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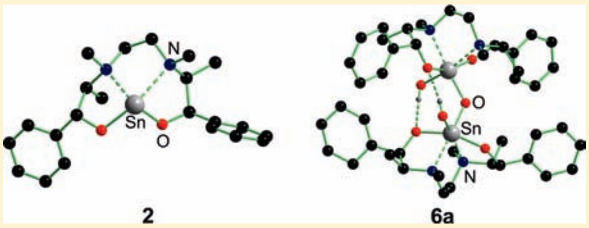
Intramolecular N→Sn Coordination in Tin(II) and Tin(IV) Compounds Based on Enantiopure Ephedrine Derivatives[†]

Thomas Zöller, Ljuba Iovkova-Berends, Thorsten Berends, Christina Dietz, Gerrit Bradtmöller, and Klaus Jurkschat*

Lehrstuhl für Anorganische Chemie II der Technischen Universität Dortmund, D-44221 Dortmund, Germany

S Supporting Information

ABSTRACT: The syntheses and molecular structures of the intramolecularly coordinated tin(II) compounds $\{CH_2N(Me)CH(Me)CH(Ph)O\}_2SnL$ (**2**, L = lone pair; **4**, L = W(CO)$_5$; **5**, L = Cr(CO)$_5$) and of the related hydroxido-substituted tin(IV) compound $[\{CH_2N(Me)CH(Me)CH(Ph)O\}_2Sn(OH)]_2O$, **6a**, are reported. Also reported are the molecular structures of the enantiopure *N*,*N*′-ethylenebis-(1*R*,2*S*)-ephedrine, $\{CH_2N(Me)CH(Me)CH(Ph)OH\}_2$ (**1**), and its hydrobromide $\{CH_2N(Me)CH(Me)CH(Ph)OH\}_2\cdot HBr$ (**1a**).



INTRODUCTION

Ephedrine and its derivatives have gained much interest as ligands and play an important role in the synthesis of optically active compounds.[1] These ligands were employed for the synthesis of a great variety of complexes with transition or main group metals and metalloids, with the metal or metalloid becoming a new stereogenic center. One of these optically active ephedrine derivatives is *N*,*N*′-ethylenebis-(1*R*,2*S*)-ephedrine, $\{CH_2N(Me)$-(*S*)-CH(Me)-(*R*)-CH(Ph)OH$\}_2$, which is easily prepared from (1*R*,2*S*)-ephedrine and 1,2-dibromoethane.[2] In 1967, Amano and co-workers[3] reported the copper(II) tricyclic compound **A** that was prepared by the reaction of *N*,*N*′-ethylenebis-(1*R*,2*S*)-ephedrine with copper(II) sulfate. The copper and the nitrogen atoms are stereogenic centers due to the intramolecular coordination (Scheme 1).[3] Other element compounds **B**−**E**[4−8] that contain ephedrine-based ligands are shown in Scheme 1 as well.

Tin(II) alkoxides are versatile ligands in transition metal chemistry,[9−18] and the corresponding "ate"-type complexes and bimetallic alkoxides halides[19] hold great potential for material science. Considering the renewed interest in tin(II) alkoxides and their transition metal complexes,[4,9−11,17,20] as well as the relevance of asymmetric induction by catalytically active compounds, we now report the syntheses and structures of ephedrine-based tin(II) and tin(IV) derivatives of *N*,*N*′-ethylenebis-(1*R*,2*S*)-ephedrine.

RESULTS AND DISCUSSION

The enantiopure *N*,*N*′-ethylenebis-(1*R*,2*S*)-ephedrine, $\{CH_2N(Me)$(*S*)-CH(Me)-(*R*)-CH(Ph)OH$\}_2$, **1**, was prepared according to a procedure reported in the literature.[2] Single crystals suitable for X-ray diffraction measurements were obtained by recrystallization from hexane. The molecular structure including selected bond distances and angles of compound **1** is given in the Supporting Information (Figure S1).

In the solid state, compound **1** shows two *intramolecular* nonsymmetric O(11)−H(11)···N(17) and O(20)−H(20A)···N(14) hydrogen bridges. As a result of this, compound **1** is monomeric and forms a kind of bicyclododecane-type structure. The O−H and N···H distances vary between 0.84 and 0.93, and 1.86 and 2.01 Å, respectively.

The reaction of compound **1** with tin(II) methoxide gave the (3*R*,4*S*,9*S*,10*R*)-3,10-diphenyl-4,5,8,9-tetramethyl-(5,8-diaza-2,11-dioxa-1-stanna(II)tricyclo[3.2.3.0^{1,5}.0^{1,8}]undecane), **2**, $\{CH_2N$(Me)(*S*)-CH(Me)-(*R*)-CH(Ph)O$\}_2$Sn, as a colorless, amorphous material in high yield (Scheme 2).

Compound **2** is quite soluble in dichloromethane (CH_2Cl_2) and toluene but less soluble in tetrahydrofurane (THF). It is rather sensitive to air and moisture. Single crystals suitable for X-ray diffraction analysis of compound **2**, as its benzene solvate **2**·C_6H_6, were obtained by recrystallization from benzene.

The molecular structure of **2**·C_6H_6 is shown in Figure 1, and selected bond distances and bond angles are given in Table 1.

In contrast to the parent dimeric compounds $\{MeN(CH_2CH_2O)_2Sn\}_2$,[9] $\{HOCMe_2CH_2N(CH_2CMe_2O)_2Sn\}_2$,[20] and $[MeN(CH_2CMe_2O)\{$(*S*)-CH(Me)-(*R*)-CH(Ph)O$\}Sn]_2$ (**B**),[4] the stanna(II)tricycloundecane **2**·C_6H_6 shows a monomeric structure in the solid state due to the steric demand of the substituent and the 2-fold intramolecular N→Sn coordination. As a result of the intramolecular coordination, a tricyclic structure

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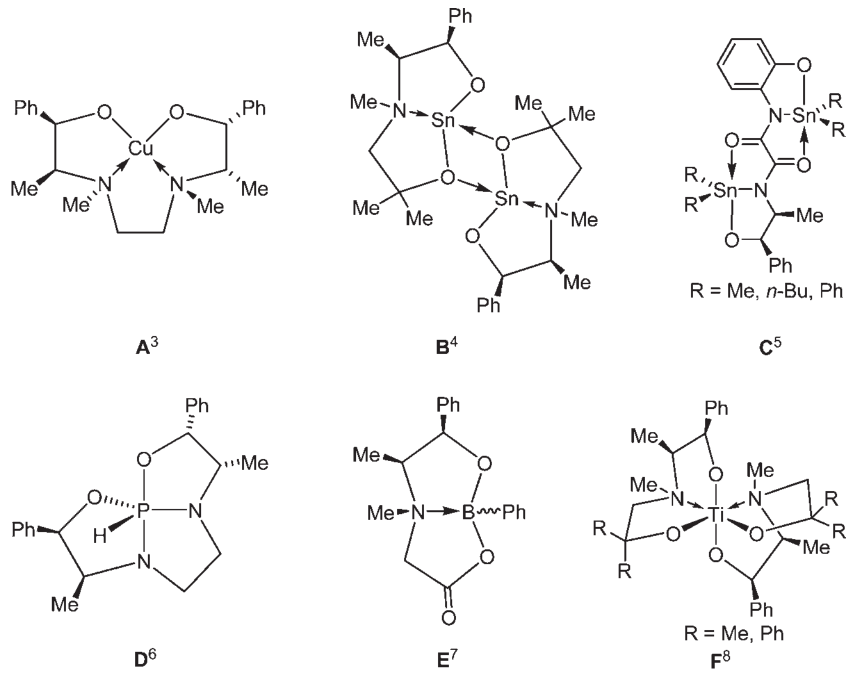
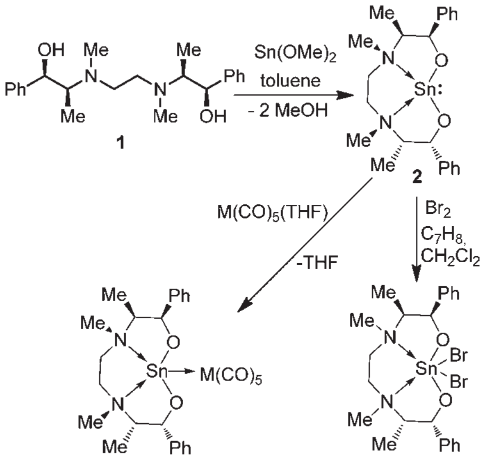
Scheme 1. Selected Ephedrine-Based Optically Active Complexes



