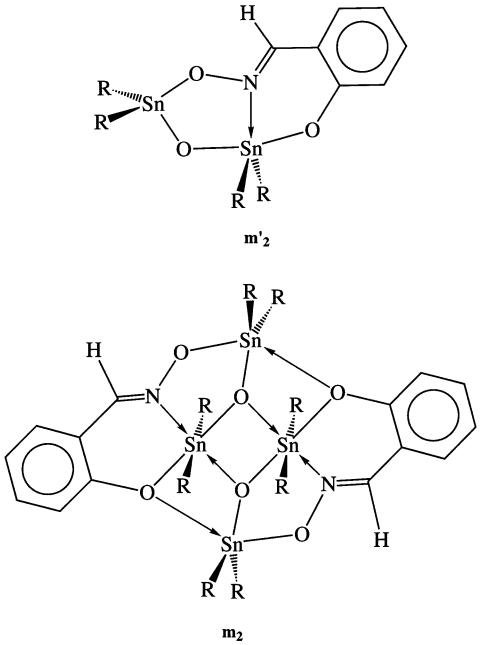


The structures of m'_2, and of its resulting dimer, m_2, proposed from comparable observations[1a] on the corresponding di-*n*-butyltin compound **1a**, are shown in Figure 3. Further evidence to the reaction of Scheme 2 is the observation of the oximic ^{1}H resonance of free salicylaldoxime.

In $CDCl_3$, the transient fractions remain low. Lowering the temperature increases the fraction of **2a** in the mixture, enabling its full NMR characterization at 270 K.

Table 2 presents an overview of the ^{1}H, ^{13}C, and ^{119}Sn chemical shifts and coupling constants associated with the dimethyltin moieties. The ^{1}H,^{13}C and ^{119}Sn resonances of **5** and **2a** were assigned with exactly the same strategy as reported previously for **2b**, **3** and **4**, using 2D gradient-enhanced ^{1}H-^{13}C HMQC and HMBC spectroscopy[5][6][7] and ^{1}H-^{119}Sn HMQC spectroscopy[1][2][3][6], evidencing the same basic tritin cluster structure for **5** and **2a** as for **2b** and

Figure 3. Transients generated from dissolving compound **2a** in C_6D_6 (see text)



of Sn(1), probably because the latter are too remote from the chiral center.

NMR spectra of **5** do not show any evidence of skeletal chirality in dimethyltin salicylaldoximate in addition to that arising from the chiral alkoxide moiety. Indeed, additional skeletal chirality observable on the NMR time scale should have provided two racemic diastereoisomers resulting in further unequal duplication of the ^{119}Sn resonances of all three Sn(1), Sn(2) and Sn(3) atoms. This expectation remained unfulfilled in spite of the very high sensitivity to the electronic environment of the ^{119}Sn nucleus evidenced by its wide chemical shift range (3000 ppm)[4][9]. Hence, it can be concluded that the observed splitting of equal intensity in the ^{1}H and ^{13}C resonances for **5** is due to a pairwise anisochrony of the two methyl groups within each of the five-coordinate tin atoms generated by their vicinity to the stereogenic carbon centre of the chiral alkoxy ligand.

Conclusion

This paper has addressed several issues unsolved so far in the chemistry of tris(dimethyltin) disalicylaldoximates. First, a chiral group could be incorporated for the first time

Table 2. ^{119}Sn-, ^{13}C- and ^{1}H-NMR data for the dimethyltin moieties of compounds **5** and **2a**[a]

Compd.	Moiety	δ(^{119}Sn)	^nJ(^{119}Sn-$^{119/117}$Sn)[b]	δ(^{13}C)	^1J(^{13}C-$^{119/117}$Sn)	δ(^{1}H)	^2J(^{1}H-^{119}Sn)
5[c]	$Me_2Sn(1)$	−458.0	356; /[d]	14.82	1107/1058	1.103	114
	$Me_2Sn(2)$	−141.8	102; 64	2.56/2.51	637/603	0.517/0.511	75
	$Me_2Sn(3)$	−130.6	351; 104	−0.16/−0.27	661/636	0.493/0.491	75
2a[e]	$Me_2Sn(1)$	−458.5	/;/[d]	14.04	1104/1062	0.813	111
	$Me_2Sn(2)$	−142.6	66; 66	4.44	677/648	0.793	76
	$Me_2Sn(3)$	−130.9	339; 72	1.89	669/640	0.623	76

