Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Organometallic Chemistry 691 (2006) 2394–2402
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

New chiral tin compounds containing the 2-(4-isopropyl-2-oxazolinyl)-5-phenyl ligand

Krzysztof Staliński [a,*], Zofia Urbańczyk-Lipkowska [a], Piotr Cmoch [a,b], Leszek Rupnicki [c], Andrey Grachev [d]

[a] *Institute of Organic Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland*
[b] *Pharmaceutical Research Institute, Rydygiera 8, 01-793 Warsaw, Poland*
[c] *Department of Chemistry, Warsaw University, Pasteura 1, 02-093 Warsaw, Poland*
[d] *Nesmeyanow Institute of Organo-Element Compounds, Russian Academy of Sciences, Vavilow 28, 117813 Moscow, Russia*

Received 18 October 2005; received in revised form 30 December 2005; accepted 11 January 2006
Available online 23 February 2006

Abstract

A series of tri- and tetraorganotin compounds containing the optically active 2-(4-isopropyl-2-oxazolinyl)-5-phenyl ligand and *tert*-butyl, methyl and/or phenyl groups on the tin has been synthesized. All the novel compounds have been characterized, especially by means of the multinuclear NMR investigation, the results of which are discussed. The tin halides, as pairs of diastereoisomers in solution, crystallize in the form of one diastereoisomer. The single-crystal X-ray analysis of tin iodide **10a** revealed *pseudo*-equatorial position of the *tert*-butyl group opposite to the isopropyl group. In the corresponding diastereomeric tin hydrides values of $^{1}J(^{1}H–^{117/119}Sn)$ differ significantly, suggesting a different *pseudo*-axial/equatorial position of the hydrogen atom.

Keywords: NMR spectroscopy; Sn–N coordination; Tin halides; Tin hydrides

1. Introduction

There have been several reports concerning potentially intramolecularly coordinated tin compounds, including hydrides in which the tin atom is coordinated to nitrogen [1–8] or phosphorus [9] from the ligand. We have recently described the synthesis and NMR study of tin hydrides **1**–**3** containing the chiral oxazoline moiety (Fig. 1) [10,11]. On the basis of the NMR results, especially the $J(^{15}N–^{117/119}Sn)$ coupling constants it appeared that the tin atom in the hydrides was indeed intramolecularly coordinated to the nitrogen from the ligand. The hydrides **1**–**3** have the same substituents (Me, *n*-Bu, Ph) on the tin and a stereogenic center in the oxazoline part. The present study was initiated by our interest in synthesis of intramolecularly Sn–N coordinated hydrides possessing an additional chirality on the tin. It was expected that bulky *tert*-butyl group linked to the tin atom might cause a strong repulsive interaction with the isopropyl group at the stereogenic center of the ligand and lead to one favorable diastereomeric hydride. We now describe the synthesis and NMR study of tri- and tetraorganotin compounds containing the optically active 2-(4-isopropyl-2-oxazolinyl)-5-phenyl ligand and *tert*-butyl, methyl and/or phenyl groups on the tin.

2. Experimental

2.1. Materials and methods

The ^{1}H, ^{13}C, ^{15}N, ^{117}Sn NMR spectra were measured in $CDCl_3$ or C_6D_6 at 303 K on a Bruker DRX Avance 500 spectrometer equipped with a TBI 500SB H-C/BB-D-05 Z-G probehead, operating at 500.133, 125.773, 50.690 and 186.501 MHz for ^{1}H, ^{13}C, ^{15}N and ^{117}Sn, respectively.

* Corresponding author. Tel.: +48 22 632 09 04; fax: +48 22 632 66 81.
E-mail address: stalinsk@icho.edu.pl (K. Staliński).

0022-328X/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2006.01.023

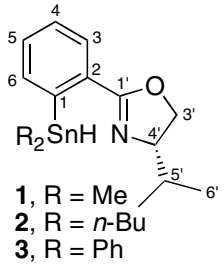


Fig. 1. The Sn–N coordinated tin hydrides **1**–**3**.

The assignment of the ^{1}H and ^{13}C NMR signals of all the compounds studied was made using results of 2D methods including ^{1}H–^{13}C gradient selected HSQC (heteronuclear single quantum correlation) and HMBC (heteronuclear multiple bond correlation). In case of the ^{15}N NMR spectra inverse gated decoupling sequence [possibility of observation of $^{1}J(^{15}N$–$^{117/119}Sn)$ couplings] was used otherwise 2D ^{1}H–^{15}N NMR gradient selected HMBC method was applied. The ^{117}Sn NMR spectra were recorded using inverse gated decoupling sequence. The ^{1}H and ^{13}C NMR measurements in $CDCl_3$ and C_6D_6 for all of the compounds studied were performed using internal tetramethylsilane as a standard, whereas for the ^{15}N and ^{117}Sn nuclei external nitromethane and tetramethyltin were applied as the standards, respectively. IR spectra were measured on a Perkin–Elmer FT-IR spectrophotometer. EI, ESI and HRMS spectra were determined on an ADM 604 Inectra GmbH spectrometer. Thin layer chromatographies were run on silica gel (Merck 60 F_{254}) plates. HPLC analyses were run using a Merck–Hitachi apparatus and Kromasil SI 60/7 μm column. All reactions were carried out under argon atmosphere. 2-(4-Bromo-phenyl)-4-isopropyl-4,5-dihydro-oxazole (**4**) was prepared according to the published procedures [12]. X-ray diffraction measurements of **10a** (crystal of dimensions $0.21 \times 0.27 \times 0.54$ mm) were performed at 293(2) K at a Nonius BV MACH3 diffractometer. Structure of **10a** was solved with direct methods using SHELXS97 [13] and refinement with SHELXL97 [14] programs included into WINGX [15] suite of programs. H-atoms were included at their calculated positions and allowed to ride with B_{iso} equal 1.2 of that of the parent atom. Crystal data of **10a** and details of refinement are shown in Table 1.

Table 1
Crystal data and structure refinement for compound **10a**

Empirical formula	$C_{22}H_{28}I_1N_1O_1Sn_1$
Formula weight	569.05
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Unit cell dimensions	
a (Å)	9.0084(9)
b (Å)	15.660(1)
c (Å)	16.562(2)
Volume (Å^3)	2336.4(4)
Z, calculated density (Mg m^{-3})	4, 1.618
Absorption coefficient (mm^{-1})	19.136
$F(000)$	1116
θ Range for data collection (°)	3.88–75.85
Reflections collected/unique (R_{int})	5190/4616 (0.0663)
Completeness to $2\theta = 74.23$ (%)	98.3
Data/restraints/parameters	4616/0/236
Goodness-of-fit on F^2	1.075
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0809$, $wR_2 = 0.1576$
Absolute structure parameter	−0.02(5)
Largest difference in peak and hole (e Å^3)	4.656 and −3.019
Wavelength (Å)	1.54178
Limiting indices	$10 \leqslant h \leqslant 11$, $-19 \leqslant k \leqslant 19$, $-20 \leqslant l \leqslant 20$
Refinement method	Full-matrix least-squares on F^2
R indices (all data)	$R_1 = 0.2174$, $wR_2 = 0.2703$
Extinction coefficient	0.0020(3)

2.2. Synthesis

2.2.1. General procedure for the preparation of stannanes *5*–*8*

To a solution of the corresponding tetraorganostannane ($Ph_3{}^tBuSn$, $Ph_2{}^tBuMeSn$ or $Ph{}^tBuMe_2Sn$, 10 mmol) in THF was added I_2 (2.54 g, 10 mmol) and the reaction mixture was stirred at ambient temperatures for 2 h and then cooled to −70 °C. Subsequently, a solution of the *o*-lithiophenyloxazole prepared by metallation of 2-(4-bromophenyl)-4-isopropyl-4,5-dihydro-oxazole (2.68 g, 10 mmol) with *n*-butyl lithium (6.3 mL, 10 mmol, 1.6 M solution in hexane) was slowly added and the reaction mixture was stirred for an additional hour and quenched by water. After addition of diethyl ether the organic layer was worked up in the usual manner to give a crude product, which was purified by column, chromatography (hexanes/ethyl acetate) to give compounds **5**–**8**.