Scheme 2. Synthesis of Compounds 2−5



is formed and the nitrogen atoms become chiral centers with *R*-configuration at the N(14) and *S*-configuration at the N(17) atom. The Sn(1) atom in compound **2**$\cdot C_6H_6$ shows a pseudo square pyramidal configuration. The equatorial positions are occupied by the N(14), N(17), O(11), and O(20) atoms, while the lone pair occupies the apical position. The O(20)−Sn(1)−N(14) angle of 135.8(1)° manifests a strong deviation from the ideal square pyramid. The intramolecular Sn(1)−N(14)/Sn(1)−N(17) distances of 2.540(2)/2.416(2) Å are not equal and comparable to N−Sn distances in the parent compounds $\{Me(NCH_2CH_2O)_2Sn\}_2$ (2.447(10), 2.413(10) Å),[9] $\{HOCMe_2CH_2N(CH_2CMe_2O)_2Sn\}_2$ (2.561(3), 2.552(3) Å),[20] and $[MeN(CH_2CMe_2O)\{(S)\text{-}CH(Me)\text{-}(R)\text{-}CH(Ph)O\}Sn]_2$ (2.523(2) Å).[4]

The ^{119}Sn NMR spectrum of **2** in CD_2Cl_2 exhibits a broad resonance at δ −231 (integral 1.00, $\Delta\nu_{1/2}$ = 1048 Hz) and a signal of low intensity at δ −334 (integral 0.04, $\Delta\nu_{1/2}$ = 177 Hz). With caution, the low intensity signal can be assigned either to the dimer of **2** or to the spiro-type compound $[\{CH_2N(Me)CH(Me)CH(Ph)O\}_2]_2Sn$. The electrospray ionization mass spectrometry (ESI-MS) spectrum (see below) favors the latter. The ^{1}H NMR spectrum (CD_2Cl_2, 300 MHz) shows rather broad resonances at δ 0.96 (CHC*H*$_3$), 1.95−3.50 (complex pattern, NC*H*$_2$, C*H*CH$_3$, NC*H*$_3$), 5.23 (C*H*Ph), 5.55 (C*H*Ph), and 7.17−7.53 (Ph-*H*). The ^{13}C NMR spectrum of the same solution displays, as expected from the solid state structure, 10 broad resonances for the non-phenyl carbon atoms. The signals for the phenyl carbon atoms are broad as well but not resolved. Also present is a set of sharp resonances of low intensity that are assigned to the free ligand **1** for both the ^{1}H and ^{13}C NMR spectra (see Experimental Section). The broad resonances in the ^{1}H, ^{13}C, and ^{119}Sn NMR spectra hint at dynamic behavior (Sn−N dissociation−inversion[21]) that was, however, not investigated further. The ESI-MS spectrum (positive mode) shows a mass cluster centered at m/z = 475.2, which is assigned to $[\mathbf{2} + H]^+$. Also present is a mass cluster centered at m/z = 829.5, which is assigned to the protonated spiro-type compound $[[\{CH_2N(Me)CH(Me)CH(Ph)O\}_2]_2Sn + H]^+$. The latter is formed under the experimental condition employed by ESI-MS.

The reaction of the stannylene **2** with elemental bromine gave, by an oxidative addition reaction (Scheme 2), the dibromido-substituted tin(IV) derivative $\{CH_2N(Me)\text{-}(S)\text{-}CH(Me)\text{-}(R)\text{-}CH(Ph)O\}_2SnBr_2$, **3**, as yellow amorphous solid material that is sparingly soluble in polar organic solvents such as CH_2Cl_2, dimethyl sulfoxide, and THF. The ^{119}Sn NMR spectrum in CD_2Cl_2 shows two low-frequency shifted signals at δ −544 (integral 1.74, $\Delta\nu_{1/2}$ = 16 Hz) and −586 (integral 1.00, $\Delta\nu_{1/2}$ = 18 Hz).

In an attempt to grow single crystals of compound **3**, partial hydrolysis took place and yellow single crystals of the

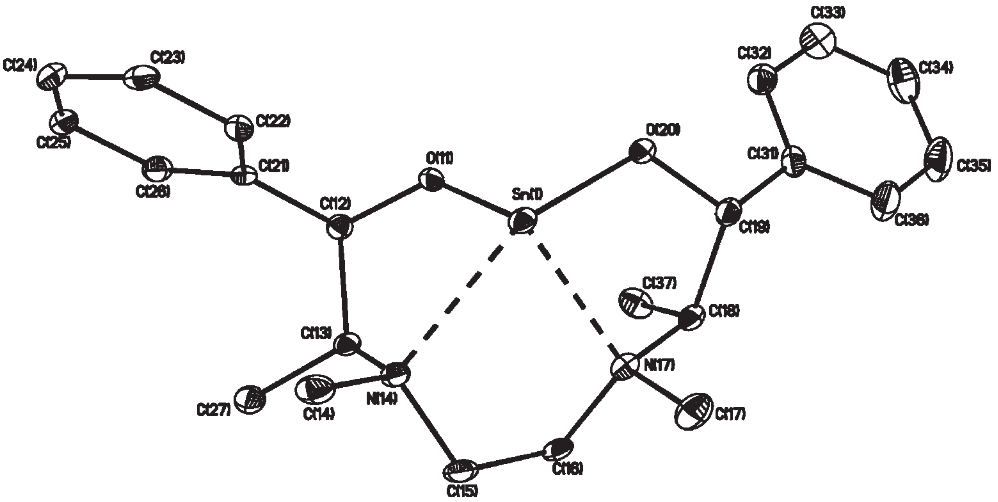


Figure 1. ORTEP presentation of the 30% probability ellipsoids of depicted atoms and atom numbering scheme of the molecular structure of **2**$\cdot C_6H_6$. The benzene solvate molecule is omitted.

Table 1. Selected Bond Length (Å) and Bond Angles (°) for 2$\cdot C_6H_6$, 4$\cdot 0.5C_6H_{14}$, 5$\cdot 0.5C_4H_8O$, and 6a$\cdot C_6D_6$

	2$\cdot C_6H_6$	**4**$\cdot 0.5C_6H_{14}$	**5**$\cdot 0.5C_4H_8O$	**6a**$\cdot C_6D_6$
Sn(1)−O(1)				1.951(2)
Sn(1)−O(2)				1.992(3)
Sn(1)−O(11)	2.048(2)	2.010(5)	2.012(3)	2.003(3)
Sn(1)−O(20)	2.078(2)	2.016(5)	2.028(3)	2.045(3)
Sn(1)−N(14)	2.540(2)	2.373(5)	2.362(4)	2.339(4)
Sn(1)−N(17)	2.416(2)	2.403(6)	2.414(3)	2.296(3)
Sn(1)−W(1)		2.7686(7)		
Sn(1)−Cr(1)			2.6324(9)	
O(1)−Sn(1)−O(2)				98.4(1)
O(1)−Sn(1)−O(11)				98.4(1)
O(1)−Sn(1)−O(20)				94.7(1)
O(1)−Sn(1)−N(14)				93.1(1)
O(1)−Sn(1)−N(17)				170.0(1)
O(2)−Sn(1)−O(11)				94.9(1)
O(2)−Sn(1)−N(14)				167.0(2)
O(2)−Sn(1)−N(17)				89.7(1)
O(2)−Sn(1)−O(20)				99.7(1)
O(11)−Sn(1)−O(20)	85.51(6)	87.2(2)	87.4(1)	158.8(1)
O(11)−Sn(1)−N(14)	73.60(6)	76.3(2)	76.3(1)	77.2(2)
O(11)−Sn(1)−N(17)	104.79(6)	118.9(2)	120.6(2)	86.6(1)
O(11)−Sn(1)−Cr(1)			123.8(1)	
O(11)−Sn(1)−W(1)		126.4(2)		
O(20)−Sn(1)−N(14)	135.79(6)	134.5(2)	132.6(1)	85.4(1)
O(20)−Sn(1)−N(17)	75.98(7)	77.0(2)	76.7(1)	78.1(1)
O(20)−Sn(1)−Cr(1)			110.3(1)	
O(20)−Sn(1)−W(1)		109.7(2)		
N(14)−Sn(1)−N(17)	72.57(6)	74.8(2)	74.4(1)	79.5(2)
N(14)−Sn(1)−Cr(1)			115.8(1)	
N(14)−Sn(1)−W(1)		114.3(1)		
N(17)−Sn(1)−Cr(1)			115.3(1)	
N(17)−Sn(1)−W(1)		114.5(1)		
Sn(1)−O(1)−Sn(1A)				129.4(2)

