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The ^{1}H, ^{13}C, ^{15}N and ^{117}Sn NMR study of the intramolecular Sn–N interaction in tri- and tetraorganotin compounds containing the chiral 2-(4-isopropyl-2-oxazolinyl)-5-phenyl ligand

Piotr Cmoch[a,b,*], Zofia Urbańczyk-Lipkowska[a], Armine Petrosyan[c], Anita Stępień[a], Krzysztof Staliński[a,*]

[a]*Institute of Organic Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warszawa, Poland*
[b]*Pharmaceutical Research Institute, Rydygiera 8, 01-793 Warsaw, Poland*
[c]*Nesmeyanow Institute of Organo-Element Compounds, Russian Academy of Sciences, Vavilov 28, 117813 Moscow, Russia*

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Abstract

A series of novel tri- and tetraorganotin compounds containing the optically active 2-(4-isopropyl-2-oxazolinyl)-5-phenyl ligand has been synthesized. All the novel compounds have been characterized, especially by means of the multinuclear NMR investigation, the results of which are discussed. A number of arguments based on the ^{13}C, ^{15}N and ^{117}Sn NMR and X-ray studies support the intramolecular donor–acceptor coordination between tin and nitrogen atoms in the stannanes. For the first time the $J(^{15}N–^{117/119}Sn)$ coupling constant values in coordinated tin hydrides clearly point to a coordination number of the tin larger than four.

Keywords: Intramolecular coordination; Organotin halides and hydrides; Multinuclear NMR spectroscopy; N ligands

1. Introduction

The organotin compounds with the potentially chelating ligands have been receiving increasing attention in recent years [1] because of their unexpected structural aspects, as well as, interesting industrial [2] and pharmacological applications [3]. Especially, interesting seem to be organotin compounds where the tin atom can interact with nitrogen donor center(s) of the ligand(s). The existence of such donor–acceptor interactions has been confirmed by X-ray techniques and NMR spectroscopy [4], especially by characteristic changes of NMR chemical shifts $\delta(^{117/119}Sn)$, $\delta(^{15}N)$ and values of $J(^{13}C–^{117/119}Sn)$ and $J(^{15}N–^{117/119}Sn)$ coupling constants [5,6]. Van Koten et al. first synthesized new organotin bromides containing the 2-(4,4-dimethyl-2-oxazolinyl)-5-(methyl)phenyl ligand [7]. Afterwards, Dakternieks et al. obtained new triorganotin chlorides and hydrides containing the above and the chiral 2-(4-isopropyl-2-oxazolinyl)-5-(methyl)phenyl ligand [8]. However, to the best of our knowledge, there is no evidence of spectral parameters of the nuclides directly involved (^{117}Sn and ^{15}N) in the latter organotin compounds. Especially, intriguing seems to be the detection of $J(^{15}N–^{117/119}Sn)$ coupling constants in the corresponding hydrides and tetraorganotin compounds. The goal of our research was to observe such parameters and to present evidence for the donor–acceptor Sn–N interaction in tin compounds containing the chiral 2-(4-isopropyl-2-oxazolinyl)-5-phenyl ligand **1–10**, **17** and **18** based on their ^{1}H, ^{13}C, ^{15}N and ^{117}Sn NMR data (Scheme 1).

2. Experimental

2.1. Spectroscopic and analytical data

The ^{1}H, ^{13}C, ^{15}N and ^{117}Sn NMR spectra were measured in $CDCl_3$ or C_6D_6 (hydrides) at 303 K on a Bruker

* Corresponding authors. Tel.: +7-48-22-632-0904/3221; fax: +7-48-22-6326681.
E-mail addresses: piocmo@icho.edu.pl (P. Cmoch), stalinsk@icho.edu.pl (K. Staliński).

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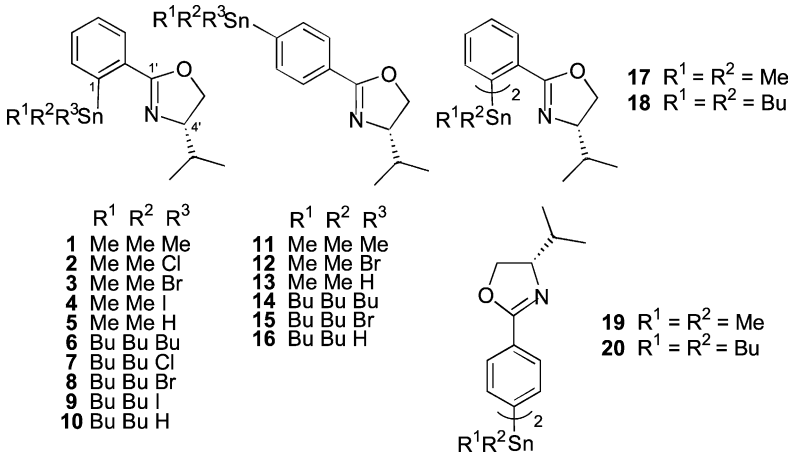


Scheme 1. Tri- and tetraorganotin compounds **1**–**20** containing the chiral 2-(4-isopropyl-2-oxazolinyl)-5-phenyl ligand.

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 ^{119}Sn nuclei, respectively. An 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 and HMBC experiments taken for **1**–**5**. The ^{15}N NMR spectra, containing in several cases $J(^{15}N$–$^{117/119}Sn)$ couplings, were measured using inverse gated decoupling sequence and in other cases 2D ^{1}H–^{15}N NMR gradient selected HMBC method. Typical parameters for 1D ^{15}N NMR measurements were as follows: acquisition time: 1.3 s, recycling delay: 3.0 s, number of scans: ca. 20,000–40,000, spectral width: ca. 250 ppm, the ^{15}N pulse (30°): 7.0 μs. The 1D ^{119}Sn NMR spectra were recorded using power-gated decopuling sequence with following parameters: acquisition time: ca. 0.6–1.0 s, recycling delay: 1.0 s, number of scans: ca. 50–1000, spectral width: ca. 300 ppm, the ^{119}Sn pulse (30°): 4.5 μs. For the ^{1}H and ^{13}C NMR spectra in $CDCl_3$ and C_6D_6, internal TMS was used as the chemical shift standard, whereas external nitromethane and tetramethyltin were applied as the standard for the ^{15}N and ^{119}Sn NMR measurements, respectively.

IR spectra were measured as films on a Perkin Elmer FT-IR spectrophotometer. EI, LSIMS(+), 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. The spots were detected under a 254 nm UV light source or by spraying with $KMnO_4$-acetone solution and then heating. Column chromatography was performed on Kieselgel 60 Merck silica gel. HPLC analyses were run using a *Merck-Hitachi* apparatus and *LiChrospher-RP18/12* μm or *Nucleosil 50/10* μm column.

X-Ray diffraction measurements were performed at rt at the Nonius BV MACH3 diffractometer. Structures were solved with direct methods using SHELXS97 [9] and refinement with SHELXL97 [10] programs. All non-H atoms were refined in anisotropic mode. All hydrogens were placed geometrically and refined with a riding mode with U_{iso} constrained to 1.2 times of that of the carrier atom.[1] Crystal data for **1**: $C_{15}H_{23}N_1O_1Sn_1$, $M_r=352.03$, $a=7.8201(7)$, $b=11.3860(6)$, $c=18.166(1)$ Å, $V=1618.5(7)$ Å^3, $Z=4$, orthorhombic, space group $P2_12_12_1$, $D_c=1.445$ Mg. m^{-3}, $T=293$ K, μ(Cu K_α)$=$ 12.466 cm^{-1}, $F(000)=712$. The intensities of 1237 unique reflections with $4.58\leq\theta\leq73.92°$ were collected (4.9% decay). Data were corrected for ψ-scan experiment based absorption: T_{min} 54.75 and T_{max} 99.70%. Final R indices– $R_1=0.0385$, $wR_2=0.0843$ for 1237 observed reflections with $I>2\sigma(I)$ and 164 parameters.