*2.2.1.1. (R)-2-[2-(tert-butyl-diphenyl-stannyl)-phenyl]-4-isopropyl-4,5-dihydro-oxazole (**5**).* Yellowish oil, 95%. $[\alpha]_D = -3.9$ ($CHCl_3$, $c = 1$). IR cm^{-1} (film): 3061, 2958, 2924, 2872, 2845, 1649, 1466, 1360, 1255, 1083, 1044, 727. ^{1}H NMR ($CDCl_3$) ppm: 8.10–7.30 (14H, m, $H_{arom.}$), 4.03 (1H, dd, $J = 9.8$ Hz, $J = 8.3$ Hz, –OCH_2CHN–), 3.89 (1H, t, $J = 8.1$ Hz, –OCH_2CHN–), 3.78 (1H, ddd, $J = 9.8$ Hz, $J = 7.9$ Hz, $J = 5.5$ Hz, –OCH$_2$C*H*N–), 1.62–1.53 (1H, m, –C*H*Me$_2$), 1.41 [9H, s, $^{3}J(^{1}H$–$^{117/119}Sn) = 75.4/79.0$ Hz, –Sn^{t}Bu], 0.75 (3H, d, $J = 6.8$ Hz, –CH*Me*$_2$), 0.58 (3H, d, $J = 6.8$ Hz, –CH*Me*$_2$). ^{13}C NMR ($CDCl_3$) ppm: 164.5 [$J(^{13}C$–$^{117/119}Sn) = 10.2$ Hz, C1′], 143.9 [$J(^{13}C$–$^{117/119}Sn) = 386/404$ Hz, C_{phenyl}], 143.1 [$J(^{13}C$–$^{117/119}Sn) = 461/482$ Hz, C_{phenyl}], 141.8 [$J(^{13}C$–$^{117/119}Sn) = 441/461$ Hz, C1], 138.7 [$J(^{13}C$–$^{117/119}Sn) = 33.9$ Hz], 137.5 [$J(^{13}C$–$^{117/119}Sn) = 30.0$ Hz], 137.1 [$J(^{13}C$–$^{117/119}Sn) = 32.1$ Hz], 134.2 [$J(^{13}C$–$^{117/119}Sn) = 20.8$ Hz], 130.6 [$J(^{13}C$–$^{117/119}Sn) = 46.0$ Hz], 128.7 [$J(^{13}C$–$^{117/119}Sn) = 32.8$ Hz], 128.5 [$J(^{13}C$–$^{117/119}Sn) = 9.8$ Hz], 128.0 [$J(^{13}C$–$^{117/119}Sn) = 46.7$ Hz], 127.9 [$J(^{13}C$–$^{117/119}Sn) = 41.1$ Hz], 127.8 [$J(^{13}C$–$^{117/119}Sn) = 10.8$ Hz], 127.7 [$J(^{13}C$–$^{117/119}Sn) = 9.7$ Hz], 72.1 (C4′), 69.5 (C3′), 32.0

[–SnC(CH_3)$_3$], 31.8 (C5′), 30.6 [J(^{13}C–$^{117/119}$Sn) = 493/516 Hz, –SnC(CH$_3$)$_3$], 18.9 and 17.0 (C6′). ^{15}N NMR ($CDCl_3$) ppm: −155.4 [J(^{15}N–$^{117/119}$Sn) = 26.2 Hz]. ^{117}Sn NMR ($CDCl_3$) ppm: −114.8. MS (ESI) m/z: 542 (M^+ + Na). Anal. Calcd. for $C_{28}H_{33}N_1O_1Sn_1$: C, 64.89; H, 6.42; N, 2.70. Found: C, 64.56; H, 6.47; N, 2.68%.

*2.2.1.2. (R)-2-[(R)-2-(tert-butyl-phenyl-methyl-stannyl)-phenyl]-4-isopropyl-4,5-dihydro-oxazole (**6**).* Major diastereoisomer, yellowish oil, 70%. $[\alpha]_D = +17.1$ ($CHCl_3$, $c = 1.1$). IR cm^{-1} (film): 3061, 2957, 2926, 2873, 2844, 1649, 1465, 1359, 1254, 1083, 1044, 726. ^{1}H NMR ($CDCl_3$) ppm: 8.03 (1H, dd, $J = 7.4$ Hz, $J = 1.7$ Hz, H$_{arom.}$), 7.68 (1H, dd, $J = 7.1$ Hz, $J = 1.6$ Hz, H$_{arom.}$), 7.48–7.24 (7H, m, H$_{arom.}$), 4.08 (1H, dd, $J = 9.8$ Hz, $J = 8.3$ Hz, –OCH_2CHN–), 3.95 (1H, t, $J = 8.3$ Hz, –OCH_2CHN–), 3.80 (1H, ddd, $J = 9.8$ Hz, $J = 8.2$ Hz, $J = 5.9$ Hz, –OCH$_2$CHN–), 1.77–1.70 (1H, m, –CHMe$_2$), 1.27 [9H, s, ^3J(^{1}H–$^{117/119}$Sn) = 70.6/73.9 Hz, –Sn^{t}Bu], 0.87 (3H, d, $J = 6.8$ Hz, –CHMe_2), 0.74 (3H, d, $J = 6.8$ Hz, –CHMe_2), 0.42 [3H, s, ^2J(^{1}H–$^{117/119}$Sn) = 46.8/48.7 Hz, –SnMe]. ^{13}C NMR ($CDCl_3$) ppm: 164.5 [J(^{13}C–$^{117/119}$Sn) = 10.2 Hz, C1′], 144.4 [J(^{13}C–$^{117/119}$Sn) = 439/460 Hz, C$_{phenyl}$], 142.7 [J(^{13}C–$^{117/119}$Sn) = 419/438 Hz, C1], 137.6 [J(^{13}C–$^{117/119}$Sn) = 33.6 Hz], 136.3 [J(^{13}C–$^{117/119}$Sn) = 32.0 Hz], 134.1 [J(^{13}C–$^{117/119}$Sn) = 18.6 Hz], 130.2 [J(^{13}C–$^{117/119}$Sn) = 44.5 Hz], 128.7 [J(^{13}C–$^{117/119}$Sn) = 31.2 Hz], 128.2 [J(^{13}C–$^{117/119}$Sn) = 9.6 Hz], 127.7 [J(^{13}C–$^{117/119}$Sn) = 44.9 Hz], 127.4 [J(^{13}C–$^{117/119}$Sn) = 10.3 Hz], 72.3 (C4′), 69.6 (C3′), 31.9 (C5′), 31.2 [–SnC(CH$_3$)$_3$], 27.6 [J(^{13}C–$^{117/119}$Sn) = 460/481 Hz, –SnC(CH$_3$)$_3$], 19.1 and 17.4 (C6′), −8.3 [J(^{13}C–$^{117/119}$Sn) = 312/326 Hz, –SnCH$_3$]. ^{15}N NMR ($CDCl_3$) ppm: −154.6 [J(^{15}N–$^{117/119}$Sn) = 19.4 Hz]. ^{117}Sn NMR ($CDCl_3$) ppm: −73.3. MS (EI) m/z: 442 (M^+ − Me, 7), 400 (100), 380 (5), 314 (37), 222 (28). Anal. Calcd. for $C_{23}H_{31}N_1O_1Sn_1$: C, 60.56; H, 6.85; N, 3.07. Found: C, 60.53; H, 6.72; N, 2.98%.

2.2.1.3. (R)-2-[(S)-2-(tert-butyl-phenyl-methyl-stannyl)-phenyl]-4-isopropyl-4,5-dihydro-oxazole (7). Minor diastereoisomer, yellowish oil, 22%. $[\alpha]_D = +2.6$ ($CHCl_3$, $c = 1.1$). IR cm^{-1} (film): 3062, 2958, 2925, 2873, 2841, 1651, 1465, 1360, 1252, 1082, 1044, 727. ^{1}H NMR ($CDCl_3$) ppm: 8.00–7.27 (9H, m, H$_{arom.}$), 4.23–4.17 (1H, m, –OCH_2CHN–), 4.04–3.98 (2H, m, –OCH$_2$CHN–), 1.93–1.86 (1H, m, –CHMe$_2$), 1.23 [9H, s, ^3J(^{1}H–$^{117/119}$Sn) = 72.3/75.6 Hz, –Sn^{t}Bu], 0.93 (3H, d, $J = 6.8$ Hz, –CHMe_2), 0.80 (3H, d, $J = 6.8$ Hz, –CHMe_2), 0.49 [3H, s, ^2J(^{1}H–$^{117/119}$Sn) = 49.8/52.0 Hz, –SnMe]. ^{13}C NMR ($CDCl_3$) ppm: 164.8 [J(^{13}C–$^{117/119}$Sn) = 9.8 Hz, C1′], 144.8 [J(^{13}C–$^{117/119}$Sn) = 374/391 Hz, C$_{phenyl}$], 143.2 [J(^{13}C–$^{117/119}$Sn) = 423/442 Hz, C1], 138.0 [J(^{13}C–$^{117/119}$Sn) = 33.0 Hz], 136.9 [J(^{13}C–$^{117/119}$Sn) = 29.2 Hz], 133.9 [J(^{13}C–$^{117/119}$Sn) = 20.5 Hz], 130.4 [J(^{13}C–$^{117/119}$Sn) = 44.4 Hz], 128.6 [J(^{13}C–$^{117/119}$Sn) = 31.7 Hz], 128.2 [J(^{13}C–$^{117/119}$Sn) = 9.7 Hz], 127.8 [J(^{13}C–$^{117/119}$Sn) = 39.8 Hz], 127.5 [J(^{13}C–$^{117/119}$Sn) = 9.4 Hz], 72.1 (C4′), 69.2 (C3′), 31.6 (C5′), 31.4 [–SnC(CH$_3$)$_3$], 27.8 [J(^{13}C–$^{117/119}$Sn) = 471/488 Hz, –SnC(CH$_3$)$_3$], 19.2 and 16.9 (C6′), −8.1 [J(^{13}C–$^{117/119}$Sn) = 342/358 Hz, –SnCH$_3$]. ^{15}N NMR ($CDCl_3$) ppm: −156.0. ^{117}Sn NMR ($CDCl_3$) ppm: −72.8. MS (EI) m/z: 442 (M^+ − Me, 8), 400 (100), 380 (7), 314 (37), 222 (31). Anal. Calcd. for $C_{23}H_{31}N_1O_1Sn_1$: C, 60.56; H, 6.85; N, 3.07. Found: C, 60.44; H, 6.81; N, 2.96%.