hydrobromide *N*,*N*′-ethylenebis-(1*R*,2*S*)-ephedrine$\cdot$HBr (**1a**) suitable for X-ray diffraction analysis were obtained instead. The molecular structure, including selected bond distances and bond angles, of compound **1a** is shown in Figure S2 (Supporting Information). Besides the four chiral centers at C(12), C(13), C(18), and C(19) provided by the enantiopure starting material, a new chiral center with the absolute configuration *R* is formed by protonation of the N(14) atom. In the solid state, compound **1a** shows three nonsymmetric O(11)−H(11)$\cdots$Br(1), O(20)−H(20) $\cdots$Br(1), and O(11)−H(11)$\cdots$Br(1) hydrogen bridges. As a result of the intermolecular hydrogen bonding and in contrast to the free ligand **1**, compound **1a** forms a polymeric chain (Figure S2). The N−H distance amounts to 0.93 Å, and the O−H and H$\cdots$Br distances vary between 0.83 and 0.93 Å and between 3.19 and 3.26 Å, respectively.

The reaction of the stannylene **2** with in situ-generated [M(CO)$_5$(thf)] (M = W, Cr) gave the corresponding tungsten- and chromiumpentacarbonyl complexes, {CH$_2$N(Me)-(*S*)-CH(Me)-(*R*)-CH(Ph)O}$_2$SnM(CO)$_5$ (**4**, M = W; **5**, M = Cr), in high yields (Scheme 2), respectively.

Compounds **4** and **5** are quite soluble in polar organic solvents such as dichloromethane but exhibit moderate solubility in toluene. Recrystallization from CH_2Cl_2/hexane provided yellowish single crystals of **4**, as its hexane solvate **4**$\cdot 0.5C_6H_{14}$. Colorless crystals of **5**, as its tetrahydrofurane solvate **5**$\cdot 0.5C_4H_8O$, were obtained by crystallization from tetrahydrofurane. The molecular structure of **4**$\cdot 0.5C_6H_{14}$ is shown in Figure 2. Compound **5**$\cdot 0.5C_4H_8O$ is isostructural, and its molecular structure is given in the Supporting Information (Figure S3). Selected bond lengths and angles of compounds **4**$\cdot 0.5C_6H_{14}$ and **5**$\cdot 0.5C_4H_8O$ are summarized in Table 1.

The Sn(1) atoms in both the tungsten and the chromium pentacarbonyl complexes **4**$\cdot 0.5C_6H_{14}$ and **5**$\cdot 0.5C_4H_8O$, respectively, exhibit a rather similar distorted square pyramidal configuration with the O(11), O(20), N(14), and N(17) atoms occupying the equatorial positions. The apical position is occupied by the W(1) (**4**$\cdot 0.5C_6H_{14}$) and Cr(1) (**5**$\cdot 0.5C_4H_8O$) atoms, respectively. The intramolecular Sn(1)−N(14)/Sn(1)−N(17) distances of 2.373(5)/2.403(6) (**4**$\cdot 0.5C_6H_{14}$) and 2.362(4)/2.414(3) (**5**$\cdot 0.5C_4H_8O$) differ slightly but are almost equal

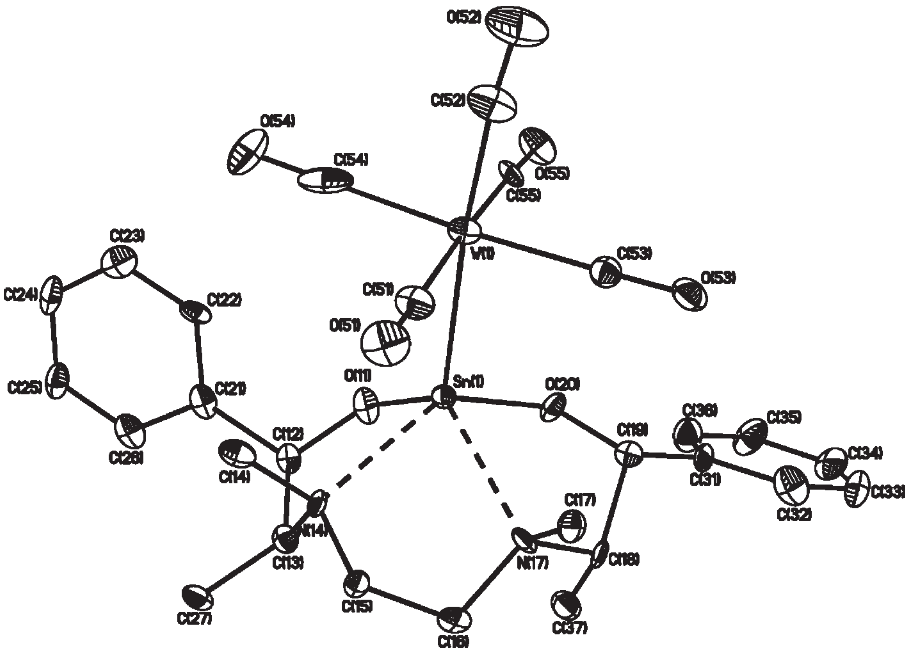


Figure 2. ORTEP presentation of the 30% probability ellipsoids of depicted atoms and atom numbering scheme of $\mathbf{4}\cdot0.5C_6H_{14}$. The disordered hexane solvate molecule was removed by Platon/Squeeze.[22]

between $\mathbf{4}\cdot0.5C_6H_{14}$ and $\mathbf{5}\cdot0.5C_4H_8O$. These distances are comparable to those reported for the related stannabicyclooocane derivative $\{MeN(CH_2CH_2O)_2SnW(CO)_5\}_2$ (2.356(5), 2.360(6) Å).[9] The Sn(1)−W(1) ($\mathbf{4}\cdot0.5C_6H_{14}$, 2.7686(7) Å) and Sn(1)−Cr(1) ($\mathbf{5}\cdot0.5C_4H_8O$, 2.6324(9) Å) distances are longer than respectively in the upper range of comparable compounds such as $\{MeN(CH_2CH_2O)_2SnW(CO)_5\}_2$ (2.737(1), 2.728(1) Å),[9] $\{t\text{-}BuN(CH_2CH_2O)_2SnW(CO)_5\}_2$ (2.7431(5), 2.7490(5) Å),[9] $(t\text{-}BuO)_2SnM(CO)_5$ (M = W 2.721(1) Å; M = Cr 2.575(2) Å),[10] $(t\text{-}BuO)_2Sn\{W(CO)_5\}\{Cr(CO)_5\}$ (Sn−W 2.740(1) Å, Sn−Cr 2.61(2) Å),[10] $(t\text{-}BuO)_2Sn\{Cr(CO)_5\}_2$ (2.60(4), 2.62(3) Å),[10] $(ox)_2SnCr(CO)_5$ (2.587(2) Å),[23] $\{(CO)_5MoIn(O\text{-}t\text{-}Bu)_3SnCr(CO)_5\}$ (2.636(3) Å),[24a] *cis*-$\{(OC)_5CrSn(O\text{-}t\text{-}Bu)_3In\}_2Cr(CO)_4$ (2.596(6) Å),[18] $\{(OC)_5CrSn(O\text{-}t\text{-}Bu)_3In\}_2Mo(CO)_4$ (2.592(6) Å), and $(OC)_5CrSn(O\text{-}t\text{-}Bu)_3Ba(O\text{-}t\text{-}Bu)_3SnCr(CO)_5$ (2.649(3) Å)[18] and might reflect a decreased M→Sn (M = Cr, W) back bonding as result of two intramolecular N→Sn interactions in compounds $\mathbf{4}\cdot0.5C_6H_{14}$ and $\mathbf{5}\cdot0.5C_4H_8O$. Similar observations have been made by Hahn and Frenking et al.[24b] Notably, in a combined experimental and theoretical study, these authors recognized diaminostannylenes to act not only as σ-donors and π-acceptors but also as π-donors toward transition metal moieties.