[a] Chemical-shift data in ppm and coupling constants in Hz. − [b] Averaged values from unresolved ^nJ(^{119}Sn-^{119}Sn) and ^nJ(^{119}Sn-^{117}Sn) coupling satellites in ^{119}Sn spectrum. − [c] Spectrum recorded from a C_6D_6 solution of **5** at 303 K. − [d] Invisible satellites because of broad ^{119}Sn(1) resonance feet. − [e] Spectrum recorded from a $CDCl_3$ solution of **2a** at 270 K.

3 (Figure 1). The ^{1}H-^{119}Sn HMQC cross peaks of **5** and **2a** reviewed in Table 3, similar to those of **1a**, **1b**, **2b** and **3**, support this conclusion, as do all the ^1J(^{13}C-$^{119/117}$Sn), ^nJ(^{119}SN−O-$^{119/117}$Sn), and ^2J(^{1}H-$^{119/117}$Sn) coupling data.

Characteristically, the ^{1}H-^{119}Sn HMQC spectrum of **5** shows a cross peak between the two diastereotopic protons, H(41A) and H(41B) of the 2-methylbutoxy group, and both Sn(2) and Sn(3) atoms. In the case of **2a**, a correlation is observed between the hydroxy proton, H(40), and both Sn(2) and Sn(3) tin atoms. These correlations are in agreement with the binding site of the entering nucleophile between Sn(2) and Sn(3).

The ^{1}H and ^{13}C methyl resonances of Sn(2) and Sn(3) in compound **5** are duplicated (Table 2). This is in agreement with the pairwise diastereotopism of the Sn(2) and Sn(3) methyl groups due to the presence of the chiral carbon atom C(42) (see below). These features are observed both in **5a**, obtained from racemic (*R*,*S*)-2-methyl-1-butanol, and **5b** from enantiomerically enriched (*S*)-2-methyl-1-butanol. Such an anisochrony is not observed for the methyl groups

into such a complex. Second, the limits of the reactivity of these complexes towards alcohols have clearly been defined. Thus, while primary alcohols smoothly react towards the corresponding μ_2-alkoxy-substituted complex, even when the substituent on the CH_2OH moiety is rather bulky, secondary alcohols, apart from 2-propanol[1b], fail to yield the corresponding μ_2-substitution products. A steric effect from a moderately bulky group is responsible for this. Third, the first clear evidence of chirality-related anisochrony of the two methyl groups on the dimethyltin moieties demonstrates that their diastereotopism can be induced on the NMR time scale only by the introduction of a μ_2-bridged chiral group into the complex. Accordingly, this rules out that the skeletal chirality displayed by these microclusters in the crystalline state remains observable in solution on the ^{119}Sn-NMR time scale, no anisochrony being visible without chiral substituent. This suggests a fast inversion of the skeletal chirality on this time scale. Last, albeit unexpected, the μ_2-hydroxy-bridged complex could be fully isolated, having been observed only as a transient so far[1][2]. Actu-

Table 3. ^{1}H-^{119}Sn correlation data as obtained from 2D ^{1}H-^{119}Sn HMQC spectra of **5** and **2a**[a][b]