*2.2.1.4. (R)-2-[2-(tert-butyl-dimethyl-stannyl)-phenyl]-4-isopropyl-4,5-dihydro-oxazole (**8**).* Colorless oil, 72%. $[\alpha]_D = +18.7$ ($CHCl_3$, $c = 1$). IR cm^{-1} (film): 3055, 2958, 2922, 2873, 2844, 1649, 1465, 1358, 1253, 1083, 1044, 725. ^{1}H NMR ($CDCl_3$) ppm: 7.98 (1H, dd, $J = 7.6$ Hz, $J = 1.4$ Hz, H$_{arom.}$), 7.63 (1H, dd, $J = 7.2$ Hz, $J = 1.4$ Hz, H$_{arom.}$), 7.43 (1H, dt, $J = 7.3$ Hz, $J = 1.4$ Hz, H$_{arom.}$), 7.38 (1H, dt, $J = 7.5$ Hz, $J = 1.5$ Hz, H$_{arom.}$), 4.42–4.36 (1H, m, –OCH_2CHN–), 4.18–4.12 (2H, m, –OCH$_2$CHN–), 2.04–1.95 (1H, m, –CHMe$_2$), 1.15 [9H, s, ^3J(^{1}H–$^{117/119}$Sn) = 69.5/72.7 Hz, –Sn^{t}Bu], 1.04 (3H, d, $J = 6.8$ Hz, –CHMe_2), 0.91 (3H, d, $J = 6.8$ Hz, –CHMe_2), 0.25 [3H, s, ^2J(^{1}H–$^{117/119}$Sn) = 49.0/51.2 Hz, –SnMe], 0.20 [3H, s, ^2J(^{1}H–$^{117/119}$Sn) = 45.2/47.1 Hz, –SnMe]. ^{13}C NMR ($CDCl_3$) ppm: 164.8 [J(^{13}C–$^{117/119}$Sn) = 8.9 Hz, C1′], 144.4 [J(^{13}C–$^{117/119}$Sn) = 400/419 Hz, C1], 137.0 [J(^{13}C–$^{117/119}$Sn) = 31.7 Hz], 133.7 [J(^{13}C–$^{117/119}$Sn) = 19.0 Hz, C2], 130.1 [J(^{13}C–$^{117/119}$Sn) = 42.5 Hz], 128.5 [J(^{13}C–$^{117/119}$Sn) = 30.2 Hz], 127.9 [J(^{13}C–$^{117/119}$Sn) = 9.3 Hz], 72.6 (C4′), 69.4 (C3′), 31.9 (C5′), 30.9 [–SnC(CH$_3$)$_3$], 25.1 [J(^{13}C–$^{117/119}$Sn) = 461/483 Hz, [–SnC(CH$_3$)$_3$], 19.3 and 17.2 (C6′), −7.4 [J(^{13}C–$^{117/119}$Sn) = 323/338 Hz, –SnCH$_3$], −8.2 [J(^{13}C–$^{117/119}$Sn) = 290/303 Hz, –SnCH$_3$]. ^{15}N NMR ($CDCl_3$) ppm: −155.9 [J(^{15}N–$^{117/119}$Sn) = 20.1 Hz]. ^{117}Sn NMR (C_6D_6) ppm: −28.6. MS (EI) m/z: 380 (M^+ − Me, 19), 338 (100), 322 (14), 308 (19), 252 (44), 222 (32). Anal. Calcd. for $C_{18}H_{29}N_1O_1Sn_1$: C, 54.86; H, 7.42; N, 3.55. Found: C, 54.69; H, 7.42; N, 3.56%.

*2.2.2. General procedure for the preparation of triorganotin bromides and iodides **9**–**12***

A solution of stannanes **5**–**8** (5.0 mmol) and Br_2 or I_2 (5.1 mmol) in THF (20 mL) was stirred at ambient temperatures. The mixture was then evaporated and the crude product was recrystallized from hexane/CH_2Cl_2 to give the corresponding halides **9**–**12** as yellowish crystals.

*2.2.2.1. (R)-2-[(R,S)(S,R)-(2-bromo-tert-butyl-phenylstannyl)-phenyl]-4-isopropyl-4,5-dihydro-oxazole (**9**).* Mixture of diastereoisomers 4.4/1, yellowish crystals, 97%. IR cm^{-1} (KBr): 3065, 2963, 2956, 2924, 2849, 1635, 1461, 1375, 1091, 945. MS (ESI) m/z: 442 (M^+ − Br). HRMS (ESI): Calcd. for $C_{22}H_{28}N_1O_1Sn_1$ 442.1142. Found 442.1187. Anal. Calcd. for $C_{22}H_{28}Br_1N_1O_1Sn_1$: C, 50.71; H, 5.42; N, 2.69; Br, 15.33. Found: C, 50.63; H, 5.65; N, 2.53; Br, 15.36%.

Major diastereoisomer ***9a***: ^{1}H NMR ($CDCl_3$) ppm: 8.70–7.22 (9H, m, $H_{arom.}$), 4.52 (1H, t, $J = 9.3$ Hz, –OCH_2CHN–), 4.37 (1H, dd, $J = 8.8$ Hz, $J = 7.2$ Hz, –OCH_2CHN–), 4.16 (1H, ddd, $J = 9.9$ Hz, $J = 7.1$ Hz, $J = 4.4$ Hz, –OCH$_2$CHN–), 1.52–1.47 (1H, m, –CHMe$_2$), 1.49 [9H, s, $^{3}J(^{1}H–^{117/119}Sn) = 102.6/107.3$ Hz, –Sn^{t}Bu], 0.69 (3H, d, $J = 6.8$ Hz, –CHMe_2), 0.26 (3H, d, $J = 6.8$ Hz, –CHMe_2). ^{13}C NMR ($CDCl_3$) ppm: 170.0 [$J(^{13}C–^{117/119}Sn) = 8.9$ Hz, C1′], 147.1 [$J(^{13}C–^{117/119}Sn) = 638/667$ Hz, C1], 144.0 [$J(^{13}C–^{117/119}Sn) = 552/578$ Hz, C_{phenyl}], 139.3 [$J(^{13}C–^{117/119}Sn) = 35.5$ Hz], 135.2 [$J(^{13}C–^{117/119}Sn) = 43.0$ Hz], 132.9 [$J(^{13}C–^{117/119}Sn) = 55.7$ Hz], 130.2 [$J(^{13}C–^{117/119}Sn) = 29.1$ Hz], 129.5 [$J(^{13}C–^{117/119}Sn) = 13.6$ Hz], 128.7 [$J(^{13}C–^{117/119}Sn) = 13.5$ Hz], 128.3 [$J(^{13}C–^{117/119}Sn) = 56.0$ Hz], 127.0 [$J(^{13}C–^{117/119}Sn) = 39.0$ Hz], 70.7 (C3′), 70.6 [$J(^{13}C–^{117/119}Sn) = 10.3$ Hz, C4′], 37.9 [$J(^{13}C–^{117/119}Sn) = 600/628$ Hz, –SnC(CH$_3$)$_3$], 31.6 [–SnC(CH$_3$)$_3$], 30.4 (C5′), 19.6 and 14.9 (C6′). ^{117}Sn NMR ($CDCl_3$) ppm: −149.9.

Minor diastereoisomer ***9b***: ^{1}H NMR ($CDCl_3$) ppm: 8.70–7.22 (9H, m, $H_{arom.}$), 4.41–4.37 (1H, m, –OCH_2CHN–), 4.32 (1H, t, $J = 8.6$ Hz, –OCH_2CHN–), 3.65–3.59 (1H, m, –OCH$_2$CHN–), 2.15–2.07 (1H, m, –CHMe$_2$), 1.47 [9H, s, $^{3}J(^{1}H–^{117/119}Sn) = 101.0/105.6$ Hz, –Sn^{t}Bu], 0.79 (6H, 2 × d, $J = 6.8$ Hz, –CHMe_2). ^{13}C NMR ($CDCl_3$) ppm: 170.1 [$J(^{13}C–^{117/119}Sn) = 9.9$ Hz, C1′], 146.0 [$J(^{13}C–^{117/119}Sn) = 648/678$ Hz, C1], 144.7 [$J(^{13}C–^{117/119}Sn) = 575/602$ Hz, C_{phenyl}], 138.5 [$J(^{13}C–^{117/119}Sn) = 34.0$ Hz], 135.4 [$J(^{13}C–^{117/119}Sn) = 42.8$ Hz], 132.9 [$J(^{13}C–^{117/119}Sn) = 48.2$ Hz], 130.4 [$J(^{13}C–^{117/119}Sn) = 30.5$ Hz], 129.4 [$J(^{13}C–^{117/119}Sn) = 13.7$ Hz], 128.6 [$J(^{13}C–^{117/119}Sn) = 13.5$ Hz], 128.3 [$J(^{13}C–^{117/119}Sn) = 56.0$ Hz], 127.0 [$J(^{13}C–^{117/119}Sn) = 40.0$ Hz], 70.9 (C3′), 70.8 [$J(^{13}C–^{117/119}Sn) = 10.3$ Hz, C4′], 37.6 [$J(^{13}C–^{117/119}Sn) = 565/593$ Hz, –SnC(CH$_3$)$_3$], 31.3 [–SnC(CH$_3$)$_3$], 30.5 (C5′), 20.2 and 14.8 (C6′). ^{117}Sn NMR ($CDCl_3$) ppm: −161.4.