As result of the intramolecular N→Sn coordination, the nitrogen atoms become chiral centers with *R*-configuration at N(14) and *S*-configuration at N(17) for both the tungsten and the chromium complex $\mathbf{4}\cdot0.5C_6H_{14}$ and $\mathbf{5}\cdot0.5C_4H_8O$, respectively. This is consistent with the absolute configuration of the nitrogen atoms in compound $\mathbf{2}\cdot C_6H_6$ in the solid state. Apparently, the chiral centers at C(12), C(13), C(18), and C(19) control the absolute configuration of the nitrogen atoms in the solid state. The carbon atoms C(14)/C(17) and C(14)/C(27) are cis, whereas the carbon atoms C(17)/C(37) are trans. Evidence for the formation of only one diastereomer for both compounds $\mathbf{4}\cdot0.5C_6H_{14}$ and $\mathbf{5}\cdot0.5C_4H_8O$ stems from ^{119}Sn CP-MAS NMR spectroscopy that shows single resonances at δ_{iso} −118 ($\mathbf{4}\cdot0.5C_6H_{14}$) and 34 ($\mathbf{5}\cdot0.5C_4H_8O$). For compound $\mathbf{4}\cdot0.5C_6H_{14}$ there is an additional resonance of low intensity at δ_{iso} −722 that was not assigned. The Sn(1) atom is a stereogenic center with three constitutionally different substituents.

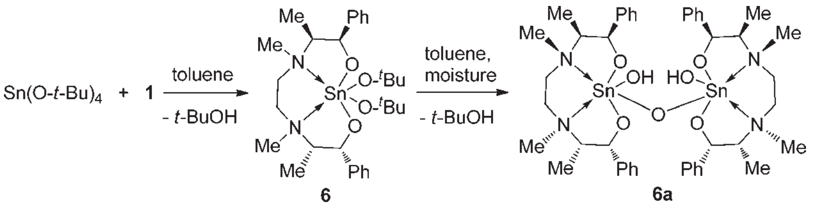
The intramolecular N→Sn coordination in compounds $\mathbf{4}\cdot0.5C_6H_{14}$ and $\mathbf{5}\cdot0.5C_4H_8O$ is preserved in solution (CD_2Cl_2/$CDCl_3$), as it is especially evidenced by the ^{119}Sn NMR chemical shifts of δ −112 (**4**, ^1J (^{119}Sn−^{183}W) = 1469 Hz) and 47 (**5**) being rather close to the chemical shifts found for the solid state. Interestingly, low frequency ^{119}Sn chemical shifts were reported for the related complexes $\{MeN(CH_2CH_2O)_2SnM(CO)_5\}_2$ that show only one intramolecular N→Sn coordination but are dimeric via intermolecular O→Sn interactions (M = W, δ ^{119}Sn −208, ^1J (^{119}Sn−^{183}W) = 1483 Hz, δ_{iso} ^{119}Sn CP-MAS −188; M = Cr, δ −27).[9]

The effect of intramolecular coordination and interaction with donor solvents on the ^{119}Sn NMR chemical shifts in related benzimidazolin-2-stannylenes has been discussed in detail.[24c]

The ^{1}H and ^{13}C NMR spectra of both **4** and **5** show the nonequivalence of the constitutionally identical methine and methyl protons PhC*H*, MeC*H*, CHC*H*$_3$, and NC*H*$_3$, respectively. This unambiguously proves the intramolecular N−Sn coordination to be retained in solution.

The reaction in toluene of tetra-*tert*-butoxystannane, $Sn(O\text{-}t\text{-}Bu)_4$, with the aminoethanol derivative **1** gave the tin(IV) alkoxide derivative $\{CH_2N(Me)\text{-}(S)\text{-}CH(Me)\text{-}(R)\text{-}CH(Ph)O\}_2Sn(O\text{-}t\text{-}Bu)_2$, **6**, as colorless, amorphous material that is soluble in CH_2Cl_2 and toluene (Scheme 3). The ^{119}Sn NMR spectrum of **6** shows two resonances at δ −539 (J (^{119}Sn−^{13}C) = 26 Hz, 47 Hz, 61 Hz, integral 1) and −543 (J (^{119}Sn−^{13}C) = 25 Hz, 40 Hz, 64 Hz, integral 0.90). The ^{1}H NMR spectrum shows two sharp signals for each of the methine and methyl protons PhC*H*, MeC*H*, CHC*H*$_3$, and NC*H*$_3$, respectively. For the NC*H*$_2$ protons, two AB-type resonances are observed. In analogy, the ^{13}C NMR spectrum exhibits two resonances for each methine, methyl, and methylene carbon atom (CHMe, CHPh, $CHCH_3$,

Scheme 3. Synthesis of Compounds 6 and 6a



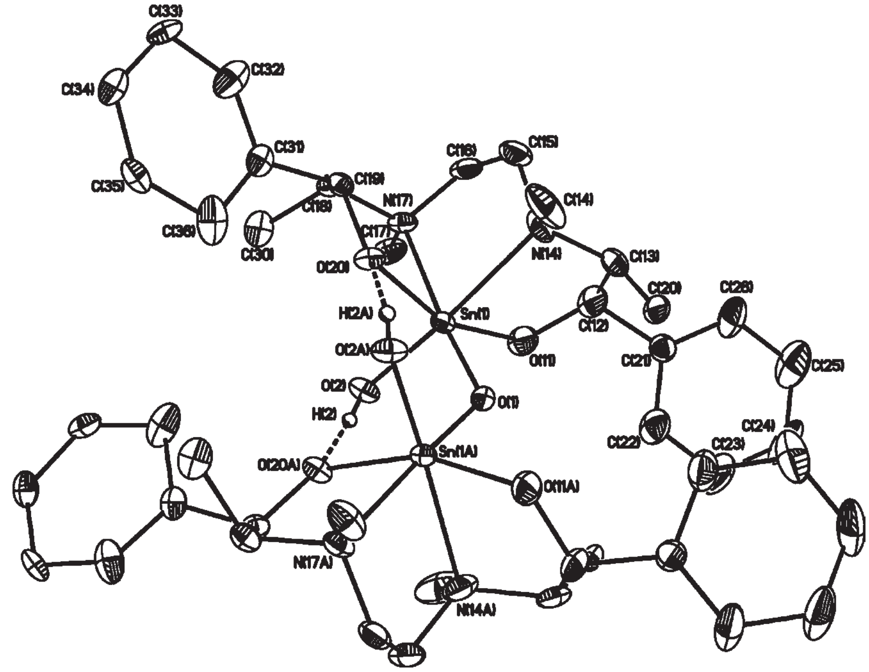


Figure 3. ORTEP presentation of the 30% probability ellipsoids of depicted atoms and atom numbering scheme of **6a**$\cdot C_6D_6$.