Crystal data for **3**: $C_{14}H_{20}Br_1N_1O_1Sn_1$, $M_r=337.00$, $a=12.9888(12)$, $b=12.9888(12)$, $c=15.8751(14)$ Å, $V=1592.0(2)$ Å^3, $Z=4$, orthorhombic, space group $P2_12_12_1$, $D_c=1.406$ Mg. m^{-3}, $T=293$ K, μ(Cu K_α)$=$ 12.651 cm^{-1}, $F(000)=676$. The intensities of 1351 unique reflections with $4.40\leq\theta\leq73.93°$ were collected (13.1% decay). Data were corrected for ψ-scan experiment based absorption: T_{min} 40.64 and T_{max} 99.51%. Final R indices— $R_1=0.0930$, $R_2=0.2535$ for 1351 observed reflections with $I>2\sigma(I)$ and 164 parameters.

2.2. Synthesis

2.2.1. General procedure for the preparation of compounds **1–18**

A solution of (−)-(*S*)-(2-bromo-phenyl)-4-isopropyl-4,5-dihydro-oxazole (536 mg, 2.0 mmol) in Et_2O (20 ml) at −78 °C was treated with *n*-BuLi (1.25 ml, 2.0 mmol, 1.6 *M* solution in hexane). After 1 h the mixture was treated

[1] CCDC-237502 and 237503 contains the crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223/336-033; deposit@ccdc.cam.ac.uk.

with Me_2SnCl_2 or n-Bu_2SnCl_2 (2.0 mmol) and after an additional hour of stirring the reaction mixture was allowed to warm to room temperature and quenched by addition of a few drops of water. The mixture was dried over $MgSO_4$, filtered and evaporated under reduced pressure. The resulting oil was purified by flash chromatography (hexanes/ethyl acetate) to yield:

17 (220 mg 45%), **7** (456 mg 50%), **6** (230 mg 24%), **18** (55 mg 9%)

To 53 mg (2.2 mmol) of magnesium, activated by 'dry stirring' were added 10 ml of THF. After addition of 536 mg (2 mmol) of (*S*)-2-(4-bromo-phenyl)-4-isopropyl-4,5-dihydro-oxazole or (*S*)-4-(4-bromo-phenyl)-4-isopropyl-4,5-dihydro-oxazole the reaction was started by addition of a small amount of 1,2-dibromoethane. The mixture was stirred at reflux until the magnesium was consumed. Subsequently, a solution of Me_2SnBr_2/n-Bu_2SnBr_2 or Me_3SnCl/n-Bu_3SnCl (2.2 mmol) in 10 ml of THF was added. After 30 min the mixture was diluted with 20 ml of ether and filtered over a short silica gel pad. The solvents were removed in vacuo and the residue was flash chromatographed. The resulting oil was purified by flash chromatography (hexanes/ethyl acetate) to yield compounds: **1** (676 mg, 94%), **2** (558 mg, 75%), **3** (667 mg, 80%), **6** (879 mg, 92%), **8** (760 mg, 76%), **11** (458 mg, 65%), **14** (593 mg, 62%).

2.2.2. (S)-4-Isopropyl-2-(2-trimethylstannanyl-phenyl)-4,5-dihydro-oxazole (*1*)

IR (film) cm^{-1}: 3063, 2964, 2910, 1645, 1466, 1351, 1257, 1085, 1043, 781, 768. ^{1}H NMR δ ppm: 7.95–7.34 (4H, *m*, $H_{arom.}$), 4.45–4.40 (1H, *dd* J=9.1, 7.8 Hz), 4.11–4.01 (2H, *m*), 1.93–1.83 (1H, *m*), 1.05 (3H, *d* J=6.7 Hz), 0.92 (3H, *d* J=6.8 Hz), 0.25 (6H, *s*). ^{13}C NMR δ ppm: 164.9, 145.3 [$J(^{13}C–^{117}Sn)$ 491 Hz], 136.5, 133.3, 130.3, 128.1, 128.0, 72.8, 70.3, 32.4, 19.4, 18.1, −6.1 [$J(^{13}C–^{117}Sn)$ 380 Hz]. ^{117}Sn NMR δ ppm: −50.6. ^{15}N NMR δ ppm: −155.7. MS (LSIMS+) *m/z*: 352 (M^++H). HRMS (LSIMS+) calcd for $C_{15}H_{24}O_1N_1^{118}Sn_1$ 352.0874 found 352.0867.

2.2.3. (S)-2-[(2-Chloro-dimethylstannanyl)-phenyl]-4-isopropyl-4,5-dihydro-oxazole (*2*)

IR (film) cm^{-1}: 3051, 2994, 2966, 2895, 1631, 1557, 1472, 1385, 1363, 1135, 1101, 1046, 957. ^{1}H NMR δ ppm: 8.37–7.36 (4H, *m*, $H_{arom.}$), 4.62–4.56 (1H, *t* J=9.4 Hz), 4.36–4.31 (1H, *t* J=8.8 Hz), 4.10–4.00 (1H, *m*), 1.97–1.88 (1H, *m*), 0.95 (3H, *d* J=6.8 Hz), 0.81 (3H, *d* J=6.8 Hz), 0.72 (3H, *s*) 0.69 (3H, *s*). ^{13}C NMR δ ppm: 170.5, 147.1 [$J(^{13}C–^{117}Sn)$ 701 Hz], 137.5, 132.8, 129.7, 129.2, 126.6, 72.1, 69.3, 31.1, 19.4, 16.5, 2.6 [$J(^{13}C–^{117}Sn)$ 556 Hz], 1.7 [$J(^{13}C–^{117}Sn)$ 589 Hz]. ^{117}Sn NMR δ ppm: −103.0. ^{15}N NMR δ ppm: −180.6. MS (EI) *m/z*: 358 (M^+–Me, 63), 338 (100). HRMS (EI) calcd for $C_{13}H_{17}O_1N_1Cl_1^{120}Sn_1$ 357.9989 found 358.0021.

2.2.4. (S)-2-[(2-Bromo-dimethylstannanyl)-phenyl]-4-isopropyl-4,5-dihydro-oxazole (*3*)

A mixture of **2** and **3** (80 mg, ~0.2 mmol) and LiBr (176 mg, 2 mmol) was refluxed overnight in acetone. The mixture was then evaporated and the crude product was purified by filtering-column chromatography on silica gel to give compound **3** (79 mg, 95%).

IR (film) cm^{-1}: 3051, 2994, 2966, 2895, 1631, 1557, 1472, 1385, 1363, 1135, 1101, 1046, 957. ^{1}H NMR δ ppm: 9.05–7.06 (4H, *m*, $H_{arom.}$), 3.70–3.66 (1H, *dd* J=9.9, 8.7 Hz), 3.60–3.55 (1H, *t* J=8.8 Hz), 3.31–3.25 (1H, *ddd* J=9.8, 9.1, 5.4 Hz), 1.40–1.30 (1H, *m*), 0.92 and 0.88 (6H, 2×*s*), 0.50–0.48 (3H, *d* J=6.8 Hz), 0.37–0.35 (3H, *d* J=6.8 Hz). ^{13}C NMR δ ppm: 170.6, 146.2 [$J(^{13}C–^{117}Sn)$ 683 Hz], 138.1, 132.9, 129.7, 129.4, 126.7, 72.1, 69.3, 31.0, 19.4, 16.4, 4.1 [$J(^{13}C–^{117}Sn)$ 547 Hz], 3.3 [$J(^{13}C–^{117}Sn)$ 578 Hz]. ^{117}Sn NMR δ ppm: −110.9. ^{15}N NMR δ ppm: −181.4. MS (EI) *m/z*: 402 (M^+ – Me, 69), 338 (100). HRMS (EI) calcd for $C_{13}H_{17}O_1N_1^{79}Br_1^{120}Sn_1$ 401.9516 found 401.9524.