*2.2.2.2. (R)-2-[(R,S)(S,R)-(2-iodo-tert-butyl-phenylstannyl)-phenyl]-4-isopropyl-4,5-dihydro-oxazole (**10**).* Mixture of diastereoisomers 5.1/1, yellowish crystals, m.p. 198–201 °C, 97%. $[\alpha]_D = +77.8$ ($CHCl_3$, $c = 1$). IR cm^{-1} (KBr): 3066, 2965, 2955, 2926, 2850, 1634, 1460, 1376, 1091, 944. MS (EI) m/z: 512 ($M^+ - {}^{t}$Bu, 71), 442 (100), 386 (54), 308 (33), 222 (50). HRMS (EI): Calcd. for $C_{18}H_{19}N_1O_1{}^{120}Sn_1I_1$ 511.9533. Found: 511.9548. Anal. Calcd. for $C_{22}H_{28}I_1N_1O_1Sn_1$: C, 46.52; H, 4.97; N, 2.47; I, 22.34. Found: C, 46.59; H, 4.97; N, 2.48; I, 20.78%.

Major diastereoisomer ***10a***: ^{1}H NMR ($CDCl_3$) ppm: 8.79–7.20 (9H, m, $H_{arom.}$), 4.52 (1H, dd, $J = 9.5$ Hz, $J = 9.2$ Hz, –OCH_2CHN–), 4.39 (1H, dd, $J = 8.8$ Hz, $J = 7.1$ Hz, –OCH_2CHN–), 4.17 (1H, ddd, $J = 9.9$ Hz, $J = 7.1$ Hz, $J = 4.3$ Hz, –OCH$_2$CHN–), 1.52 [9H, s, $^{3}J(^{1}H–^{117/119}Sn) = 104.1/108.9$ Hz, –Sn^{t}Bu], 1.47–1.40 (1H, m, –CHMe$_2$), 0.69 (3H, d, $J = 6.7$ Hz, –CHMe_2), 0.25 (3H, d, $J = 6.7$ Hz, –CHMe_2). ^{13}C NMR ($CDCl_3$) ppm: 169.6 [$J(^{13}C–^{117/119}Sn) = 8.1$ Hz, C1′], 148.8 [$J(^{13}C–^{117/119}Sn) = 623/652$ Hz, C1], 142.4 [$J(^{13}C–^{117/119}Sn) = 523/547$ Hz, C_{phenyl}], 140.5 [$J(^{13}C–^{117/119}Sn) = 36.3$ Hz], 134.6 [$J(^{13}C–^{117/119}Sn) = 41.4$ Hz], 132.7 [$J(^{13}C–^{117/119}Sn) = 54.7$ Hz], 129.7, 129.6 128.3 [$J(^{13}C–^{117/119}Sn) = 19.3$ Hz], 128.1, 127.0 [$J(^{13}C–^{117/119}Sn) = 37.0$ Hz], 70.8 (C3′), 70.4 [$J(^{13}C–^{117/119}Sn) = 10.1$ Hz, C4′], 37.5 [$J(^{13}C–^{117/119}Sn) = 579/606$ Hz, –SnC(CH$_3$)$_3$], 31.8 [–SnC(CH$_3$)$_3$], 30.1 (C5′), 19.5 and 14.6 (C6′). ^{117}Sn NMR ($CDCl_3$) ppm: −133.2. ^{15}N NMR ($CDCl_3$) ppm: −179.7 [$J(^{15}N–^{117/119}Sn) = 112.6$ Hz].

Minor diastereoisomer ***10b***: ^{1}H NMR ($CDCl_3$) ppm: 8.79–7.20 (9H, m, $H_{arom.}$), 4.54–4.50 (1H, m, –OCH_2CHN–), 4.37 (1H, t, $J = 8.7$ Hz, –OCH_2CHN–), 3.55–3.49 (1H, m, –OCH$_2$CHN–), 2.13–2.06 (1H, m, –CHMe$_2$), 1.50 [9H, s, $^{3}J(^{1}H–^{117/119}Sn) = 102.1/106.7$ Hz, –Sn^{t}Bu], 0.79 (6H, 2 × d, $J = 6.7$ Hz, –CHMe_2). ^{13}C NMR ($CDCl_3$) ppm: 170.1 (C1′), 147.5, 143.2, 139.7, 134.8 132.6, 130.4, 129.7, 128.4, 128.2, 126.7, 71.1 (C3′), 69.3 (C4′), 35.7 [–SnC(CH$_3$)$_3$], 31.4 [–SnC(CH$_3$)$_3$], 29.8 (C5′), 20.1 and 15.5 (C6′). ^{117}Sn NMR ($CDCl_3$) ppm: −117.6.

*2.2.2.3. (R)-2-[(R,S)(S,R)-(2-bromo-tert-butyl-methyl-stannyl)-phenyl]-4-isopropyl-4,5-dihydro-oxazole (**11**).* Mixture of diastereoisomers 10/1, white crystals, m.p. 85–88 °C, 98%. $[\alpha]_D = +80.7$ ($CHCl_3$, $c = 1$). IR cm^{-1} (film): 3057, 2961, 2925, 2874, 2850, 1634, 1466, 1380, 1262, 1095, 1046, 953, 729. MS (EI) m/z: 444 ($M^+ - Me$, 1), 402 (100), 380 (22), 358 (7), 316 (27), 222 (19). Anal. Calcd. for $C_{27}H_{26}Br_1N_1O_1Sn_1$: C, 44.49; H, 5.71; N, 3.05; Br, 17.41. Found: C, 44.53; H, 5.72; N, 3.11; Br, 17.56%.

Major diastereoisomer ***11a***: ^{1}H NMR ($CDCl_3$) ppm: 8.60–8.45 (1H, m, $H_{arom.}$), 7.83–7.77 (1H, m, $H_{arom.}$), 7.64 (1H, dt, $J = 7.4$ Hz, $J = 1.3$ Hz, $H_{arom.}$), 7.46 (1H, dt, $J = 7.6$ Hz, $J = 1.3$ Hz, $H_{arom.}$), 4.59 (1H, dd, $J = 10.0$ Hz, $J = 9.0$ Hz, –OCH_2CHN–), 4.50 (1H, dd, $J = 8.9$ Hz, $J = 7.0$ Hz, –OCH_2CHN–), 4.28 (ddd, $J = 10.2$ Hz, $J = 6.4$ Hz, $J = 3.2$ Hz, –OCH$_2$CHN–), 2.20–2.10 (1H, m, –CHMe$_2$), 1.31 [9H, s, $^{3}J(^{1}H–^{117/119}Sn) = 98.0/102.6$ Hz, –Sn^{t}Bu], 1.07 (3H, d, $J = 6.8$ Hz, –CHMe_2), 0.87 (3H, d, $J = 6.8$ Hz, –CHMe_2), 0.90 [3H, s, $^{3}J(^{1}H–^{117/119}Sn) = 63.6/66.4$ Hz, –SnMe]. ^{13}C NMR ($CDCl_3$) ppm: 170.1 [$J(^{13}C–^{117/119}Sn) = 8.3$ Hz, C1′], 145.8 [$J(^{13}C–^{117/119}Sn) = 537/562$ Hz, C1], 138.4 [$J(^{13}C–^{117/119}Sn) = 35.5$ Hz], 132.5 [$J(^{13}C–^{117/119}Sn) = 55.1$ Hz], 129.5 [$J(^{13}C–^{117/119}Sn) = 29.0$ Hz], 129.1 [$J(^{13}C–^{117/119}Sn) = 11.1$ Hz], 126.7 [$J(^{13}C–^{117/119}Sn) = 29.0$ Hz], 70.3 (C3′), 69.6 [$J(^{13}C–^{117/119}Sn) = 10.7$ Hz, C4′], 34.1 [$J(^{13}C–^{117/119}Sn) = 573/600$ Hz, –SnC(CH$_3$)$_3$], 30.7 [–SnC(CH$_3$)$_3$], 30.0 (C5′), 19.4 and 14.6 (C6′), 4.3 [$J(^{13}C–^{117/119}Sn) = 460/481$ Hz, –SnCH$_3$]. ^{117}Sn NMR ($CDCl_3$) ppm: −75.7. ^{15}N NMR ($CDCl_3$) ppm: −181.3 [$J(^{15}N–^{117/119}Sn) = 116.3$ Hz].

Minor diastereoisomer ***11b***: ^{1}H NMR ($CDCl_3$) ppm: 8.42–7.43 (4H, m, $H_{arom.}$), 4.62–4.57 (1H, m, –OCH_2CHN–), 4.39 (1H, t, $J = 8.8$ Hz, –OCH_2CHN–), 4.08 (1H, ddd, $J = 9.6$ Hz, $J = 4.3$ Hz, $J = 0.6$ Hz,

–OCH_2CHN–), 2.20–2.10 (1H, m, –C*H*Me_2), 1.32 [9H, s, $^3J(^1H–^{117/119}Sn)$ = 96.2/100.5 Hz, –Sn^{t}Bu], 1.00 (3H, d, J = 6.8 Hz, –CHMe_2), 0.91 [3H, s, $^2J(^1H–^{117/119}Sn)$ = 62.4/65.3 Hz, –SnMe], 0.81 (3H, d, J = 6.8 Hz, –CHMe_2). ^{13}C NMR ($CDCl_3$) ppm: 170.2 (C1′), 145.9 (C1), 138.0, 132.3, 129.5, 129.0, 126.6, 71.3 (C3′), 70.1 (C4′), 32.9 [–Sn*C*$(CH_3)_3$], 30.4 [–SnC(*C*$H_3)_3$], 27.9 (C5′), 20.4 and 15.8 (C6′), 4.1 (–Sn*C*H_3). ^{117}Sn NMR ($CDCl_3$) ppm: −60.9.