NCH_3, NCH_2). With caution, we interpret the NMR data in terms of two out of four possible diastereomers of compound **6** that can be formed upon 2-fold N−Sn coordination. The ^1H, ^{13}C, and ^{119}Sn NMR data are consistent with the formation of two diastereomers with the same absolute configurations at the nitrogen atoms (*R*(N14), *R*(N17) or *S*(N14), *S*(N17)), respectively. The ESI-MS spectrum (positive mode) shows mass clusters centered at 491.2 $[\{CH_2N(Me)CH(Me)CH(Ph)O\}_2SnOH]^+$, 977.4 [M + **1** + H]$^+$, and 1465.6 [M + $[\{CH_2N(Me)CH(Me)CH(Ph)O\}_2SnOH]$ + **1**]$^+$, which indicates the partial hydrolysis of **6** in solution under the experimental conditions employed by ESI-MS.

Compound **6** reacts with moisture to give the hydrolysis product $[\{CH_2N(Me)$-(*S*)-$CH(Me)$-(*R*)-$CH(Ph)O\}_2Sn(OH)]_2O$, **6a**, as its benzene solvate, **6a**$\cdot C_6D_6$, which crystallized in the NMR tube as colorless single crystals suitable for X-ray diffraction measurements (Scheme 3).

The molecular structure of compound **6a**$\cdot C_6D_6$ is shown in Figure 3, and selected bond distances and angles are given in Table 1. In compound **6a**$\cdot C_6D_6$, the Sn(1) atom shows a distorted octahedral configuration, with the distortion manifested by the deviation of the O(1)−Sn(1)−N(17) (170.0(1)°), O(2)−Sn(1)−N(14) (167.0(1)°), and O(11)−Sn(1)−O(20) (158.8(1)°) from the ideal angle of 180°. The intramolecular Sn(1)−N(14) and Sn(1)−N(17) distances of 2.296(3) and 2.339(4) Å, respectively, are slightly shorter than the corresponding distances in the transition metal complexes **4**$\cdot 0.5C_6H_{14}$ and **5**$\cdot 0.5C_4H_8O$ and reflect a stronger Lewis acidity of the Sn(IV) atom in compound **6a**$\cdot C_6D_6$. Because of the intramolecular N→Sn coordination, the nitrogen atoms become chiral centers with *R*-configuration at the N(14) atom as well as at the N(17) atom. The observation of the same absolute configuration at the nitrogen atoms for the Sn(IV) compound **6a**$\cdot C_6D_6$ in the solid state is consistent with the proposed stereochemistry for the Sn(IV) compound **6** in solution.

In compound **6a**$\cdot C_6D_6$, the μ-O(1) atom bridges the Sn(1) and Sn(1A) atoms at a Sn(1)−O(1) distance of 1.951(1) Å and with a Sn(1)−O(1)−Sn(1A) angle of 129.4(2)°. The distance is slightly shorter than the Sn(1)−O(2), Sn(1)−O(11), and Sn(1)−O(20) distances of 1.992(3), 2.003(3), and 2.045(3) Å, respectively. The O(2)H-hydroxido group supports the μ-O(1) bridge by an intramolecular nonsymmetric O(2)−H(2)···O(20A) hydrogen bridge at a O(2)···O(20A) distance of 2.948(4) Å [O(2)−H(2) 0.79(5), O(20A)···H(2) 2.20(5) Å]. To the best of our knowledge, the structural motif $HO(RO)_2SnOSn(OR)_2OH$ represented by compound **6a** has not been realized before. However, there are two monomeric tetraorganodistannoxanes $HO(R_2)SnOSn(R_2)OH$ (R = 2-$Me_2NCH_2C_6H_4$, 2,6-$(MeOCH_2)_2C_6H_3$) reported in the literature.[24d,e]

Table 2. Crystal Data and Structure Refinement for Compounds **1**, **2**·C_6H_6, and **1a**

	1	**2**·C_6H_6	**1a**
empirical formula	$C_{22}H_{32}N_2O_2$	$C_{28}H_{36}N_2O_2Sn$	$C_{22}H_{33}BrN_2O_2$
formula weight	365.50	551.28	437.41
temperature/K	173(2)	173(2)	173(2)
wavelength/Å	0.71073	0.71073	0.71073
crystal system	orthorhombic	monoclinic	monoclinic
space group	$P2_12_12_1$	$P2_1$	$P2_1$
unit cell dimensions			
a /Å	7.0717(2)	7.0576(3)	7.6385(5)
b /Å	13.6182(4)	17.9392(6)	10.359(1)
c /Å	21.1941(7)	10.6368(4)	14.046(1)
β /°	90	101.899(4)	98.715(8)
volume/Å^3	2041.1(1)	1317.76(9)	1098.6(2)
Z	4	2	2
D_c /g·cm^3	1.160	1.389	1.322
absorption coefficient/mm^{-1}	0.074	0.995	1.889
F(000)	776	568	460
crystal size/mm	0.42 × 0.38 × 0.28	0.50 × 0.48 × 0.42	0.28 × 0.24 × 0.16
Θ range for data collection /°	2.44−25.50	2.95−25.50	2.45−25.49
reflections collected	38273	9668	5323
independent reflections	3799 [R(int) = 0.0420]	4835 [R(int) = 0.0163]	3733 [R(int) = 0.0421]
refinement method	full-matrix least-squares on F^2		
data/restraints/parameters	3799/0/245	4835/1/302	3733/1/253
goodness-of-fit on F^2	0.910	0.989	0.693
final R indices [$I > 2\sigma(I)$]	R_1 = 0.0297, wR_2 = 0.0607	R_1 = 0.0197, wR_2 = 0.0472	R_1 = 0.0358, wR_2 = 0.0442
R indices (all data)	R_1 = 0.0404, wR_2 = 0.0623	R_1 = 0.0213, wR_2 = 0.0475	R_1 = 0.0727, wR_2 = 0.0471
largest diff peak and hole/e·Å^{-3}	0.087 and −0.145	0.331 and −0.336	0.314 and −0.220

There was not sufficient material of compound **6a**·C_6D_6 to record ^{1}H, ^{13}C, and ^{119}Sn NMR spectra. However, the ESI-MS spectrum shows a major mass cluster centered at m/z = 979.4 (100%) that is assigned to $[M - OH]^+$ and that confirms the identity of compound **6a** in solution.

CONCLUSION

Monomeric tin(II) alkoxides, their transition metal complexes as well as tin(IV) alkoxides, can be stabilized by 2-fold intramolecular N→Sn coordination that prohibits intermolecular O→Sn interactions. The chiral information provided by the ephedrine-based ligand controls the absolute configuration at the nitrogen atoms that become chiral centers as a result of the N→Sn coordination. Most interestingly, the combination of the steric bulk of the ephedrine-derived aminoalcoholate, the 2-fold intramolecular N→Sn coordination, and the intramolecular O−H···O hydrogen bridges allows the isolation of the unprecedented tetraalkoxido(dihydroxido)distannoxane (**6a**). Provided that up-scaling of the reaction can be achieved, the latter holds potential for subsequent reactions at the SnOH functions to give tailor-made tinoxo clusters.

EXPERIMENTAL SECTION

General Methods. All solvents were purified by distillation under argon from appropriate drying agents. All reactions were carried out under an inert atmosphere of argon. The NMR spectra were recorded with Bruker DRX 400 and Bruker DPX 300 spectrometers. Chemical shifts δ are given in ppm and are referenced to the solvent peaks with the usual values calibrated against tetramethylsilane (^{1}H, ^{13}C) and tetramethylstannane (^{119}Sn). Elemental analyses were performed on a LECO−CHNS-932 analyzer. All compounds were dried in vacuo (0.01 mmHg) prior to analyses. The electrospray mass spectra were recorded on a Thermoquest−Finnigan instrument using CH_3CN or CH_2Cl_2 as a mobile phase.

The NMR spectra and elemental analyses of all compounds were recorded/determined after the samples had been kept in vacuo (0.1 mmHg) at 50 °C for 1 h in order to remove all volatiles including the solvate molecules.