2.2.5. (S)-2-[(2-Iodo-dimethylstannanyl)-phenyl]-4-isopropyl-4,5-dihydro-oxazole (*4*)

A solution of **1** (100 mg, 0.285 mmol) and I_2 (74 mg, 0.29 mmol) in benzene (5 ml) was stirred in the dark at rt. The mixture was then evaporated and the crude product was purified by filtering-column chromatography on silica gel to give compound **4** (129 mg, 98%).

IR (film) cm^{-1}: 3048, 2964, 2926, 2873, 1635, 1556, 1384, 1130, 1097, 1049, 941. ^{1}H NMR δ ppm: 8.53–7.38 (4H, *m*, $H_{arom.}$), 4.64–4.59 (1H, *dd* J=9.8, 9.0 Hz), 4.40–4.35 (1H, *t* J=8.8 Hz), 4.11–4.05 (1H, *ddd* J=9.8, 8.9, 5.0 Hz), 2.00–1.91 (1H, *m*), 1.07 (3H, *d* J=11.5 Hz), 1.00 (3H, *d* J=11.6 Hz), 0.97 (3H, *d* J=6.9 Hz), 0.82 (3H, *d* J=6.8 Hz). ^{13}C NMR δ ppm: 170.4, 144.3 [$J(^{13}C–^{117}Sn)$ 659 Hz], 138.9, 132.8, 129.6, 129.5, 126.6, 72.2, 69.1, 30.8, 19.4, 16.2, 6.4 [$J(^{13}C–^{117}Sn)$ 535 Hz], 5.9 [$J(^{13}C–^{117}Sn)$ 565 Hz]. ^{117}Sn NMR δ ppm: −129.2. ^{15}N NMR δ ppm: −182.8. MS (EI) *m/z*: 438 (M^+–Me, 100), 308 (17), 264 (7), 252 (33), 222 (19). HRMS (EI) calcd for $C_{14}H_{20}O_1N_1^{120}Sn_1$ 338.0567 found 338.0569.

2.2.6. [2-(4-(S)-Isopropyl-2-oxazoline)-5-phenyl]dimethyltin hydride (*5*)

A solution of $NaBH_4$ (757 mg, 20 mmol) in ethanol (10 ml) was added to a solution of compound **3** (802 mg, 2 mmol) in ethanol (20 ml) and stirred at room temperature for 1 h. 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 hydride **5** (656 mg, 97%) as colorless oil.

IR (film) cm^{-1}: 3055, 2960, 2909, 1843, 1756, 1647, 1467, 1359, 1257, 1086, 1044. ^{1}H NMR (C_6D_6) δ ppm: 8.16–7.20 (4H, *m*, $H_{arom.}$), 6.22–6.18 [1H, *septet* J=1.9 Hz, -[$J(^1H–^{119}Sn)$ 1753 Hz], 4.05–3.96 (1H, *m*), 3.84–3.66 (2H, *m*), 1.73–1.55 (1H, *m*), 0.95 (3H, *d* J=6.7 Hz), 0.78

(3H, *d* $J=6.8$ Hz), 0.56 [3H, *d* $J=2$ Hz, $J(^{1}H–^{117}Sn)$ 59 Hz], 0.53 [3H, *d* $J=2$ Hz, $J(^{1}H–^{117}Sn)$ 56 Hz]. ^{13}C NMR (C_6D_6) δ ppm: 165.7, 144.3 [$J(^{13}C–^{117}Sn)$ 537 Hz], 138.2, 133.5, 131.0, 128.2, 127.9, 72.7, 70.7, 32.6, 19.2, 18.3, −7.0 [$J(^{13}C–^{117}Sn)$ 421 Hz], −7.4 [$J(^{13}C–^{117}Sn)$ 390 Hz]. ^{117}Sn NMR (C_6D_6) δ ppm: −129.0. ^{15}N NMR (C_6D_6) δ ppm: −155.3. MS (EI) *m/z*: 338 (M^+–H, 29), 324 (M^+–Me, 100), 308 (28), 264 (7), 252 (14), 238 (18), 222 (26). HRMS (EI) calcd for $C_{14}H_{20}O_1N_1^{120}Sn_1$ 338.0567 found 338.0572.

2.2.7. (S)-4-Isopropyl-2-(2-tributylstannanyl-phenyl)-4,5-dihydro-oxazole (**6**)

IR (film) cm^{-1}: 3055, 2956, 2920, 2871, 2853, 1649, 1464, 1355, 1083, 1043, 967. ^{1}H NMR δ ppm: 7.95–7.30 (4H, *m*, $H_{arom.}$), 4.41–4.36 (1H, *dd* $J=8.9$, 7.5 Hz), 4.11–4.02 (2H, *m*), 1.95–1.86 (1H, *m*), 1.51–0.98 (18H, *m*), 1.03 (3H, *d* $J=6.7$ Hz), 0.91 (3H, *d* $J=6.8$ Hz), 0.86 (9H, *t* $J=7.3$ Hz). ^{13}C NMR δ ppm: 165.0, 145.0 [$J(^{13}C–^{117}Sn)$ 403 Hz], 137.0, 133.8, 130.1, 128.3, 127.8, 72.8, 69.9, 32.3, 29.2, 27.5, 19.4, 17.9, 13.7, 11.9 [$J(^{13}C–^{117}Sn)$ 365 Hz]. ^{117}Sn NMR δ ppm: −52.5. ^{15}N NMR δ ppm: −156.1. MS (EI) *m/z*: 478 (M^+, 1), 422 (M^+ – Bu, 100), 308 (22), 264 (3), 222 (18). HRMS (EI) calcd for $C_{20}H_{32}O_1N_1^{120}Sn_1$ 422.1457 found 422.1491.

2.2.8. (S)-2-[(2-Chloro-dibutylstannanyl)-phenyl]-4-isopropyl-4,5-dihydro-oxazole (**7**)

IR (film) cm^{-1}: 3058, 2956, 2925, 2855, 1636, 1463, 1378, 1133, 1096, 1046, 958. ^{1}H NMR δ ppm: 8.43–7.42 (4H, *m*, $H_{arom.}$), 4.66–4.60 (1H, *d* $J=9.8$, 9.0 Hz), 4.43–4.38 (1H, *t* $J=8.7$ Hz), 4.17–4.10 (1H, *ddd* $J=9.8$, 8.6, 4.9 Hz), 2.10–2.00 (1H, *m*), 1.71–1.25 (12H, *m*), 1.05–1.02 (3H, *d* $J=6.9$ Hz), 0.90–0.88 (3H, *d* $J=6.8$ Hz), 0.86–0.80 (6H, $2\times t$ $J=7.3$ Hz). ^{13}C NMR δ ppm: 170.5, 147.2 [$J(^{13}C–^{117}Sn)$ 603 Hz], 137.7, 132.7, 130.0, 129.0, 126.7, 71.5, 69.7, 31.1, 28.1, 28.0, 26.7, 26.6, 21.2 [$J(^{13}C–^{117}Sn)$ 560 Hz], 21.2 [$J(^{13}C–^{117}Sn)$ 533 Hz] 19.6, 16.2, 13.6, 13.5. ^{117}Sn NMR δ ppm: −97.2. ^{15}N NMR δ ppm: −180.4. MS (EI) *m/z*: 456 (M^+, 1), 422 (11), 400 (100), 343 (3), 308 (27), 264 (6), 222 (23), 210 (9), 183 (3), 167 (5), 149 (12). HRMS (EI) calcd for $C_{16}H_{23}O_1N_1^{120}Sn_1^{35}Cl_1$ 400.0490 found 400.0462.