*2.2.2.4. (R)-2-[(R,S)(S,R)-(2-iodo-tert-butyl-methyl-stannyl)-phenyl]-4-isopropyl-4,5-dihydro-oxazole (**12**).* Mixture of diastereoisomers 21/1, yellowish oil, 98%. $[\alpha]_D$ = +70.1 ($CHCl_3$, c = 1). IR cm^{-1} (film): 3053, 2962, 2923, 2875, 2849, 1633, 1464, 1381, 1263, 1095, 1046, 952, 728. *Major diastereoisomer* ***12a***: ^1H NMR ($CDCl_3$) ppm: 8.60 (1H, d, J = 7.4 Hz, $H_{arom.}$), 7.80 (1H, d, J = 7.7 Hz, $H_{arom.}$), 7.66 (1H, dt, J = 7.4 Hz, J = 1.2 Hz, $H_{arom.}$), 7.47 (1H, dt, J = 7.6 Hz, J = 1.1 Hz, $H_{arom.}$), 4.61 (1H, dd, J = 9.8 Hz, J = 9.1 Hz, –O*C*H_2CHN–), 4.54 (1H, dd, J = 8.9 Hz, J = 6.9 Hz, –O*C*H_2CHN–), 4.31 (1H, ddd, J = 10.3 Hz, J = 6.9 Hz, J = 3.8 Hz, –OCH_2CHN–), 2.22–2.13 (1H, m, –C*H*Me_2), 1.33 [9H, s, $^3J(^1H–^{117/119}Sn)$ = 99.4/104.1 Hz, –Sn^{t}Bu], 1.10 [3H, s, $^2J(^1H–^{117/119}Sn)$ = 61.5/71.1 Hz, –SnMe], 1.01 (3H, d, J = 6.8 Hz, –CHMe_2), 0.81 (3H, d, J = 6.8 Hz, –CHMe_2). ^{13}C NMR ($CDCl_3$) ppm: 170.3 (C1′), 144.7 [$J(^{13}C–^{117/119}Sn)$ = 508/530 Hz, C1], 140.0 [$J(^{13}C–^{117/119}Sn)$ = 32.3 Hz], 132.8 [$J(^{13}C–^{117/119}Sn)$ = 53.5 Hz], 129.5, 129.3, 127.0 [$J(^{13}C–^{117/119}Sn)$ = 35.9 Hz], 70.7 (C3′), 69.8 (C4′), 34.0 [–Sn*C*$(CH_3)_3$], 31.1 [–SnC(*C*$H_3)_3$], 30.1 (C5′), 19.8 and 14.8 (C6′), 8.6 [$J(^{13}C–^{117/119}Sn)$ = 512/532 Hz, –Sn*C*H_3]. ^{117}Sn NMR ($CDCl_3$) ppm: −58.4 (major diastereoisomer) and −48.3 (minor diastereoisomer). ^{15}N NMR ($CDCl_3$) ppm: −181.9. MS (EI) m/z: 492 (M^+ − Me, 1), 450 (100), 380 (86), 364 (24), 324 (33), 308 (39), 222 (22). HRMS (EI): Calcd. for $C_{13}H_{17}O_1N_1{}^{120}Sn_1I_1$ 449.9377. Found: 449.9370. Anal. Calcd. for $C_{17}H_{26}I_1N_1O_1Sn_1$: C, 40.35; H, 5.18; N, 2.77; I, 25.08. Found: C, 40.23; H, 5.18; N, 2.73; I, 22.79%.

2.2.3. Synthesis of hydrides *13* and *14*

A solution of $NaBH_4$ (757 mg, 20.0 mmol) in ethanol (5 mL) was added to a solution of the corresponding tin halide **9**–**12** (4.0 mmol) in ethanol (10 mL) and stirred at 0 °C for 5 min. The reaction mixture was treated with water (1 mL) and the crude product was extracted with hexane. The extracts were dried over anhydrous $MgSO_4$ and evaporated to afford the corresponding hydride **13** or **14** as colorless oil.

*2.2.3.1. (R,S)(S,R)-[2-(4-(R)-isopropyl-2-oxazoline)-5-phenyl]tert-butylphenyltin hydride (**13**).* Mixture of diastereoisomers 1.7/1.0, yellowish oil, 98%. IR cm^{-1} (film): 3061, 2960, 2923, 2873, 2847, 1836, 1739, 1645, 1580, 1563, 1464, 1362, 1087, 1046, 963. MS (EI) m/z: 442 (M^+ − H, 7), 386 (100), 366 (6), 308 (33), 222 (17). HRMS (EI): Calcd. for $C_{22}H_{28}O_1N_1{}^{120}Sn_1$ 442.1193. Found: 442.1182.

Major diastereoisomer ***13a***: ^1H NMR (C_6D_6) ppm: 8.48–7.25 (9H, m, $H_{arom.}$), 7.15 [1H, s, $^1J(^1H–^{117/119}Sn)$ = 1480/1549 Hz, –SnH], 4.10–3.85 (3H, m, –OCH_2CHN–), 1.68–1.63 (1H, m, –C*H*Me_2), 1.56 [9H, s, $^3J(^1H–^{117/119}Sn)$ = 77.9/81.1 Hz, –Sn^{t}Bu], 0.72 (3H, d, J = 6.8 Hz, –CHMe_2), 0.57 (3H, d, J = 6.8 Hz, –CHMe_2). ^{13}C NMR (C_6D_6) ppm: 165.8 [$J(^{13}C–^{117/119}Sn)$ = 9.9 Hz, C1′], 143.3 [$J(^{13}C–^{117/119}Sn)$ = 498/521 Hz, C_{phenyl}], 143.2 [$J(^{13}C–^{117/119}Sn)$ = 466/487 Hz, C1], 138.6 [$J(^{13}C–^{117/119}Sn)$ = 31.7 Hz], 137.1 [$J(^{13}C–^{117/119}Sn)$ = 35.8 Hz], 133.4 [$J(^{13}C–117/119Sn)$ = 21.5 Hz], 131.5 [$J(^{13}C–^{117/119}Sn)$ = 48.9 Hz], 128.8, 128.3, 128.2, 127.9, 72.3 (C4′), 69.8 (C3′), 35.5 (C5′), 32.0 [–SnC(*C*$H_3)_3$], 29.2 [$J(^{13}C–^{117/119}Sn)$ = 505/529 Hz, –Sn*C*$(CH_3)_3$], 19.4 and 14.1 (C6′). ^{117}Sn NMR (C_6D_6) ppm: −102.0.

Minor diastereoisomer ***13b***: ^1H NMR (C_6D_6) ppm: 8.48–7.25 (9H, m, $H_{arom.}$), 7.35 [1H, s, $^1J(^1H–^{117/119}Sn)$ = 1823/1908 Hz, –SnH], 4.10–3.85 (3H, m, –OCH_2CHN–), 1.82–1.75 (1H, m, –C*H*Me_2), 1.52 [9H, s, $^3J(^1H–^{117/119}Sn)$ = 78.6/81.4 Hz, –Sn^{t}Bu], 0.94 (3H, d, J = 6.8 Hz, –CHMe_2), 0.88 (3H, d, J = 6.8 Hz, –CHMe_2). ^{13}C NMR (C_6D_6) ppm: 165.6 [$J(^{13}C–^{117/119}Sn)$ = 7.9 Hz, C1′], 144.7 [$J(^{13}C–^{117/119}Sn)$ = 336/351 Hz, C_{phenyl}], 143.0 [$J(^{13}C–^{117/119}Sn)$ = 467/487 Hz, C1], 140.1 [$J(^{13}C–^{117/119}Sn)$ = 37.2 Hz], 138.3 [$J(^{13}C–^{117/119}Sn)$ = 35.6 Hz], 133.1 [$J(^{13}C–^{117/119}Sn)$ = 20.3 Hz], 131.2 [$J(^{13}C–^{117/119}Sn)$ = 49.1 Hz], 128.5, 128.3, 128.1, 127.9, 72.1 (C4′), 70.5 (C3′), 35.5 (C5′), 32.3 [–SnC(*C*$H_3)_3$], 29.0 [$J(^{13}C–^{117/119}Sn)$ = 515/539 Hz, [–Sn*C*$(CH_3)_3$], 19.1 and 16.7 (C6′). ^{117}Sn NMR (C_6D_6) ppm: −118.9.

*2.2.3.2. (R,S)(S,R)-[2-(4-(R)-isopropyl-2-oxazoline)-5-phenyl]tert-butylmethyltin hydride (**14**).* Mixture of diastereoisomers 6.2/1, yellowish oil, 98%. IR cm^{-1} (film): 3055, 2960, 2926, 2873, 2845, 1834, 1737, 1643, 1580, 1561, 1480, 1465, 1362, 1087, 1044, 963, 728. MS (EI) m/z: 380 (M^+ − H, 11), 358 (27), 338 (20), 324 (100), 308 (69), 222 (61). HRMS (EI): Calcd. for $C_{13}H_{18}O_1N_1{}^{120}Sn_1$ 324.0410. Found: 324.0418.