Crystallography. Intensity data for the crystals of **1**, **2**·C_6H_6, **1a**, **4**·0.5C_6H_{14}, **5**·0.5C_4H_8O, and **6a**·C_6D_6 were collected on an Xcalibur2 CCD diffractometer (Oxford Diffraction) with graphite monochromated MoKα radiation at 173 K. The data collection covered almost the whole sphere of the reciprocal space with 18 sets at different κ-angles and 1030 frames via ω-rotation ($\Delta/\omega = 1°$) at two times 16 s per frame for **1**, 7 sets and 405 frames at two times 1.5 s per frame for **2**·C_6H_6, 7 sets and 408 frames at two times 25 s per frame for **1a**, 3 sets and 210 frames at two times 30 s per frame for **4**·0.5C_6H_{14}, 3 sets and 207 frames at two times 120 s per frame for **5**·0.5C_4H_8O, and 3 sets and 236 frames at two times 30 s per frame for **6a**·C_6D_6. The crystal-to-detector distance was 4.5 cm. Crystal decay was monitored by repeating the initial frames at the end of data collection. Analyzing the duplicate reflections, there was no indication of any decay. The structures were solved by direct methods SHELXS97[25] and successive difference Fourier syntheses. Refinement applied full-matrix least-squares methods SHELXL97.[26] All H atoms were located in the difference Fourier map, and their positions were isotropically refined with U_{iso} constrained at 1.2 times U_{eq} of the carrier C atom for non-methyl groups and at 1.5 times U_{eq} of the carrier C atom for methyl groups. Atomic scattering factors for neutral atoms and real and

Table 3. Crystal Data and Structure Refinement for Compounds $\mathbf{4}\cdot 0.5C_6H_{14}$, $\mathbf{5}\cdot 0.5C_4H_8O$, and $\mathbf{6a}\cdot C_6D_6$

	$\mathbf{4}\cdot 0.5C_6H_{14}$	$\mathbf{5}\cdot 0.5C_4H_8O$	$\mathbf{6a}\cdot C_6D_6$
empirical formula	$C_{30}H_{37}N_2O_7SnW$	$C_{29}H_{34}CrN_2O_{7.5}Sn$	$C_{50}H_{62}D_6N_4O_7Sn_2$
formula weight	797.07	665.22	996.36
temperature/K	173(2)	173(2)	173(2)
wavelength/Å	0.71073	0.71073	0.71073
crystal system	orthorhombic	orthorhombic	tetragonal
space group	$P2_12_12_1$	$P2_12_12_1$	$P4_22_12$
unit cell dimensions			
a /Å	7.0554(4)	7.0618(4)	12.8431(4)
b /Å	16.776(2)	16.738(1)	12.8431(4)
c /Å	25.249(6)	25.383(2)	32.889(1)
volume/Å^3	2988.5(8)	3000.3(3)	5424.9(3)
Z	4	4	4
D_c /g·cm^3	1.772	1.473	1.220
absorption coefficient/mm^{-1}	4.726	1.238	0.964
F(000)	1544	1344	2040
crystal size/mm	0.22 × 0.20 × 0.06	0.20 × 0.08 × 0.06	0.23 × 0.17 × 0.12
Θ range for data collection /°	2.02−25.50	2.01−25.49	2.24−25.50
reflections collected	11420	11288	23826
independent reflections	5544 [R(int) = 0.0509]	5525 [R(int) = 0.0456]	5065 [R(int) = 0.0457]
refinement method		full-matrix least-squares on F^2	
data/restraints/parameters	5544/0/343	5525/0/343	5065/70/264
goodness-of-fit on F^2	0.803	0.700	0.828
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0352$, $wR_2 = 0.0508$	$R_1 = 0.0320$, $wR_2 = 0.0375$	$R_1 = 0.0311$, $wR_2 = 0.0720$
R indices (all data)	$R_1 = 0.0537$, $wR_2 = 0.0525$	$R_1 = 0.0578$, $wR_2 = 0.0393$	$R_1 = 0.0441$, $wR_2 = 0.0739$
largest diff peak and hole/e·Å^{-3}	1.244 and −0.727	0.548 and −0.424	0.392 and −0.441

imaginary dispersion terms were taken from *International Tables for X-ray Crystallography*.[27] To improve the main part of structures $\mathbf{4}\cdot 0.5C_6H_{14}$, $\mathbf{5}\cdot 0.5C_4H_8O$, and $\mathbf{6a}\cdot C_6D_6$, disordered solvent molecules were removed by Platon/Squeeze.[22] In compound $\mathbf{6a}\cdot C_6D_6$, two groups of atoms are affected by disorder. One group consists of the phenyl atoms C21−C26 with methyl atom C27 and carbon atoms C33−C35 forming the second group. Both of them are refined by a split model over two positions with an occupancy ratio of 55:45 for the first group and 50:50 for the second group. Standard similar distance restraints and equal anisotropic displacement parameters were used to stabilize the split model. The anisotropic U-values of C33 and C35 are restrained to behave more isotropically. The figures were created by SHELXTL.[28] Crystallographic data are given in Tables 2 and 3. Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary material publication no. CCDC 825802−825807. Copies of the data can be obtained free charge on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, U.K. (fax: +44 1223 336033, e-mail: deposit@ccdc.cam.ac.uk).

*Synthesis of (3R,4S,9S,10R)-3,10-Diphenyl-4,5,8,9-tetramethyl-5,8-diaza-2,11-dioxa-1-stanna(II)tricyclo[3.2.3.0^{1,5}.0^{1,8}]undecane (**2**).* To a suspension of $Sn(OMe)_2$ (4.16 g, 23.03 mmol) in dry toluene (150 mL) was added dropwise a solution of *N*,*N*′-ethylenebis-(1*R*,2*S*)-ephedrine (8.21 g, 23.03 mmol) in dry toluene (60 mL) within 10 min. After complete addition, the reaction mixture was heated and two-thirds of the solvent and the resulting MeOH were removed by aceotropic distillation. The remaining solvent was removed under reduced pressure to obtain compound **2** (10.47 g, 22.13 mmol, 96.2%) as colorless oil that slowly solidified. Single crystals of **2**, as its benzene solvate $\mathbf{2}\cdot C_6H_6$, were obtained by recrystallization from benzene.