Compd.	Tin atom	δ(^{119}Sn)	Oximic protons	Other protons
5[c]	Sn(1)	−460.0	H(17): 8.226, $^{3}J < 2$ H(7): 8.143, $^{3}J < 2$	H(9): 13.881, $^{3}J < 2$ CH_3[d]: 1.103, ^{2}J = 114
	Sn(2)	−141.8	H(17): 8.226, $^{5}J < 2$	H(3): 6.244, $^{4}J < 2$ H(41A): 3.074, ^{3}J = 12 H(41B): 2.955, ^{3}J = 11 CH_3−Sn(1): 1.103, $^{4}J < 2$ CH_3[d]: 0.517/0.511, ^{2}J = 75
	Sn(3)	−130.6	H(17): 8.226, $^{4}J < 2$	H(41A): 3.074, ^{3}J = 13 H(41B): 2.955, ^{3}J = 14 CH_3−Sn(1): 1.103, $^{4}J < 2$ CH_3[d]: 0.493/0.491, ^{2}J = 75
2a[e]	Sn(1)	−458.5	H(17): 8.133, $^{3}J < 2$ H(7): 8.006, $^{3}J < 2$	H(9): 13.536, $^{3}J < 2$ CH_3[d]: 0.813, ^{2}J = 111 CH_3−Sn(2): 0.793, $^{4}J < 2$
	Sn(2)	−142.6	H(17): 8.133, $^{5}J < 2$	H(3): 6.366, $^{4}J < 2$ H(40): 2.406, $^{2}J < 2$ CH_3[d]: 0.793, ^{2}J = 76 CH_3−Sn(3): 0.623, $^{4}J < 2$
	Sn(3)	−130.9	H(17): 8.133, ^{4}J <2	H(40): 2.406, $^{2}J < 2$ CH_3−Sn(1): 0.813, $^{4}J < 2$ CH_3[d]: 0.623, ^{2}J = 76

[a] ^{1}H chemical shift and $^{n}J(^{1}H$-$^{119}Sn)$ are given for each proton that correlates with a ^{119}Sn resonance (see Figure 1 for labelling). − [b] Chemical shifts are given in ppm and coupling constants in Hz. − [c] Spectrum recorded from a C_6D_6 solution of **5** at 303 K. − [d] Methyl group bound to the considered tin atom. − [e] Spectrum recorded from a $CDCl_3$ solution of **2a** at 270 K.

ally, this complex appears to be the only one that can be generated from the reaction mixture when the synthesis of complexes involving chiral μ_2-bridged secondary alkoxy groups is attempted. Noteworthy is that the resulting complex reaction mixture smoothly evolves by crystallization to the single μ_2-hydroxy complex, just by taking up water present in the medium, either in the solvent and/or in the atmosphere.

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Experimental Section

General: The samples were prepared by dissolving ca. 40 mg of product in 0.5 ml of solvent. NMR spectra of compounds **5a** and **5b** were recorded at 303 K in C_6D_6 and those of compound **2a** were recorded at 270 K in $CDCl_3$. ^{1}H-, ^{13}C- and ^{119}Sn-NMR spectra were recorded with a Bruker AMX500 spectrometer equipped with a digital lock and operating at 500.13, 125.77 and 186.50 MHz, respectively. Chemical shifts are in ppm, coupling constants in Hz. The ^{119}Sn reference frequency was calculated from the absolute frequency of Me_4Sn, Ξ = 37.290 665 MHz[10]. ^{13}C and ^{1}H chemical shifts were respectively referenced to the ^{13}C resonance of the solvent at δ = 128.0 (C_6D_6) or 77.0 ($CDCl_3$) and to the residual ^{1}H solvent resonance at δ = 7.15 (C_6D_5H) or 7.24 ($CHCl_3$); multiplicity patterns in ^{1}H spectra are: d: doublet; dd: doublet of doublets; ddd: doublet of doublets of doublets; s: singlet; m: complex pattern; nr: non resolved. $^{n}J(^{1}H$-$^{1}H)$ coupling constants are given between parentheses. $^{n}J(^{1}H$-$^{119}Sn)$, $^{1}J(^{13}C$-$^{119/117}Sn)$, and $^{2}J(^{119}Sn$-$^{119/117}Sn)$ coupling constants are given in Table 2 and not repeated here. Broad-band ^{1}H-decoupled ^{13}C and ^{119}Sn spectra were recorded using Bruker standard pulse sequences. All heteronuclear correlation-spectroscopy experiments consisted of gradient-enhanced versions of the standard ^{1}H-^{119}Sn HMQC and ^{1}H-^{13}C HMQC or HMBC pulse sequences, implemented in exactly the same way as explained elsewhere and processed in the magnitude mode[1b].