2.2.9. (S)-2-[(2-Bromo-dibutylstannanyl)-phenyl]-4-isopropyl-4,5-dihydro-oxazole (**8**)

IR (film) cm^{-1}: 3056, 2958, 2923, 1635, 1464, 1381, 1294, 1134, 1096, 954, 732. ^{1}H NMR δ ppm: 8.55–7.41 (4H, *m*, $H_{arom.}$), 4.70–4.64 (1H, *dd* $J=9.9$, 9.0 Hz), 4.48–4.42 (1H, *t* $J=8.7$ Hz), 4.21–4.14 (1H, *ddd* $J=9.9$, 8.4, 4.8 Hz), 2.15–2.00 (1H, *m*), 1.85–0.81 (18H, *m*), 1.04 (3H, *d* $J=6.8$ Hz), 0.89 (3H, *d* $J=6.8$ Hz). ^{13}C NMR δ ppm: 170.5, 146.4 [$J(^{13}C–^{117}Sn)$ 583 Hz], 138.3, 132.6, 129.7, 129.0, 126.6, 71.5, 69.4, 30.9, 28.3, 28.1, 26.5, 26.3, 22.4 [$J(^{13}C–^{117}Sn)$ 522 Hz], 22.3 [$J(^{13}C–^{117}Sn)$ 549 Hz], 19.6, 16.0, 13.5, 13.4. ^{117}Sn NMR δ ppm: −93.2. ^{15}N NMR δ ppm: −181.0. MS (EI) *m/z*: 444 (M^+–Bu, 100), 422 (32), 308 (64), 264 (10), 222 (36). HRMS (EI) calcd for $C_{16}H_{23}O_1N_1^{79}Br_1^{120}Sn_1$ 443.9985 found 443.9964.

2.2.10. (S)-2-[(2-Iodo-dibutylstannanyl)-phenyl]-4-isopropyl-4,5-dihydro-oxazole (**9**)

A solution of **6** (48 mg, 0.1 mmol) and I_2 (28 mg, 0.11 mmol) in benzene (3 ml) was stirred in the dark at rt. The mixture was then evaporated and the crude product was purified by filtering-column chromatography on silica gel to give compound **9** (X=I, ~55 mg, 100%).

IR (film) cm^{-1}: 3051, 2957, 2922, 2871, 2855, 1634, 1559, 1463, 1381, 1134, 1095, 952. ^{1}H NMR δ ppm: 8.60–7.45 (4H, *m*, $H_{arom.}$), 4.71–4.65 (1H, *dd* $J=9.8$, 9.0 Hz), 4.50–4.46 (1H, *t* $J=8.7$ Hz), 4.23–4.17 (1H, *ddd* $J=9.8$, 8.5, 4.7 Hz), 2.16–2.05 (1H, *m*), 1.70–1.26 (12H, *m*), 1.09–1.05 (3H, *d* $J=6.8$ Hz), 0.94–0.90 (3H, *d* $J=6.8$ Hz), 0.89–0.81 (6H, *m*). ^{13}C NMR δ ppm: 170.6, 144.9 [$J(^{13}C–^{117}Sn)$ 553 Hz], 139.8, 132.9, 129.5, 129.3, 126.7, 71.6, 69.5, 30.9, 28.7, 28.6, 26.4, 26.3, 24.3 [$J(^{13}C–^{117}Sn)$ 535 Hz], 23.8 [$J(^{13}C–^{117}Sn)$ 508 Hz], 19.7, 16.0, 13.6, 13.5. ^{117}Sn NMR δ ppm: −89.7. ^{15}N NMR δ ppm: −181.6. MS (EI) *m/z*: 492 (M^+ – Bu, 18), 422 (100), 400 (20), 308 (44), 222 (24). HRMS (EI) calcd for $C_{16}H_{23}O_1N_1^{120}Sn_1I_1$ 491.9846 found 491.9852.

2.2.11. [2-(4-(S)-Isopropyl-2-oxazoline)-5-phenyl]dibutyltin hydride (**10**)

A solution of $NaBH_4$ (757 mg, 20 mmol) in ethanol (10 ml) was added to a solution of compound **8** (1.0 g, 2 mmol) in ethanol (20 ml) and stirred at room temperature for 1 h. 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 hydride **10** (807 mg, 98%) as colorless oil.

IR (film) cm^{-1}: 3056, 2957, 2920, 1828, 1739, 1646, 1464, 1359, 1256, 1086, 1043. ^{1}H NMR (C_6D_6) δ ppm: 8.20–7.22 (4H, *m*, $H_{arom.}$), 6.42 [1H, *m*, $J(^{1}H–^{117}Sn)$ 1503 Hz], 4.04–3.95 (1H, *m*), 3.86–3.76 (2H, *m*), 4.23–4.17 (1H, *ddd* $J=9.8$, 8.5, 4.7 Hz), 1.90–1.32 (13H, *m*), 1.03–1.00 (3H, *t* $J=7.3$ Hz), 1.01–0.98 (3H, *t* $J=7.3$ Hz), 0.97–0.95 (3H, *d* $J=6.8$ Hz), 0.89–0.82–0.80 (6H, *m* $J=6.8$ Hz). ^{13}C NMR (C_6D_6) δ ppm: 166.0, 145.1 [$J(^{13}C–^{117}Sn)$ 478 Hz], 139.2, 133.6, 131.1, 128.6, 127.8, 72.6, 70.4, 32.4, 30.5, 30.4, 27.5, 27.4, 19.3, 18.0, 14.0, 13.9, 13.5 [$J(^{13}C–^{117}Sn)$ 433 Hz], 13.3 [$J(^{13}C–^{117}Sn)$ 424 Hz]. ^{117}Sn NMR (C_6D_6) δ ppm: −92.0. ^{15}N NMR (C_6D_6) δ ppm: −158.3. MS (EI) *m/z*: 422 (M^+, 16), 366 (100), 308 (47), 222 (18). HRMS (EI) calcd for $C_{20}H_{32}O_1N_1^{120}Sn_1$ 422.1506 found 422.1521.

2.2.12. (S)-4-Isopropyl-2-(4-trimethylstannanyl-phenyl)-4,5-dihydro-oxazole (**11**)

IR (film) cm^{-1}: 3070, 3014, 2959, 2908, 1649, 1388, 1354, 1058. ^{1}H NMR δ ppm: 7.91–7.47 (4H, *m*, $H_{arom.}$), 4.42–4.35 (1H, *m*), 4.16–4.08 (2H, *m*), 1.92–1.83 (1H, *m*), 1.02 (3H, *d* $J=6.8$ Hz), 0.92 (3H, *d* $J=6.8$ Hz), 0.31 [9H, *s*,

$J(^1H–^{117}Sn)$ 55 Hz]. ^{13}C NMR δ ppm: 163.5, 146.9 [$J(^{13}C–^{117}Sn)$ 445 Hz], 135.7, 127.7, 127.4, 72.5, 69.9, 32.8, 18.9, 18.0, −9.6 [$J(^{13}C–^{117}Sn)$ 353 Hz]. ^{117}Sn NMR δ ppm: −28.6. ^{15}N NMR δ ppm: −156.0. MS (EI) *m/z*: 353 (M^+, 8), 338 (100), 308 (26), 280 (5), 265 (6), 222 (9), 165 (15). HRMS (EI) calcd for $C_{15}H_{23}O_1N_1^{120}Sn_1$ 353.0802 found 353.0810.