Major diastereoisomer ***14a***: ^1H NMR (C_6D_6) ppm: 8.15 (1H, dd, J = 7.5 Hz, J = 1.1 Hz, $H_{arom.}$), 8.03 (1H, dd, J = 7.1 Hz, J = 1.1 Hz, $H_{arom.}$), 6.35 [1H, s, $^1J(^1H–^{117/119}Sn)$ = 1380/1444 Hz, –SnH], 7.30 (1H, dt, J = 5.7 Hz, J = 1.4 Hz, $H_{arom.}$), 7.25 (1H, dt, J = 7.5 Hz, J = 1.4 Hz, $H_{arom.}$), 4.02–3.83 (3H, m, –OCH_2CHN–), 1.90–1.84 (1H, m, –C*H*Me_2), 1.41 [9H, s, $^3J(^1H–^{117/119}Sn)$ = 75.4/79.1 Hz, –Sn^{t}Bu], 0.84 (3H, d, J = 6.8 Hz, –CHMe_2), 0.76 (3H, d, J = 6.8 Hz, –CHMe_2), 0.58 [3H, *d*, J = 2.0 Hz, $^2J(^1H–^{117/119}Sn)$ = 56.4 Hz, –SnMe]. ^{13}C NMR (C_6D_6) ppm: 165.9 [$J(^{13}C–^{117/119}Sn)$ = 9.1 Hz, C1′], 144.8 [$J(^{13}C–^{117/119}Sn)$ = 447/468 Hz, C1], 139.8 [$J(^{13}C–^{117/119}Sn)$ = 36.0 Hz], 133.4 [$J(^{13}C–^{117/119}Sn)$ = 21.4 Hz], 131.2 [$J(^{13}C–^{117/119}Sn)$ = 47.4 Hz], 128.6, 128.2 [$J(^{13}C–^{117/119}Sn)$ = 7.0 Hz], 72.3 (C4′), 69.3 (C3′), 31.8 [–SnC(*C*$H_3)_3$], 30.7 (C5′), 26.3 [$J(^{13}C–^{117/119}Sn)$ = 489/512 Hz, –Sn*C*$(CH_3)_3$],

19.3 and 16.7 (C6′), −7.4 [$J(^{13}C–^{117/119}Sn) = 363/380$ Hz, –Sn*C*H$_3$]. ^{117}Sn NMR (C_6D_6) ppm: −60.0.

Minor diastereoisomer ***14b***: ^{1}H NMR (C_6D_6) ppm: 8.17–7.20 (4H, m, $H_{arom.}$), 6.46 [1H, s, $^1J(^1H–^{117/119}Sn) = 1692/1770$ Hz, –SnH], 4.02–3.83 (3H, m, –OCH$_2$CHN–), 1.81–1.75 (1H, m, –C*H*Me$_2$), 1.39 [9H, s, $^3J(^1H–^{117/119}Sn) = 76.4/80.2$ Hz, –Sn*t*Bu], 0.94 (3H, d, $J = 6.8$ Hz, –CH*Me*$_2$), 0.87 (3H, d, $J = 6.8$ Hz, –CH*Me*$_2$), 0.46 [3H, *d*, $J = 2.0$ Hz, $^2J(^1H–^{117/119}Sn) = 22.2$ Hz, –SnMe]. ^{13}C NMR (C_6D_6) ppm: 165.5 [$J(^{13}C–^{117/119}Sn) = 7.9$ Hz, C1′], 144.1 [$J(^{13}C–^{117/119}Sn) = 443/464$ Hz, C1], 138.2 [$J(^{13}C–^{117/119}Sn) = 34.7$ Hz], 133.7 [$J(^{13}C–^{117/119}Sn) = 18.8$ Hz], 130.9 [$J(^{13}C–^{117/119}Sn) = 29.8$ Hz], 128.7 [$J(^{13}C–^{117/119}Sn) = 9.8$ Hz], 128.5, 72.7 (C4′), 70.1 (C3′), 31.7 [–SnC(*C*H$_3$)$_3$], 30.5 (C5′), 26.1 [$J(^{13}C–^{117/119}Sn) = 489/511$ Hz, –Sn*C*(CH$_3$)$_3$], 20.5 and 19.2 (C6′), −9.1 [$J(^{13}C–^{117/119}Sn) = 287/301$ Hz, –Sn*C*H$_3$]. ^{117}Sn NMR (C_6D_6) ppm: −91.0.

3. Results and discussion

3.1. Synthesis of the tin hydrides

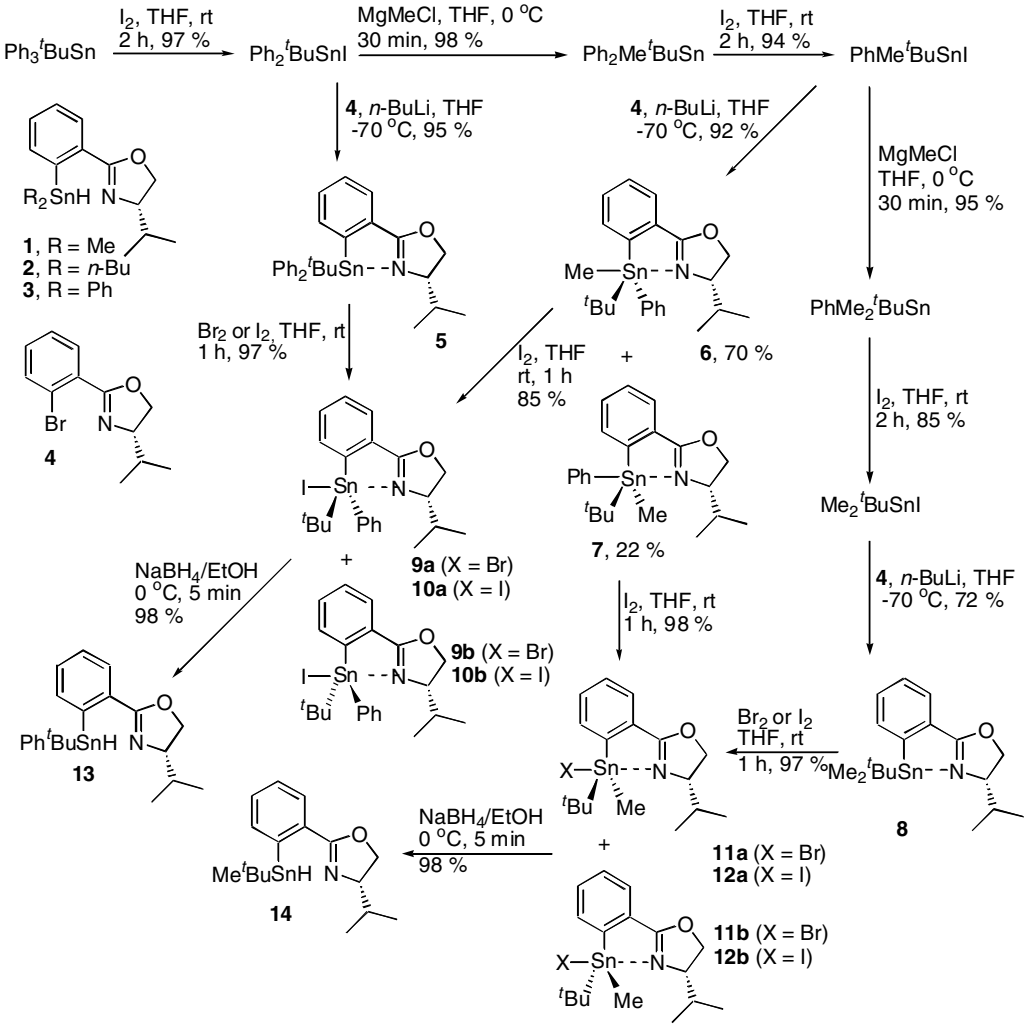
Initially, two isomeric tetraorganotin compounds **6** and **7** were expected to be appropriate precursors of triorganotin halides **9**–**12**. The synthesis of these compounds involved treatment of Ph*t*BuMeSnI with the *o*-lithiophenyloxazole prepared by metallation of 2-(4-bromo-phenyl)-4-isopropyl-4,5-dihydro-oxazole with *n*-butyl lithium in THF at −70 °C. They were formed as a 3.2/1.0 mixture of two diastereoisomers. The mixture could be separated into pure diastereoisomers using HPLC [16,17]. However, when stannanes **6** and **7** reacted with bromine or iodine at ambient temperatures they followed different chemical pathways. In the case of **6** the usual sequence of reactivity was reversed, i.e., the methyl group was cleaved preferentially to the aryl group (**9** and **10**). In the case of **7** tin bromide **11** or iodide **12** was formed according to the general rule. Such phenomena could be explained by intramolecular assistance at the tin [10,18]. In view of these results the reported triorganotin bromides and iodides **9**–**12** were prepared in a much simpler way via addition of stoichiometric amount of bromine or iodine to stannanes **5** and **8** (Scheme 1). Tin halides were obtained as mixtures of diastereoisomers: **9** (**a**/**b** = 4.4/1.0), **10** (**a**/**b** = 5.1/1.0), **11** (**a**/**b** = 10/1), **12** (**a**/**b** = 21/1). They could be purified on silica gel to give satisfactory elemental analyses. The tin halides appeared to be stable and could be stored at room temperature with exclusion of light for months without decomposition. Crystallization of tin iodide **10a**,**b** results in the preferential formation of one diastereoisomer **10a**. However, in solution at room temperature the 5.1/1.0 ratio of **10a**/**10b** reestablishes itself. Similar preferential crystallization has been reported [6,19]. Reduction of tin halides **9**–**12** with $NaBH_4$ in ethanol at 0 °C afforded tin hydrides **13** and **14** as mixtures of diastereoisomers: **13** (**a**/**b** = 1.7/1.0), **14** (**a**/**b** = 6.2/1.0). However, when the reaction time was longer (1 h) epimerization was observed, presumable due to the presence of sodium borohydride or ethoxide anions formed in the reaction mixture. A similar process has been reported by Metzger and co-workers [3]. The isolated organotin hydrides do not racemize and are stable enough to be used in further radical reactions but they cannot be stored for a long period of time at room temperature due to their high reactivity.