X-ray Diffraction Studies: Intensity data for a colourless crystal of **5a** were collected at 200 K with a Rigaku AFC6R diffractometer employing Mo-K_α radiation (λ = 0.71073 Å) and the ω-2θ scan technique to $2\theta_{max}$ = 50.0°. The data set was corrected for Lorentz and polarisation effects[11] as well as for absorption employing an empirical procedure (range of transmisison factors: 0.756 to 1)[12]. Data that satisfied the $I \geq 3.0\sigma(I)$ criterion of observability were used in the subsequent analysis. Crystal data and refinement details are given in Table 4.

Table 4. Crystallographic data for **5a**

Formula	$C_{25}H_{40}N_2O_6Sn_3$
Formula weight	820.7
Crystal system	monoclinic
Space group	$P2_1/c$
a [Å]	8.865(5)
b [Å]	17.64(1)
c [Å]	19.52(1)
β [°]	92.49(6)
V [Å^3]	3048(3)
Z	4
Crystal dimensions [mm]	0.11 × 0.37 × 0.47
$\rho_{calcd.}$ [g cm^{-3}]	1.788
$F(000)$	1608
No. of data collected	5970
No. of unique data	5591
No. of reflections with $I \geq 3.0\sigma(I)$	4144
No. of refined parameters	325
R	0.035
R_w	0.041
Residual ρ_{max} [e Å^{-3}]	0.73

The structure was solved by direct methods[13] and refined by a full-matrix least-squares procedure based on F[11]. Non-hydrogen atoms were refined with anisotropic displacement parameters and hydrogen atoms were included in the model at their calculated positions (C−H 0.95 Å). The refinement was continued until convergence employing sigma weights, i.e. $1/\sigma^2(F)$. Selected interatomic parameters are collected in Table 1 and the crystallographic numbering scheme employed is shown in Figure 2 which was drawn with ORTEP[14] at 50% probability ellipsoids. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101351. Copies of the data can be obtained free of charge on application

to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: + 44-1223-336−033; E-mail: deposit@ccdc.cam.ac.uk].

Compound **3**: Compound **3** was synthesized as previously described[1b].

Compound **5a**: To a solution of 1.000 g (1.31 mmol) of **3** in 10 ml of dichloromethane was added a solution of 0.598 g (6.8 mmol, 5.2 equiv.) of (*d,l*)-2-methyl-1-butanol in 10 ml of dichloromethane. The mixture was stirred for 5 min and the solvent was evaporated under vacuum. Recrystallization in dichloromethane/hexane (1:1) of the precipitate obtained provided 0.942 g of pure **5a** crystals suitable for X-ray analysis (yield: 88%). The compound starts melting under decomposition at 116°C. − $C_{25}H_{40}N_2O_6Sn_3$ (820.67): calcd. C 36.6, H 4.9, N 3.4; found C 36.6, H 5.2, N 3.4. − ^{1}H NMR (C_6D_6, 500.13 MHz; for complex patterns, the centre of ^{1}H-^{13}C HMQC cross peaks is given): δ = 13.88 [s, OH(9)], 8.23 (s, 17-H), 8.14 (s, 7-H), 7.07 (mnr, 3′-H), 7.06 (mnr, 4′-H), 7.04 (mnr, 4-H), 6.847 (dd, *J* = 7.7, 1.9 Hz, 6-H), 6.823 (dd, *J* = 7.6, 1.1 Hz, 6′-H), 6.605 (ddd, *J* = 7.4, 7.4, 0.8 Hz, 5-H), 6.570 (ddd, *J* = 7.6, 6.5, 1.8 Hz, 5′-H), 6.244 (d, *J* = 8.2 Hz, 3-H), 3.074 (dd, *J* = 10.9, 6.5 Hz, 41A-H), 2.955 (dd, *J* = 10.9, 7.0 Hz, 41B-H), 1.30 (mnr, 43A-H), 1.103 [s, CH_3 (Sn-1)]; 1.06 (mnr, 42-H), 0.81 (mnr, 43B-H), 0.78 (mnr, 44-H), 0.684 (d, *J* = 6.6 Hz, 45-H), 0.517 [s, Sn(2)−CH_3], 0.511 [s, Sn(2)−CH_3], 0.493 [s, Sn(3)−CH_3], 0.491 [s, Sn(3)−CH_3]. − ^{13}C NMR (C_6D_6, 125.76 MHz): δ = 162.6 (C-2′), 161.0 (C-2), 154.6 (C-17), 149.9 (C-7), 135.6 (C-6), 132.4 (C-4′), 132.1 (C-6′), 131.0 (C-4), 120.9 (C-3′), 120.7 (C-1), 119.4 (C-1′), 117.9 (C-3), 117.2 (C-5′), 117.1 (C-5), 68.5 (C-41), 38.8 (C-42), 26.3 (C-43), 16.5 (C-45), 14.8 [C−Sn(1)], 11.4 (C-44), 2.56 [C−Sn(2)], 2.51 [C−Sn(2)], −0.16 [C−Sn(3)], −0.27 [C−Sn(3)]. − ^{119}Sn NMR (C_6D_6, 186.50 MHz): −130.6 Sn(3), −141.8 Sn(2), −458.0 Sn(1).