2.2.13. (S)-2-(2-Bromo-dimethylstannanyl-phenyl)-4-isopropyl-4,5-dihydro-oxazole (**12**)

IR (film) cm^{-1}: 3051, 2992, 2910, 2874, 1643, 1554, 1466, 1391, 1363, 1255, 190, 1062, 779. ^1H NMR δ ppm: 8.04–7.59 (4H, $AA'BB'$ system, $H_{arom.}$), 4.48–4.40 (1H, *m*), 4.20–4.11 (2H, *m*), 1.95–1.86 (1H, *m*), 1.05 (3H, *d* $J=6.8$ Hz), 0.97 [6H, *s*, $J(^1H–^{117}Sn)$ 59 Hz], 0.95 (3H, *d* $J=6.8$ Hz). ^{13}C NMR δ ppm: 163.1, 144.0 [$J(^{13}C–^{117}Sn)$ 533 Hz], 135.0, 129.3, 128.1, 72.6, 70.1, 32.8, 18.9, 18.0, −2.0 [$J(^{13}C–^{117}Sn)$ 393 Hz]. ^{117}Sn NMR δ ppm: 64.0. MS (EI) *m/z*: 416 (M^+, 1), 402 (15), 374 (100), 344 (9), 330 (21), 229 (16). HRMS (EI) calcd for $C_{14}H_{20}O_1N_1^{79}Br_1^{120}Sn_1$ 416.9760 found 416.9749.

2.2.14. [4-(4-(S)-Isopropyl-2-oxazoline)-5-phenyl]dimethyltin hydride (**13**)

A solution of $NaBH_4$ (45 mg, 1.2 mmol) in ethanol (2 ml) was added to a solution of compound **12**(50 mg, 0.12 mmol) in ethanol (5 ml) and stirred at room temperature for 1 h. 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 hydride **13** (40 mg, 99%) as colorless oil.

NMR (C_6D_6) δ ppm: 8.40–7.35 (4H, *m*, H_{arom}), 5.45 [1H, *septet* $J=2.3$ Hz, $J(^1H–^{119}Sn)$ 1827 Hz], 4.05–4.00 (1H, *dd* $J=9.5$, 7.9 Hz), 3.95–3.89 (1H, *ddd* $J=9.4$, 8.0, 6.5 Hz), 1.72–1.63 (1H, *m*), 1.04 (3H, *d* $J=6.7$ Hz), 0.85 (3H, *d* $J=6.7$ Hz), 0.19 [3H, *s*, $J(^1H–^{117}Sn)$ 59 Hz], 0.18 [3H, *s*, $J(^1H–^{117}Sn)$ 59 Hz]. ^{13}C NMR (C_6D_6) δ ppm: 163.2, 143.7 [$J(^{13}C–^{117}Sn)$ 478 Hz], 136.7, 129.0, 128.0, 73.2, 70.3, 33.3, 18.9, 18.6, −11.7 [$J(^{13}C–^{117}Sn)$ 365 Hz]. ^{117}Sn NMR (C_6D_6) δ ppm: −121.4. MS (EI) *m/z*: 339 (M^+, 6), 324 (50), 308 (10), 296 (100), 280 (4), 265 (4), 222 (7). HRMS (EI) calcd for $C_{14}H_{21}O_1N_1^{120}Sn_1$ 339.0645 found 339.0631.

2.2.15. (S)-4-Isopropyl-2-(4-tributylstannanyl-phenyl)-4,5-dihydro-oxazole (**14**)

IR (film) cm^{-1}: 3070, 2957, 2927, 2872, 2853, 1650, 1464, 1388, 1354, 1081, 1056, 1017. ^1H NMR δ ppm: 7.90–7.45 (4H, *m*, $H_{arom.}$), 4.42–4.34 (1H, *m*), 4.15–4.06 (2H, *m*), 1.90–1.82 (1H, *m*), 1.60–1.45 (6H, *m*), 1.36–1.05 (12H, *m*), 1.04–1.01 (3H, *d* $J=6.8$ Hz), 0.94–0.91 (3H, *d* $J=6.8$ Hz), 0.90–0.85 (9H, *t* $J=7.3$ Hz). ^{13}C NMR δ ppm: 163.6, 146.9 [$J(^{13}C–^{117}Sn)$ 369 Hz], 136.3, 127.4, 127.2, 72.5, 69.9, 32.8, 29.1, 27.3, 18.9, 18.0, 13.6, 9.6 [$J(^{13}C–^{117}Sn)$ 342 Hz]. ^{117}Sn NMR δ ppm: −42.0. MS (EI) *m/z*: 422 (M^+, 100), 366 (57), 310 (94), 265 (11), 222 (8). HRMS (EI) calcd for $C_{20}H_{32}O_1N_1^{120}Sn_1$ 422.1506 found 422.1525.

2.2.16. (S)-2-(2-Bromo-dibutylstannanyl-phenyl)-4-isopropyl-4,5-dihydro-oxazole (**15**)

To 27 mg (1.1 mmol) of magnesium, activated by 'dry stirring' was added 10 ml of THF. After addition of 268 mg (1.0 mmol) of (*S*)-2-(4-Bromo-phenyl)-4-isopropyl-4,5-dihydro-oxazole, the reaction was started by addition of a small amount of 1,2-dibromoethane. The mixture was stirred at reflux until the magnesium was consumed. Subsequently, a solution of 309 mg (1.0 mmol) of *n*-$Bu_2SnAllCl$ in 1 ml of THF was added. After 15 min the mixture was diluted with 20 ml of ether and filtered over a short silica gel pad. The solvents were removed in vacuo and the residue was flash chromatographed. The resulting product was obtained as a colorless oil (180 mg, 36%).

IR (film) cm^{-1}: 2958, 2924, 2872, 2855, 1642, 1464, 1390, 1060, 1017, 963. ^1H NMR δ ppm: 7.98–7.59 (4H, *m*, $H_{arom.}$), 4.45–4.36 (1H, *m*), 4.16–4.08 (2H, *m*), 1.91–1.32 (13H, *m*), 1.04–1.01 (3H, *d* $J=6.8$ Hz), 0.97–0.85 (9H, *m*), 0.92–0.90 (3H, *d* $J=6.9$ Hz). ^{13}C NMR δ ppm: 163.1, 135.4, 129.0, 128.0 (2×), 72.6, 70.1, 32.8, 28.1, 26.7, 18.9, 18.0, 17.7 [$J(^{13}C–^{117}Sn)$ 374 Hz], 13.5. ^{117}Sn NMR δ ppm: 64.4. MS (EI) *m/z*: 500 (M^+, 3), 444 (100), 414 (5), 400 (16), 388 (23), 344 (9), 308 (13), 199 (14). HRMS (EI) calcd for $C_{16}H_{23}O_1N_1^{79}Br_1^{120}Sn_1$ 443.9985 found 443.9980.

2.2.17. [4-(4-(S)-Isopropyl-2-oxazoline)-5-phenyl]dibutyltin hydride (**16**)

A solution of $NaBH_4$ (45 mg, 1.2 mmol) in ethanol (2 ml) was added to a solution of compound **12** (50 mg, 0.10 mmol) in ethanol (5 ml) and stirred at room temperature for 1 h. 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 hydride **16** (40 mg, 96%) as colorless oil.

IR (film) cm^{-1}: 3070, 2957, 2928, 1821, 1722, 1650, 1464, 1354, 1255, 1057, 1017. ^1H NMR (C_6D_6) δ ppm: 8.39–7.55 (4H, *m*, $H_{arom.}$), 5.77 [1H, *septet* $J=1.9$ Hz, $J(^1H–^{119}Sn)$ 1706 Hz], 4.08–4.03 (1H, *dd* $J=9.5$, 7.8 Hz), 3.99–3.93 (1H, *ddd* $J=9.5$, 7.9, 6.4 Hz), 3.88–3.83 (1H, *t* $J=7.9$ Hz), 1.76–1.10 (13H, *m*), 1.08–1.06 (3H, *d* $J=6.7$ Hz), 0.95–0.91 (6H, *t* $J=7.3$ Hz), 0.90–0.88 (3H, *d* $J=6.7$ Hz). ^{13}C NMR (C_6D_6) δ ppm: 163.0, 143.7 [$J(^{13}C–^{117}Sn)$ 426 Hz], 137.0, 128.7, 127.6, 73.0, 70.1, 33.1, 29.6, 27.0, 18.7, 18.4, 13.5, 9.2 [$J(^{13}C–^{117}Sn)$ 370 Hz]. ^{117}Sn NMR (C_6D_6) δ ppm: −112.0. MS (EI) *m/z*: 422 (M^+, 2), 366 (50), 310 (100), 265 (8), 222 (6). HRMS (EI) calcd for $C_{20}H_{32}O_1N_1^{120}Sn_1$ 422.1506 found 422.1520.