^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.53−7.17 (complex pattern, 60H, Ph−*H*, **1**, **2**), 6.54 (d, ^3J (^{1}H−^{1}H) = 2.1 Hz, 2H, OH, **1**), 5.55 (s, $\Delta\nu_{1/2}$ = 30 Hz, 5H, (Ph)C*H*, **2**), 5.23 (s, $\Delta\nu_{1/2}$ = 33 Hz, 5H, (Ph)C*H*, **2**), 5.13 (s, 2H, 2(Ph)C*H*, **1**), 3.50−1.95 (complex pattern, 60H, NCH_2, *C*HCH$_3$, NCH_3, **2**), 3.15 (d, ^2J (^{1}H−^{1}H) = 11.0 Hz, 2H, NCH−*H*, **1**), 2.88 (dq, ^3J (^{1}H−^{1}H) = 6.8 Hz, 6.8 Hz, 2H, (Me)C−*H*, **1**), 2.44 (s, 6H, NCH_3, **1**), 2.27 (d, ^2J (^{1}H−^{1}H) = 11.0 Hz, 2H, NCH−*H*, **1**), 0.96 (s, $\Delta\nu_{1/2}$ = 19 Hz, 30H, CHCH_3, **2**), 0.78 (d, ^3J (^{1}H−^{1}H) = 7.0 Hz, 6H, CHCH_3, **1**). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6): δ 145.8 ($\Delta\nu_{1/2}$ = 50 Hz, Ph−C_i), 142.8 (Ph−C_i), 129.2, 128.4, 128.3, 128.1 ($\Delta\nu_{1/2}$ = 5 Hz), 128.0, 127.9, 127.7 ($\Delta\nu_{1/2}$ = 4 Hz), 126.8 ($\Delta\nu_{1/2}$ = 31 Hz), 126.7, 126.3, 126.1 ($\Delta\nu_{1/2}$ = 5 Hz), (s, Ph−C), 80.1 ($\Delta\nu_{1/2}$ = 29 Hz, (Ph)CO, **2**), 76.2 ((Ph)CO, **1**), 73.6 ($\Delta\nu_{1/2}$ = 31 Hz, (Ph)CO, **2**), 68.3 ($\Delta\nu_{1/2}$ = 30 Hz, (Me)CH, **2**), 64.3 ((Me)CH, **1**), 63.6 ($\Delta\nu_{1/2}$ = 26 Hz, (Me)CH, **2**), 55.1 ($\Delta\nu_{1/2}$ = 27 Hz, NCH$_2$, **2**), 51.7 (NCH$_2$, **1**), 50.8 ($\Delta\nu_{1/2}$ = 21 Hz, NCH$_2$, **2**), 43.9 ($\Delta\nu_{1/2}$ = 20 Hz, NCH$_3$, **2**), 43.2 (NCH$_3$, **1**), 38.5 ($\Delta\nu_{1/2}$ = 27 Hz, NCH$_3$, **2**), 10.7 ($\Delta\nu_{1/2}$ = 23 Hz, CCH$_3$, **2**), 10.1 ($\Delta\nu_{1/2}$ = 27 Hz, CCH$_3$, **2**), 6.8 (CCH$_3$, **1**). ^{119}Sn NMR (112 MHz, CD_2Cl_2): δ −231 (integral 1.00, $\Delta\nu_{1/2}$ = 1048 Hz), −334 (integral 0.04, $\Delta\nu_{1/2}$ = 177 Hz). Anal. Calcd. for $C_{22}H_{30}N_2O_2Sn$ (%): C 55.8, H 6.4, N 5.9. Found: C 55.4, H 6.7, N 5.3. MS (ESI +): m/z = 829.5 [[{CH$_2$N(Me)CH(Me)CH(Ph)O}$_2$]$_2$Sn + H]$^+$, 475.2 [M + H]$^+$, 357.3 [**1** + H]$^+$, 192.2 [$C_{12}H_{18}NO$]$^+$.

*Synthesis of (3R,4S,9S,10R)-1,1-Dibromido-3,10-diphenyl-4,5,8,9-tetramethyl-5,8-diaza-2,11-dioxa-1-stanna(II)tricyclo[3.2.3.0^{1,5}.0^{1,8}-]undecane (**3**).* To a magnetically stirred solution of **2** (1.14 g, 2.41 mmol) in dry toluene (100 mL) was added dropwise a solution of bromine (Br_2) in dichloromethane (6.20 mL, 0.062 g Br_2/mL, 2.41 mmol, 1 equiv). The color of the reaction mixture turned yellowish, and a yellow amorphous solid precipitated. After a short heating at reflux and filtrating the hot solution, compound **3** (1.32 g, 2.08 mmol, 86.3%) was obtained as yellow amorphous solid.

^{119}Sn NMR (112 MHz, CD$_2$Cl$_2$): δ −544 (integral 1.74, $\Delta\nu_{1/2}$ = 16 Hz) and −586 (integral 1.00, $\Delta\nu_{1/2}$ = 18 Hz). Mp = 136 °C (decomposition). Anal. Calcd. for C$_{22}$H$_{30}$Br$_2$N$_2$O$_2$Sn (%): C 41.7, H 4.8, N 4.4. Found: C 42.2, H 5.1, N 3.8. MS (ESI +): *m*/*z* = 633.0 [M + H]$^+$, 357.3 [**1** + H]$^+$.

*Synthesis of Pentacarbonyl{(3R,4S,9S,10R)-3,10-diphenyl-4,5,8,9-tetramethyl-5,8-diaza-2,11-dioxa-1-stanna(II)tricyclo[3.2.3.0^{1,5}.0^{1,8}]-undecane}tungsten(0) (**4**).* A solution of W(CO)$_6$ (2.50 g, 7.04 mmol) in dry THF (250 mL) was irradiated with UV light, and the volume of the carbon monoxide formed was measured. After 150 mL of CO had been formed (within a period of 1.5 h), the UV irradiation was stopped and the reaction mixture was evaporated under reduced pressure to a volume of 100 mL. The concentrated solution was added to a suspension of the stannylene **2** (3.33 g, 7.04 mmol) in dry THF (80 mL), and the mixture was stirred at room temperature for 24 h. The solvent was removed under reduced pressure to provide **4** (5.46 g, 6.62 mmol, 94.0%) as yellowish amorphous solid. Crystallization from dichloromethane/hexane gave colorless needles of **4**, as its hexane solvate **4**·0.5C$_6$H$_{14}$.

^{1}H NMR (300 MHz, CD$_2$Cl$_2$): δ 7.55−7.32 (m, 10H, Ph−*H*), 5.57 (d, ^3J (^{1}H−^{1}H) = 4.5 Hz, 1H, (Ph)C*H*), 5.20 (d, ^3J (^{1}H−^{1}H) = 2.5 Hz, 1H, (Ph)C*H*), 3.60−3.43 (m, 1H, (Me)C*H*), 3.35−3.22 (m, 1H, (Me)C*H*), 3.22−3.08 (m, 1H, NCH−*H*), 3.02−2.70 (m, 3H, NCH−*H*), 2.90 (s, 3H, NC*H*$_3$), 2.37 (s, 3H, NC*H*$_3$), 1.08 (d, ^3J (^{1}H−^{1}H) = 6.9 Hz, 3H, C*H*$_3$) 1.04 (d, ^3J (^{1}H−^{1}H) = 6.7 Hz, 3H, C*H*$_3$). ^{13}C{^{1}H} NMR (101 MHz, CD$_2$Cl$_2$): δ 199.9 (s, W−CO), 198.3 (s, W−CO), 143.9 (Ph−*C*$_{\text{ipso}}$), 143.5 (Ph−*C*$_{\text{ipso}}$), 127.9 (Ph−*C*), 126.6 (Ph−*C*), 126.1 (Ph−*C*), 143.1 (Ph−*C*), 128.4 (Ph−*C*), 127.0 (Ph−*C*), 126.4 (Ph−*C*), 77.2 ((Ph)CO), 72.9 ((Ph)CO), 68.8 ((Me)CH), 63.7 ((Me)CH), 54.1 (NCH$_2$), 50.2 (NCH$_2$), 46.6 (NCH$_3$), 39.4 (NCH$_3$), 10.7 (CCH$_3$), 10.3 (CCH$_3$). ^{119}Sn NMR (112 MHz, CD$_2$Cl$_2$): δ −112 (s, ^1J (^{119}Sn−^{183}W) = 1469 Hz). ^{119}Sn CP-MAS NMR (149 MHz): δ_{iso} −118 (**4**), −722 (impurity, not defined). Mp = 199 °C (decomposition). Anal. Calcd. for C$_{27}$H$_{30}$N$_2$O$_7$SnW (%): C 40.7, H 3.8, N 3.5. Found: C 41.1, H 3.8, N 2.9. MS (ESI +): *m*/*z* = 860.0 [M + Na + CH$_3$CN]$^+$, 763.1 [**2** + W(CO)$_3$ + Na]$^+$, 583.2 [**2** + Na + CH$_3$CN]$^+$, 497.1 [**2** + Na]$^+$, 475.2 [**2** + H]$^+$.

*Synthesis of Pentacarbonyl{(3R,4S,9S,10R)-3,10-diphenyl-4,5,8,9-tetramethyl-5,8-diaza-2,11-dioxa-1-stanna(II)tricyclo[3.2.3.0^{1,5}.0^{1,8}]-undecane}chromium(0) (**5**).* The procedure is the same as described for compound **4** with freshly generated [Cr(CO)$_5$(thf)]. Compound **5** crystallized from tetrahydrofurane, as its THF solvate **5**·0.5C$_4$H$_8$O, as colorless needles.