Compound **5b**: Synthesis is the same as for **5a**, using 0.592 g of (*S*)-(−)-2-methyl-1-butanol; yield 53%. The compound starts melting under decomposition at 109°C. − $C_{25}H_{40}O_6N_2Sn_3$ (820.67): calcd. C 36.6, H 4.9, N 3.4; found C 36.1, H 5.0, N 3.4. − NMR spectra of **5b** are identical to those of **5a**.

Compound **2a**: Same procedure as for **5a**, using 1.000 g of **3** and 0.492 g (6.6 mmol, 5.1 equiv.) of (*d,l*)-2-butanol; recrystallization from dichloromethane/hexane (1:4); yield 59%. The compound starts melting under decomposition at 99°C. − $C_{20}H_{30}O_6N_2Sn_3$ (750.54): calcd. C 32.0, H 4.0, N 3.7; found C 32.1, H 4.1, N 3.6. − ^{1}H NMR ($CDCl_3$, 500.13 MHz): δ = 13.536 [s, OH(9)], 8.133 (s, 17-H), 8.006 (s, 7-H), 7.227 (ddd, *J* = 8.6, 7.2, 1.8 Hz, 4′-H), 7.17 (mnr, 4-H), 7.15 (mnr, 6-H), 7.104 (dd, *J* = 7.7, 1.7 Hz, 6′-H), 6,824 (d, *J* = 8.0 Hz, 3′-H), 6.746 (t, *J* = 7.4 Hz, 5-H and 5′-H), 6.366 (d, *J* = 8.1 Hz, 3-H), 2.406 (s, 40-H), 0.813 [s, Sn(1)−CH_3], 0.793 [s, Sn(2)−CH_3], 0.623 [s, Sn(3)−CH_3]. − ^{13}C NMR ($CDCl_3$, 125.76 MHz): δ = 161.4 (C-2′), 160.4 (C-2), 154.1 (C-17), 149.6 (C-7), 134.9 (C-6), 131.9 (C-4′), 131.7 (C-6′), 131.1 (C-4), 120.3 (C-3′), 119.4 (C-1), 118.7 (C-1′), 117.5 (C-3), 116.9 (C-5′), 116.5 (C-5), 14.0 [Sn(1)−CH_3], 4.4 [Sn(2)−CH_3], 1.9 [Sn(3)−CH_3]. − ^{119}Sn NMR ($CDCl_3$, 186.50 MHz): δ = −130.9 [Sn(3)], −142.6 [Sn(2)], −458.5 [Sn(1)].

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