2.2.18. Dimethyl-di-[2-(4-isopropyl-4,5-dihydro-oxazoline)-phenyl]-stannane (**17**)

IR (film) cm^{-1}: 3053, 2959, 2905, 1650, 1467, 1354, 1255, 1083, 1043, 781, 728. ^1H NMR δ ppm: 7.96–7.33

(8H, *m*, $H_{arom.}$), 4.26–4.21 (2H, *dd* $J=9.7$, 8.3 Hz), 3.92 (2H, *t* $J=8.6$ Hz), 3.78–3.72 (2H, *m*), 1.65–1.56 (2H, *m*), 0.84 (6H, *d* $J=6.7$ Hz), 0.77 (6H, *d* $J=6.8$ Hz), 0.43 [3H, *s*, $J(^1H–^{117}Sn)$ 59 Hz]. ^{13}C NMR δ ppm: 164.9, 148.3 [$J(^{13}C–^{117}Sn)$ 530 Hz], 136.7, 133.1, 130.2, 127.8, 127.5, 72.5, 70.3, 32.3, 19.0, 18.1, −3.5 [$J(^{13}C–^{117}Sn)$ 437 Hz]. ^{117}Sn NMR δ ppm: −94.9. ^{15}N NMR δ ppm: −155.1. MS (EI) *m/z*: 525 (M^+, 1), 511 (M^+ – Me, 100), 453 (4), 425 (4), 338 (19), 308 (7), 264 (3), 248 (5), 222 (10), 146 (12). HRMS (EI) calcd for $C_{25}H_{31}O_2N_2^{120}Sn_1$ 511.1407 found 511.1396.

2.2.19. Dibutyl-di-[2-(4-isopropyl-4,5-dihydro-oxazoline)-phenyl]-stannane (**18**)

IR (film) cm^{-1}: 3053, 2965, 2926, 2871, 2853, 1650, 1464, 1355, 1082, 1042, 728. ^1H NMR δ ppm: 7.97–7.28 (8H, *m*, $H_{arom.}$), 4.15–4.10 (2H, *dd* $J=9.7$, 8.3 Hz), 3.88–3.83 (2H, *t* $J=8.4$ Hz), 3.74–3.65 (2H, *m*), 1.62–1.54 (4H, *m*), 1.44–1.36 (4H, *m*), 1.30–1.16 (6H, *m*), 1.05–0.71 (18H, *m*). ^{13}C NMR δ ppm: 165.0, 148.0 [$J(^{13}C–^{117}Sn)$ 469 Hz], 137.0, 133.4, 130.1, 127.8, 72.3, 70.0, 32.2, 29.1, 27.4, 19.0, 18.0, 15.1 [$J(^{13}C–^{117}Sn)$ 434 Hz], 13.6. ^{117}Sn NMR δ ppm: −87.5. ^{15}N NMR δ ppm: −156.3. MS (EI) *m/z*: 609 (M^+, 2), 553 (100), 422 (7), 409 (3), 324 (3), 308 (7), 248 (6), 222 (12), 146 (5). HRMS (EI) calcd for $C_{28}H_{37}O_2N_2^{120}Sn_1$ 553.1877 found 553.1854. HRMS (EI) calcd for $C_{32}H_{45}O_2N_2^{120}Sn_1$ 609.2503 found 609.2526.

2.2.20. Dimethyl-di-[4-(4-isopropyl-4,5-dihydro-oxazoline)-phenyl]-stannane (**19**)

To 53 mg (2.2 mmol) of magnesium, activated by 'dry stirring' was added 10 ml of THF. After addition of 536 mg (2 mmol) of (*S*)-2-(4-bromo-phenyl)-4-isopropyl-4,5-dihydro-oxazole the reaction was started by addition of a small amount of 1,2-dibromoethane. The mixture was stirred at reflux until the magnesium was consumed. Subsequently, a solution of Me_2SnBr_2 (309, 1.0 mmol) in 2 ml of THF was added. After 30 min the mixture was diluted with 10 ml of ether and filtered over a short silica gel pad. The solvents were removed in vacuo and the residue was flash chromatographed. The resulting oil was purified by flash chromatography (hexanes/ethyl acetate) to yield compound **19** (294 mg, 56%) as white solid (m.p. 112–114 °C).

IR (film) cm^{-1}: 3066, 3016, 1646, 1387, 1353, 1056. ^1H NMR δ ppm: 7.96–7.50 (8H, $AA'BB'$ system, $H_{arom.}$), 4.41–4.34 (2H, *m*), 4.14–4.07 (4H, *m*), 1.90–1.81 (2H, *m*), 1.03 (6H, *d* $J=$ 6.8 Hz), 0.92 (6H, *d* $J=6.8$ Hz), 0.86 (6H, *t* $J=7.3$ Hz). ^{13}C NMR δ ppm: 163.1, 144.7 [$J(^{13}C–^{117}Sn)$ 475 Hz], 135.9, 128.0, 127.5, 72.4, 69.8, 32.6, 18.7, 17.9, −10.0 [$J(^{13}C–^{117}Sn)$ 370 Hz]. ^{117}Sn NMR δ ppm: −57.9. MS (EI) *m/z*: 526 (M^+, 2), 511 (M^+ – Me, 100), 483 (28), 453 (2), 397 (1). HRMS (EI) calcd for $C_{26}H_{34}O_2N_2^{120}Sn_1$ 526.1642 found 526.1658.

2.2.21. Dibutyl-di-[4-(4-isopropyl-4,5-dihydro-oxazoline)-phenyl]-stannane (**20**)

To 53 mg (2.2 mmol) of magnesium, activated by 'dry stirring' was added 10 ml of THF. After addition of 536 mg (2 mmol) of (*S*)-2-(4-bromo-phenyl)-4-isopropyl-4,5-dihydro-oxazole the reaction was started by addition of a small amount of 1,2-dibromoethane. The mixture was stirred at reflux until the magnesium was consumed. Subsequently, a solution of Bu_2SnBr_2 (393 mg, 1.0 mmol) in 2 ml of THF was added. After 30 min the mixture was diluted with 10 ml of ether and filtered over a short silica gel pad. The solvents were removed *in vacuo* and the residue was flash chromatographed. The resulting oil was purified by flash chromatography (hexanes/ethyl acetate) to yield compound **20** (396 mg, 65%) as yellowish oil.

IR (film) cm^{-1}: 3070, 3015, 1650, 1389, 1355, 1057. ^1H NMR δ ppm: 7.93–7.46 (8H, $AA'BB'$ system, $H_{arom.}$), 4.42–4.34 (2H, *m*), 4.15–4.07 (4H, *m*), 1.90–1.82 (2H, *m*), 1.65–1.25 (12H, *m*), 1.02 (6H, *d* $J=6.7$ Hz), 0.93 (6H, *d* $J=6.8$ Hz), 0.86 (6H, *t* $J=7.3$ Hz). ^{13}C NMR δ ppm: 163.4, 144.7 [$J(^{13}C–^{117}Sn)$ 419 Hz], 136.7, 128.0, 127.5, 72.6, 70.0, 32.8, 28.8, 27.2, 18.9, 18.0, 13.5, 10.4 [$J(^{13}C–^{117}Sn)$ 372 Hz]. ^{117}Sn NMR δ ppm: −70.2. MS (ASC) *m/z*: 611 ($M^+ + H$). HRMS (ASC) calcd for $C_{32}H_{47}O_2N_2^{120}Sn_1$ 611.2654 found 611.2683.