3.2. Crystal structure of triorganotin iodide (*10a*)

The molecular structure of tin iodide **10a** is shown in Fig. 2 and selected interatomic parameters are collected in Table 2. The compound has trigonal bipyramidal coordination geometry at the tin atom, with the N- and I-atoms located in the apex of the bipyramid and the three carbon atoms occupying equatorial positions. In the absence of classic hydrogen bond donors several CH-acceptor interactions are observed in the crystal. Conformation of the complex is stabilized by two intramolecular hydrogen bonds: C6–H6–I1 [H6–I1 = 2.93(8) Å, C6–H6–I1 angle = 133(4)] and C3–H3–O8 [H3-O8 = 2.57(8) Å, C3–H3–O8 angle = 102]. Due to chiral ligand the compound crystallizes in the non-centrosymmetric space group. Absolute configuration at the C10 stereogenic center is (R), as assigned on the basis of ψ-scan based absorption.

3.2.1. Structure in solution of the tetraorganotin compounds

We have recently described that the tin atom in tetraorganotin compounds containing the chiral oxazoline was in fact pentacoordinated due to the weak Sn–N coordination [10,11]. Newly synthesized compounds **5**–**8**, which are substrates in two-step reaction leading to hydrides **13** and **14** also share this feature. The $^{117/119}$Sn chemical shifts of tetraorganotins are generally not sensitive to the anticipated Sn–N coordination [20]. For compounds **5**–**8** the ^{117}Sn NMR shifts depend only on a number of phenyl groups attached to the tin atom: **5** (−114.8 ppm), **6** (−73.3 ppm), **7** (−72.8 ppm), **8** (−28.6 ppm). Comparison of the ^{117}Sn NMR data for **5**–**8** with those of counterparts without the oxazoline substituent (Ph$_3$*t*BuSn −108.9 ppm, Ph$_2$*t*BuMeSn −65.0 ppm, Ph*t*BuMe$_2$Sn −19.1 ppm) indicates only small ^{117}Sn shielding increases (5.9–9.5 ppm) for potentially coordinated stannanes **5**–**8**. More informative, from the standpoint of the Sn–N interaction parameters, are the ^{13}C and ^{15}N NMR data, especially the $^1J(^{13}C–^{117/119}Sn)$ and the $^1J(^{15}N–^{117/119}Sn)$ couplings. An increase in coupling constants is ascribed to an increase of s character in the C1–Sn bond. Comparison of the $J(^{13}C–^{117/119}Sn)$ for stannanes **5**–**8** with those from Ph$_3$*t*BuSn: 139.2 ppm [418/434 Hz], 29.1 ppm [441/462 Hz]; Ph$_2$*t*BuMeSn: 140.5 ppm [405/424 Hz], 26.7 ppm [432/452 Hz], −12.2 ppm [299/312 Hz]; Ph*t*BuMe$_2$Sn: 141.7 ppm [390/408 Hz], 23.9 ppm [423/443 Hz], −12.1 ppm [290/304 Hz] shows either increase or decrease of the $^1J(^{13}C–^{117/119}Sn)$ couplings at carbons directly bounded to the tin for **5**–**8** (Table 3). As previously proved



Scheme 1. The preparation of tin compounds **5**–**14**.

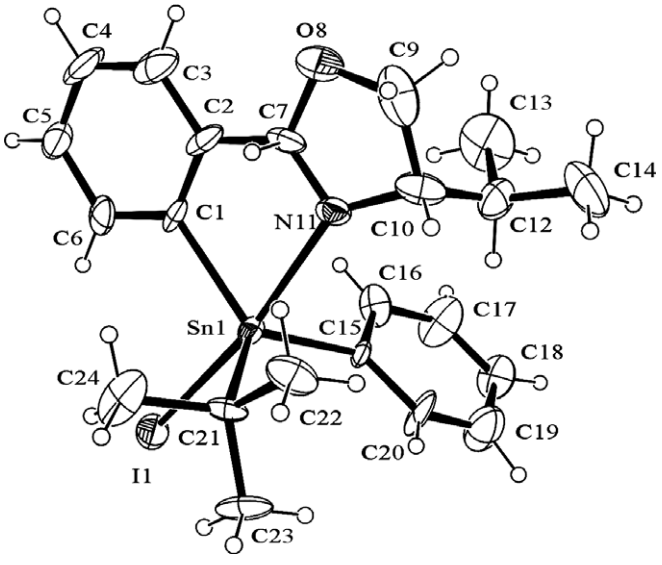


Fig. 2. Molecular structure and atomic numbering scheme for tin iodide **10a**.

Table 2
Selected bond lengths and angles for **10a**

Bond lengths (Å)		Angles (°)			
Sn–1–C15	2.11(2)	C1–Sn1–C15	120.1(7)	C21–Sn1–N11	95.1(6)
Sn1–C1	2.19(2)	C15–Sn1–C21	118.7(9)	C15–Sn1–I1	92.6(6)
Sn1–C21	2.21(2)	C1–Sn1–C21	118.5(9)	C1–Sn1–I1	94.3(7)
Sn1–N11	2.44(2)	C15–Sn1–N11	87.1(7)	C21–Sn1–I1	94.3(7)
Sn1–I1	2.867(2)	C1–Sn1–N11	74.9(8)	N11–Sn1–I1	167.1(4)

by NOE differential and NOESY experiments the *tert*-butyl group in stannanes **5**–**8** occupies a *pseudo*-equatorial position opposite to the isopropyl one due to steric reasons. Therefore, it is reasonably safe to assume that the considerably large differences between the $^{1}J(^{13}C–^{117/119}Sn)$ couplings observed at the phenyl/methyl carbons directly bounded to the tin of **5**–**8** are due to *pseudo*-axial/equatorial positions of two remaining groups (Ph or Me) caused by the Sn–N interaction. An additional proof supporting the Sn–N coordination was obtained from long accumu-

Table 3
The selected $^{1}J(^{117/119}Sn–^{13}C)$ values of stannanes **5**–**9**, **13**, **14**

Stannane	$^{1}J(^{117/119}Sn–^{13}C)$			
	C_1 *tert*-butyl	C_1 ligand	C_1 phenyl	C_1 methyl
5	30.6 (493/516)	141.8 (441/461)	143.9 (386/404), 143.1 (461/482)	–
6	27.6 (460/481)	142.7 (419/438)	144.4 (439/460)	−8.3 (312/326)
7	27.8 (471/488)	143.2 (423/442)	144.8 (374/391)	−8.1 (342/358)
8	25.1 (461/483)	144.4 (400/419)	–	−7.4 (323/338), −8.2 (290/303)
9a	37.9 (600/628)	147.1 (638/667)	144.0 (552/578)	–
9b	37.6 (565/593)	146.0 (648/678)	144.7 (575/602)	–
13a	29.2 (505/529)	143.2 (466/487)	143.3 (498/521)	–
13b	29.0 (515/539)	143.0 (467/487)	144.7 (336/351)	–
14a	26.3 (489/512)	144.8 (447/468)	–	−7.4 (363/380)
14b	26.1 (489/511)	144.1 (443/464)	–	−9.1 (287/301)

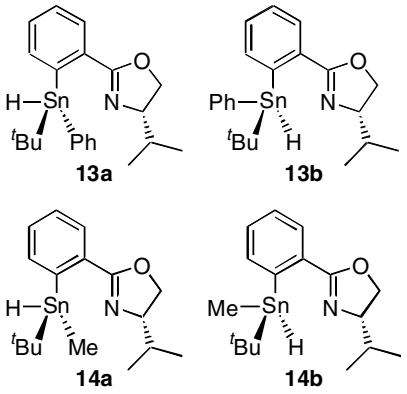
lated ^{15}N NMR spectra taken for **5**, **6** and **8** in which appearance of the $^{1}J(^{15}N–^{117/119}Sn)$ couplings of 26.2, 19.4 and 20.1 Hz was observed, respectively.