^{1}H NMR (300 MHz, CD$_2$Cl$_2$): δ 7.53−7.31 (m, 10H, Ph−*H*), 5.57 (d, ^3J (^{1}H−^{1}H) = 4.5 Hz, 1H, (Ph)C*H*), 5.20 (d, ^3J (^{1}H−^{1}H) = 2.5 Hz, 1H, (Ph)C*H*), 3.55−3.39 (m, 1H, (Me)C*H*), 3.31−3.18 (m, 1H, (Me)C*H*), 3.16−3.01 (m, 1H, NCH−*H*), 2.97−2.68 (m, 3H, NCH−*H*), 2.82 (s, 3H, NC*H*$_3$), 2.33 (s, 3H, NC*H*$_3$), 1.02 (d, ^3J (^{1}H−^{1}H) = 6.9 Hz, 3H, C*H*$_3$), 0.98 (d, ^3J (^{1}H−^{1}H) = 6.7 Hz, 3H, C*H*$_3$). ^{13}C{^{1}H} NMR (100.63 MHz, CD$_2$Cl$_2$): δ (ppm) = 199.8 (s, Cr−CO), 143.5 (Ph−*C*$_{\text{ipso}}$), 128.4 (Ph−*C*), 127.0 (Ph−*C*), 126.1 (Ph−*C*), 77.9 ((Ph)CO), 72.2 ((Ph)CO), 68.8 ((Me)CH), 63.7 ((Me)CH), 54.1 (NCH$_2$), 50.2 (NCH$_2$), 46.6 (NCH$_3$), 39.4 (NCH$_3$), 10.7 (CCH$_3$), 10.3 (CCH$_3$). ^{119}Sn NMR (112 MHz, CDCl$_3$): δ 47. ^{119}Sn CP-MAS NMR (149 MHz): δ_{iso} 34. Mp = 185 °C (decomposition). No elemental analysis was performed.

*Reaction of Sn(O-t-Bu)$_4$ with N,N′-Ethylenebis-(1R,2S)-ephedrine (**1**).* To a stirred solution of Sn(O-*t*-Bu)$_4$ (1.18 g, 2.87 mmol) in dry toluene (100 mL) was added a solution of *N*,*N*′-ethylenebis-(1*R*,2*S*)-ephedrine (**1**) (1.02 g, 2.87 mmol) in dry toluene (40 mL), dropwise. After complete addition, the reaction mixture was heated and two-thirds of the solvent and the resulting *t*-BuOH were removed by aceotropic distillation. The remaining solvent was removed under reduced pressure to give **6** as a colorless, amorphous solid. Partial hydrolysis of the product by reaction in benzene-*d*$_6$ with moisture gave colorless crystals of **6a**·C$_6$D$_6$.

*Compound **6**.* ^{1}H NMR (300 MHz, CD$_2$Cl$_2$, 300 K): δ 7.55 (d, ^3J (^{1}H−^{1}H) = 7.4 Hz, 4H, Ph−*H*), 7.42 (d, ^3J (^{1}H−^{1}H) = 7.4 Hz, 4H, Ph−*H*), 7.32 (dt, ^3J (^{1}H−^{1}H) = 7.5 Hz, ^3J (^{1}H−^{1}H) = 3.0 Hz, 8H, Ph−*H*), 7.26−7.16 (m, 4H, Ph−*H*), 5.39 (d, ^3J (^{1}H−^{1}H) = 9.2 Hz, 2H, (Ph)C*H*), 5.23 (d, ^3J (^{1}H−^{1}H) = 5.6 Hz, 2H, (Ph)C*H*), 3.81 (dq, ^3J (^{1}H−^{1}H) = 9.1 Hz, ^3J (^{1}H−^{1}H) = 7.4 Hz, 2H, (Me)C*H*), 3.59 (d, ^2J (^{1}H−^{1}H) = 9.8 Hz, 2H, NCH−*H*$_A$), 3.00 (d, ^2J (^{1}H−^{1}H) = 10.0 Hz, 2H, NCH−*H*$_A$), 2.89 (s, ^3J (^{1}H−^{119}Sn) = 16.4 Hz, 6H, NC*H*$_3$), 2.93−2.82 (m, 2H, (Me)C*H*), 2.67 (s, ^3J (^{1}H−^{119}Sn) = 16.4 Hz, 6H, NC*H*$_3$), 2.53 (d, ^2J (^{1}H−^{1}H) = 9.8 Hz, 2H, NCH−*H*$_B$), 2.17 (d, ^2J (^{1}H−^{1}H) = 10.2 Hz, 2H, NCH−*H*$_B$), 1.42 (s, 18H, C(C*H*$_3$)$_3$), 1.37 (s, 18H, C(C*H*$_3$)$_3$), 1.11 (d, ^3J (^{1}H−^{1}H) = 7.1 Hz, 6H, C*H*$_3$), 0.76 (d, ^3J (^{1}H−^{1}H) = 7.4 Hz, 6H, C*H*$_3$). ^{13}C{^{1}H} NMR (100.63 MHz, CD$_2$Cl$_2$, 300 K): δ 146.9 (Ph−*C*$_{\text{ipso}}$), 146.5 (Ph−*C*$_{\text{ipso}}$), 127.9 (Ph−*C*), 127.8 (Ph−*C*), 127.7 (Ph−*C*), 127.3 (Ph−*C*), 126.6 (Ph−*C*$_{\text{para}}$), 126.5 (Ph−*C*$_{\text{para}}$), 72.9 ((Ph)CO, ^2J (^{13}C−^{119}Sn) = 22.8 Hz), 72.9 ((Ph)CO, ^2J (^{13}C−^{119}Sn) = 27.4 Hz), 71.2 (OC(CH$_3$)$_3$), 70.8 (OC(CH$_3$)$_3$, ^2J (^{13}C−^{119}Sn) = 40.5 Hz), 65.3 ((Me)CH), 61.1 ((Me)CH), 52.8 (NCH$_2$), 49.0 (NCH$_2$), 42.4 (NCH$_3$), 40.4 (NCH$_3$), 33.9 (^2J (^{13}C−^{119}Sn) = 24.4 Hz, OC(CH$_3$)$_3$), 33.9 (^2J (^{13}C−^{119}Sn) = 25.6 Hz, OC(CH$_3$)$_3$), 12.8 (CCH$_3$), 10.9 (^3J (^{13}C−^{119}Sn) = 13.8 Hz, CCH$_3$). ^{119}Sn NMR (112 MHz, C$_6$D$_6$): δ −539 (J (^{119}Sn−^{13}C) = 26 Hz, 47 Hz, 61 Hz, integral 1), −543 (J (^{119}Sn−^{13}C) = 25 Hz, 40 Hz, 64 Hz, integral 0.90). MS (ESI +): *m*/*z* = 1465.6 [M + {CH$_2$N(Me)CH(Me)CH(Ph)O}$_2$SnOH + **1**]$^+$, 977.4 [M + **1** + H]$^+$, 491.2 [{CH$_2$N(Me)CH(Me)CH(Ph)O}$_2$SnOH]$^+$, 357.3 [**1** + H]$^+$, 192.2 [C$_{12}$H$_{18}$NO]$^+$.

*Compound **6a**.* Mp = 204−207 °C (decomposition). Anal. Calcd. for C$_{44}$H$_{62}$N$_4$O$_7$Sn$_2$ (%): C 53.0, H 6.3, N 5.6. Found: C 52.7, H 6.2, N 5.2. MS (ESI +): *m*/*z* = 979.4 [M − OH]$^+$, 516.2 (not assigned), 509.2 [{CH$_2$N(Me)CH(Me)CH(Ph)O}$_2$Sn(OH)$_2$ + H]$^+$, 491.2 [{CH$_2$N(Me)CH(Me)CH(Ph)O}$_2$SnOH]$^+$, 357.3 [**1** + H]$^+$, 192.2 [C$_{12}$H$_{18}$NO]$^+$.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Molecular structures of compounds **1** (Figure S1), **1a** (Figure S2), and **5**·0.5C$_6$H$_6$ (Figure S3) and crystal data. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: Klaus.jurkschat@tu-dortmund.de.

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