2.2.22. (S)-2-(4-Iodo-phenyl)-4-isopropyl-4,5-dihydro-oxazole (**21**)

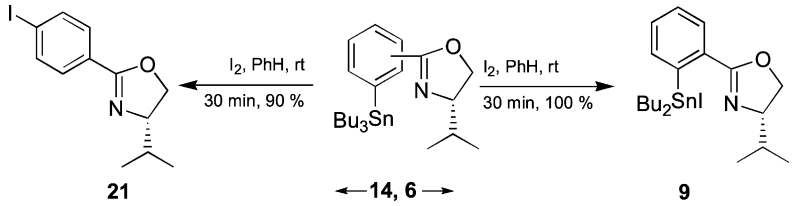
A solution of **14** (48 mg, 0.1 mmol) and I_2 (28 mg, 0.11 mmol) in benzene (3 ml) was stirred in the dark at rt for 30 min. The mixture was then evaporated and the crude product was purified by filtering-column chromatography on silica gel to give compound **21**. (28 mg, 90%) as colorless needles (m.p. 73–74 °C).

IR (film) cm^{-1}: 2984, 2955, 2889, 2870, 1647, 1588, 1393, 1260, 1075, 1005, 962. ^1H NMR δ ppm: 7.76–7.64 (4H, $AA'BB'$ system, $H_{arom.}$), 4.42–4.37 (1H, *d* $J=9.1$, 7.9 Hz), 4.15–4.05 (2H, *m*), 1.88–1.80 (1H, *m*), 1.03–1.01 (3H, *d* $J=6.8$ Hz), 0.93–0.91 (3H, *d* $J=6.8$ Hz). ^{13}C NMR δ ppm: 162.7, 137.5, 129.8, 127.5, 98.0, 72.7, 70.3, 32.8, 18.9, 18.1. MS (EI) *m/z*: 315 (M+, 9), 272 (100), 244 (16), 230 (3), 217 (4), 149 (19), 117 (24). HRMS (EI) calcd for $C_{12}H_{14}O_1N_1I_1$ 315.0120 found 315.0112.

2.2.23. (S)-4-Isopropyl-2-phenyl-4,5-dihydro-oxazole (**22**)

To a solution of (S)-(2-bromo-phenyl)-4-isopropyl-4,5-dihydro-oxazole (100 mg, 0.37 mmol) in Et_2O (7 ml) was added dropwise at −78 °C a solution of *n*-BuLi in hexane (1.6 M, 256 μl, 0.41 mmol). After addition was complete, the solution was stirred for an additional hour and quenched by saturated aqueous NH_4Cl solution. The organic layer was worked up in the usual manner to give a crude product which was purified by filtering-column chromatography on silica gel to give compound **22** (58 mg, 82%).

^1HNMR δ ppm: 7.99–7.41 (5H, *m*, H_{arom}), 4.46–4.10 (3H, *m*), 1.92–1.85 (1H, *m*), 1.07–1.06 (3H, *d* $J=6.8$ Hz), 0.97–0.95 (3H, *d* $J=6.8$ Hz). ^{15}N NMR δ ppm: −156.3.



Scheme 2. The influence of coordination at the tin on the reaction course.

3. Results and discussion

Synthesis of the organotin compounds. The synthesis of the investigated compounds (**1**–**10**) involved the preparation of (−)-(*S*)-(2-bromo-phenyl)-4-isopropyl-4,5-dihydro-oxazole and then formation of Sn derivatives by substitution [11]. Initially, the *o*-lithiophenyloxazole prepared by metallation of (−)-(*S*)-(2-bromo-phenyl)-4-isopropyl-4,5-dihydro-oxazole with *n*-butyl lithium [12] was treated with twofold excess of *n*-Bu_2SnCl_2 at −78 °C giving compounds **6** (24%), **7** (50%) and **18** (9%). Experiments with stoichiometric amount of *n*-Bu_2SnCl_2 gave similar results. The attempts to substitute only one of the chlorine atoms in Me_2SnCl_2 failed due to the preferential formation of disubstituted product **17**. When the oxazole was converted to an organomagnesium derivative using activated magnesium [13] and then treated with R_2SnCl_2 (R = Me or Bu) **2** and **7** were formed in satisfactory yields (75–80%). However, the halide **2** appeared to be a mixture of the corresponding chloride and bromide. Both of them could be transformed into the corresponding bromide or iodide using LiBr or KI in boiling acetone, respectively. Fortunately, the cleavage of organic groups from tin by halogen can be predicted accurately [14]. Two isomeric tetraorganotin compounds **6** and **14** when reacted with iodine at ambient temperatures followed different chemical pathways (Scheme 2). In the case of **14** aryl iodide **21** was formed according to the general rule, whereas compound **6** gave iodide **9**. The usual sequence of reactivity was reversed, i.e. the *n*-butyl group was cleaved preferentially to the aryl group. Such phenomena have already been observed by Jousseaume and explained by intramolecular assistance at the tin [15]. Also easily available **1** and **6** when treated with stoichiometric amount of bromine or iodine in benzene at ambient temperatures gave the corresponding halides (**3**, **4**, **8** and **9**) in excellent yields (> 95%) [16].

There are several methods for the preparation of triorganotin hydrides [7,17–21] but, in the case of halides **2**–**4**, **7**–**9** only reduction with $NaBH_4$ in ethanol was successful. The crude hexane extracts from the reaction mixtures contained pure tin hydrides **5** and **10**, as it was judged from their ^1H and ^{13}C NMR spectra. They appeared to be stable and could be stored at low temperatures under argon for several weeks without significant decomposition (<10%) [22].

To distinguish unambiguously effects caused by the postulated coordination and these caused by the substituents we also decided to synthesize tin compounds **11**–**16** and **19** and **20** starting from (−)-(*S*)-(4-bromo-phenyl)-4-isopropyl-4,5-dihydro-oxazole (Scheme 1). We measured the ^1H, ^{13}C, ^{15}N and ^{117}Sn NMR spectra of tin compounds **1**–**10**, **17** and **18** and compared the results obtained with those for compounds **11**–**16** and **19**–**20**.

Crystal structures of [2-(4-isopropyl-2-oxazolinyl)-5-phenyl]trimethyltin (1) and [2-(4-isopropyl-2-oxazolinyl)-5-phenyl]dimethyltin bromide (3). Attempts to obtain crystals of **6**–**9** suitable for X-ray study were not successful. On the other hand compounds **1**–**4** were obtained as white crystalline solids and an X-ray structure determination of **1** and **3** was carried out. Both structures were characterized by affecting geometry large thermal motions. This suggests thermal instability of the compounds. Regardless of this difficulty, the structure determination shows main features of molecular geometry. As depicted in Figs. 1 and 2, the nitrogen atom of the oxazoline ring is preferentially coordinated to the tin atom in both cases. However, these two complexes are different by the Sn–N distance that is much shorter in the case of bromide **3** (for distances see figures captions). The bromide has trigonal bipyramidal coordination geometry at the tin atom, in which the electronegative ligands occupy the axial sites and the three carbon atoms equatorial sites. The Sn–N distance of 2.39(2) Å is a little bit shorter than in the previous reported triorganotin halides containing sp^2-hybridized nitrogen atom [7,8]. The Sn–N distance in **1** is very long 2.888(9)

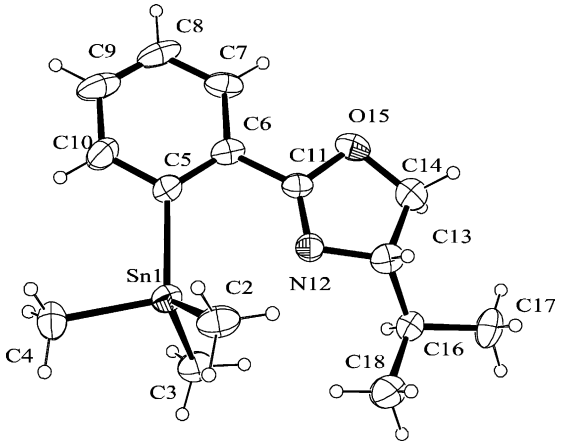


Fig. 1. ORTEP diagram of compound **1**. Thermal ellipsoids shown at 30% probability level. Selected bond lengths: Sn1–C2 2.13(1), Sn1–C3 2.15(1), Sn1–C4 2.15(1), Sn1–C5 2.16(1), and Sn1–N12 2.888(9) Å.