3.2.2. Structure in solution of the triorganotin halides

Due to the preferential cleavage of *pseudo*-axial groups over *pseudo*-equatorial ones, the triorganotin halides **9**–**12** can be obtained in a nearly quantitative yield from the reaction of **5** and **8** with bromine or iodide. It was expected that the bulky *tert*-butyl group linked to the tin atom might cause a strong repulsive interaction with the isopropyl group at the stereogenic center of the ligand and lead to one favorable diastereomeric halide. Indeed, the halides were obtained with good to high diastereoselectivity: **9** (**a**/**b** = 4.4/1.0, 63% de), **10** (**a**/**b** = 5.1/1.0, 67% de), **11** (**a**/**b** = 10/1, 82% de), **12** (**a**/**b** = 21/1, 91% de). It is rather difficult to determine the structure of second minor isomer but the dominant form is that with halogen at *axial* position of the trigonal bipyramid, what in the case of **10a** was proved by the X-ray diffraction measurements. The ^{1}H and ^{117}Sn NMR spectra of solutions of tin halides **9**–**12** showed no change in the diastereomeric ratios even after 10 days at rt. However, on cooling the ^{1}H NMR spectra of the halides revealed increases of the major diastereoisomers at the expense of the minor ones. It reflects the dynamic equilibrium of the tin halides in solution [21,22]. Particularly interesting are the $^{1}J(^{13}C–^{117/119}Sn)$ couplings of **9**, which are different for both forms **a** and **b** (ca. 20–30 Hz). This could suggest different chemical environments of the substituents at the tin. Unfortunately, in the case of minor diastereoisomers of **10b**–**12b** it was not possible to detect the $^{1}J(^{13}C–^{117/119}Sn)$ due to broad carbon signals (half-heights ca. 15 Hz). Comparison of the ^{117}Sn NMR chemical shifts of **9** (**a**/**b** = −149.9/−164.4 ppm), **10** (**a**/**b** = −133.2/−117.6 ppm), **11** (**a**/**b** = −75.7/−60.9 ppm) and **12** (**a**/**b** = − 58.4/−48.3 ppm,) with those of counterparts ($Ph_2{}^{t}BuSnI$: −36.7 ppm, $Ph{}^{t}BuMeSnI$: −20.3 ppm) shows remarkable ^{117}Sn shielding increases for coordinated tin halides **9**–**12**. Additionally, in the ^{15}N NMR spectra of **10a** and **11a** we observed the $^{1}J(^{15}N–^{117/119}Sn)$ couplings as small satellite line (**10a** 112.6 Hz, **11a** 116.3 Hz). This confirms the existence of the Sn–N interaction in these molecules in solution.

3.2.3. Structure in solution of the triorganotin hydrides

The tin hydrides **13** and **14** were obtained as mixtures of diastereoisomers: **13** (**a**/**b** = 1.7/1.0), **14** (**a**/**b** = 6.2/1). In the ^{117}Sn NMR spectra of hydrides **13** and **14** two separate signals for each compound are observed in a typical range for tin hydrides. The ^{117}Sn NMR chemical shifts for both hydrides depend on the substituents at the tin and are as follows: **13** (**a**/**b** = −102.0/−118.9 ppm), **14** (**a**/**b** = −60.0/−91.0 ppm). They are quite close to those of counterparts without the oxazoline moiety: $Ph_2{}^{t}BuSnH$ −118.6 ppm, $Ph{}^{t}BuMeSnH$ −86.9 ppm. Based only on this comparison it is not possible to correlate these values with geometry at the tin. More informative are the ^{1}H NOE differential experiments taken for **13a**/**b**–**14a**/**b** at low temperatures in toluene–d_8. Analysis of the NOEs observed for the hydrides clearly proves that in solution two diastereoisomeric hydrides with hydrogen in *pseudo*-axial/equatorial positions are present. This conclusion is strongly supported by the $^{1}J(^{1}H–^{117/119}Sn)$ couplings for triorganotin hydrides **13** and **14**. The corresponding values differ significantly at 30 °C (**13a** 1480/1549 Hz, **13b** 1823/1908 Hz, **14a** 1380/1444 Hz, **14b** 1692/1770 Hz), suggesting a different position of the hydrogen atom. Similar but smaller differences in the $^{1}J(^{1}H–^{117/119}Sn)$ couplings of the investigated hydrides have been reported by Metzger and co-workers [3] and Dakternieks et al. [6]. Moreover, the $^{1}J(^{1}H–^{117/119}Sn)$ couplings seem to be temperature dependent. The ^{1}H NMR measurements of **13a**/**b** in toluene–d_8 at different temperatures show noticeable differences in the $^{1}J(^{1}H–^{117/119}Sn)$ couplings, although the diastereomeric ratios of **13a**/**b** does not change with temperature [23]. At low (−60 and −20 °C) and high (+80 °C) temperatures they are as follows: **13a** (1384/1448 Hz, 1426/1493 Hz), **13b** (1887/1974 Hz, 1850/1936 Hz) and **13a** (1545/1617 Hz), **13b** (1792/1876 Hz), respectively. The same phenomenon was observed for hydride **14a**/**b**: −60 °C **14a** (1284/1344 Hz), **14b** (1727/1806 Hz) and −20 °C **14a** (1360/1423 Hz), **14b** (1707/1785 Hz). Analysis of the values of the $^{1}J(^{13}C–^{117/119}Sn)$ observed at C1 (phenyl or methyl) resonances of the *pseudo*-axial substituents shows that they are smaller than the *pseudo*-equatorial substituents in hydrides **13a**/**b** and **14a**/**b**, respectively (Table 3). On the basis of these results we propose distorted tetrahedral



Scheme 2. Axial versus equatorial position of the hydrogen atom in hydrides **13**–**14**.

coordination geometry at tin and the *pseudo*-axial/equatorial position of hydrogen atom for the investigated diastereomeric hydrides (Scheme 2).

In conclusion, the new hydrides can be easily prepared from the corresponding tetraorganotin compounds. In the diastereomeric triorganotin hydride values of the $^{1}J(^{1}H–^{117/119}Sn)$ differ significantly, suggesting a different *pseudo*-axial/equatorial position of the hydrogen atom. The isolated hydrides do not racemize and are stable enough to be used in radical and nucleophilic reductions. Further investigations concerning application of the hydrides are in progress.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structure **5** in this paper has been deposited with the Cambridge Crystallographic Data Center as Supplementary Publication No. CCDC 285182. Copies of the data can be obtained free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44 0 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

Financial support by the Institute of Organic Chemistry, Polish Academy of Sciences and the Scientific Research (Grant No. 4 TO9A 063 25) is gratefully acknowledged.

References

[1] H. Schumann, B.C. Wassermann, F.E. Hahn, Organometallics 11 (1992) 2803.
[2] E. Vedejs, S.M. Duncan, A.R. Haight, J. Org. Chem. 58 (1993) 3046.
[3] K. Schwarzkopf, J.O. Metzger, W. Saak, S. Pohl, Chem. Ber./Recueil 130 (1997) 1539.
[4] D. Dakternieks, K. Dunn, V.T. Perchyonok, C.H. Schiesser, Chem. Commun. (1999) 1665.
[5] D. Dakternieks, K. Dunn, C.H. Schiesser, E.R.T. Tiekink, J. Organomet. Chem. 605 (2000) 209.
[6] D. Dakternieks, K. Dunn, C.H. Schiesser, E.R.T. Tiekink, J. Chem. Soc., Dalton Trans. (2000) 3693.
[7] D. Dakternieks, C.H. Schiesser, Aust. J. Chem. 54 (2001) 89.
[8] D. Dakternieks, V.T. Perchyonok, C.H. Schiesser, Tetrahedron: Asymm. 14 (2003) 3057.
[9] G. Muller, J. Brand, Z. Anorg. Allg. Chem. 631 (2005) 2820.
[10] P. Cmoch, Z. Urbańczyk-Lipkowska, A. Petrosyan, A. Stępień, K. Staliński, J. Mol. Struct. 733 (2005) 29.
[11] L. Rupnicki, Z. Urbańczyk-Lipkowska, A. Stępień, P. Cmoch, Z. Pianowski, K. Staliński, J. Organomet. Chem. 690 (2005) 3690.
[12] M. Peer, J.C. de Jong, M. Kiefer, T. Langer, H. Rieck, H. Schell, P. Sennhenn, J. Sprinz, H. Steinhagen, B. Wiese, G. Helmchen, Tetrahedron 52 (1996) 7547.
[13] G.M. Sheldrick, Acta Crystallogr. A46 (1990) 467.
[14] G.M. Sheldrick, SHELXL97, Program for Crystal Structure Refinement, University of Göttingen, Germany, 1997.
[15] L.J. Farrugia, J. Appl. Crystallogr. 32 (1999) 837.
[16] I.V. Eynde, M. Gielen, J. Organomet. Chem. 198 (1980) C55.
[17] I.V. Eynde, M. Gielen, G. Stühler, A. Mannschreck, Polyhedron 1 (1982) 1.
[18] B. Jousseaume, P.J. Villeneuve, J. Chem. Soc., Chem. Commun. (1987) 513.
[19] G. van Koten, J.T.B.H. Jastrzebski, J.G. Noltes, J. Am. Chem. Soc. 100 (1978) 5021.
[20] J.T.B.H. Jastrzebski, J. Boersma, P.M. Esch, G. Van Koten, Organometallics 10 (1991) 930.
[21] M. Gielen, Top. Curr. Chem. 104 (1983) 57.
[22] M. Gielen, M. Biesemans, R. Willem, Appl. Organomet. Chem. 19 (2005) 440.
[23] M. Gielen, Y. Tondeur, J. Organomet. Chem. 169 (1979) 265.