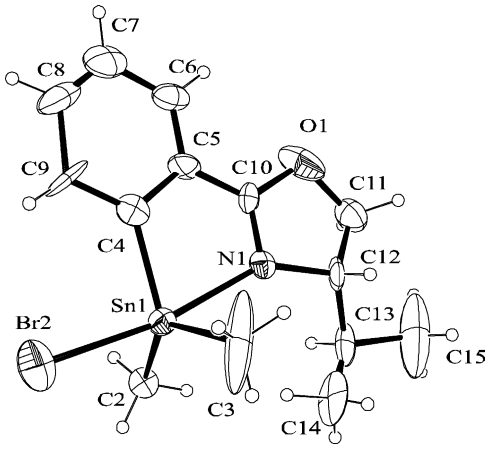


Fig. 2. ORTEP diagram of compound **3**. Thermal ellipsoids shown at 30% probability level. Selected bond lengths: Sn1–Br2 2.599(4), Sn1–C2 2.14(2), Sn1–C3 2.05(4), Sn1–C4 2.14(3), Sn1–N1 2.39(2) Å.

Å but still shorter than the longest one found in $Ph_2SnCl_2 \cdot$pyrazine (2.965 Å) [23].

Structure in solution of the organotin halides. At first we measured multinuclear NMR spectra for halides **2–4**, **7–9** and **12**, **15** containing tin substituents in the *o*- or *p*-positions to the oxazole ring, respectively. In Tables 1–3, selected multinuclear NMR data (chemical shifts and coupling constants) are collected. Full multinuclear NMR characteristic of all the compounds studied is presented in the experimental section. The exact comparison of the NMR data for **2–4** and **7–9** with those reported earlier by van Koten et al. [7] and Dakternieks et al. [8] was not possible due to different substituents at the tin [24]. Nevertheless, for the halides we noticed very similar values of the ^{117}Sn NMR chemical shifts. The comparison of the ^{117}Sn NMR chemical shifts of bromides **3/8** (coordinated) representatives of compounds **2–4**, **7–9** and **12/15** (non-coordinated) shows a very large difference (ca. 174 and 156 ppm, respectively) in the ^{117}Sn shieldings between both pairs of bromides **3/8** and **12/15**. In compounds **2–4** and **7–9** the signals of the ^{117}Sn nuclei are strongly shifted upfield, when compared to their positions observed in compounds **12** and **15**.

In the case of halides **2–4** the ^{117}Sn NMR shielding increases in the following order: Cl, Br and I ($-103.0 \rightarrow -128.8$ ppm). This change of the ^{117}Sn NMR shielding reveals the reversed order as would be assumed from the electronegativity of the halides. On the other hand for compounds **7–9** an opposite effect was observed ($-96.2 \rightarrow -89.7$ ppm). A higher acidity at tin for the corresponding bromides and iodides was reported by Dräger and Jousseaume in a series of (2-carbomethoxy-1,4-cyclohexadien-1-yl)dimethyltin halides [25]. It could be explained in terms of decreasing of p_π–d_π overlap from Sn–F to Sn–I contrary to the decreasing electronegativity effect. Moreover, the ^{117}Sn NMR signals of halides **2–4** and **7–9** were much broader (half-height widths are ca. 30–50 Hz) than these of tetraorganotins **1** and **6** and **11** and **14** (half-hight widths are ca. 1–2 Hz) [26].

Further comparison of the NMR data leads to the following observations: (i) the increase of the $^1J(^{13}C–^{117/119}Sn)$ at carbon C1 of the phenyl ring by ca. 150 Hz. (ii) the increase of the $^1J(^{13}C–^{117/119}Sn)$ at CH_3/CH_2 carbons directly bounded to the tin atom by ca. 140–170 Hz. (iii) an appearance of the $J(^{13}C4'–^{117/119}Sn)$ ca. 10 Hz in

Table 1
The ^{13}C NMR chemical shifts and the $J(^{13}C–^{117/119}Sn)$ couplings of **1–20**

Compound	$SnCH_2$–/$SnCH_3$[a,b]	C1phenyl[a,b]	C1′$_{ligand}$[a]	C4′$_{ligand}$[c]
1	−6.1 (363, 380)	145.3 (470, 491)	164.9	72.8 (–)
2	2.6 (532, 556), 1.7 (561, 589)	147.1 (670, 701)	170.5	69.3 (10.7)
3	4.1 (523, 547), 3.3 (552, 578)	146.2 (653, 683)	170.6	69.2 (10.2)
4	6.4 (514, 535), 5.9 (542, 565)	144.3 (629, 659)	170.5	69.2 (10.5)
5	−7.0 (402.0, 421.0), −7.4 (373, 390)	144.3 (514, 537)	165.7	72.7 (–)
6	11.9 (348, 365)	145.0 (385, 403)	165.0	72.8 (–)
7	21.2 (499, 533), 21.2 (535, 560)	147.2 (576, 603)	170.5	69.6 (10.9)
8	22.3 (499, 522), 22.4 (525, 549)	146.4 (557, 583)	170.5	69.5 (10.8)
9	24.3 (511, 535), 23.8 (485, 508)	144.9 (530, 553)	170.6	69.5 (10.6)
10	13.5 (414, 433), 13.3 (405, 424)	145.1 (457, 478)	166.0	72.7 (–)
11	−9.6 (337, 353)	146.9 (425, 445)	163.5	72.5 (–)
12	−2.0 (376, 393)	144.0 (510, 533)	163.1	72.5 (–)
13	−11.7 (349, 365)	143.7 (455, 478)	163.2	73.2 (–)
14	9.6 (326, 342)	146.9 (353, 369)	163.7	72.5 (–)
15	17.7 (358, 374)	not detected	163.1	72.6 (–)
16	9.2 (355, 370)	143.7 (406, 426)	163.0	73.0 (–)
17	−3.5 (418, 437)	148.3 (506, 530)	164.9	72.5 (–)
18	15.1 (414, 434)	148.0 (447, 469)	165.0	72.3 (–)
19	−10.0 (354, 370)	144.7 (454, 475)	163.3	72.6 (–)
20	10.4 (355, 372)	144.7 (401, 419)	163.4	72.6 (–)

[a] All values are in δ relative to $(Me)_4Si$ in $CDCl_3$ at 30 °C.
[b] Values of the $^1J(^{13}C–^{117/119}Sn)$ couplings.
[c] Values of the $^nJ(^{13}C–^{117/119}Sn)$ couplings.

Table 2
The ^{117}Sn NMR data of compounds **1–20**

Compound	^{117}Sn (ppm)[a]	Compound	^{117}Sn (ppm)[a]
1	−50.6	**12**	64.0
2	−103.0	**13**	−121.4
3	−110.9	**14**	−42.0
4	−129.2	**15**	64.4
5	−129.0	**16**	−112.0
6	−52.5	**17**	−94.9
7	−97.2	**18**	−87.5
8	−93.2	**19**	−57.9
9	−89.7	**20**	−70.2
10	−92.0		
11	−28.6		

[a] All values are in δ relative to $(Me)_4Sn$ in $CDCl_3$ at 30 °C.

halides **2–4** and **7–9**. (iv) a strong shielding increase of the ^{15}N nucleus by ca. 20 ppm. Two first tendencies are well-known in literature [1] but the last two related to the appearance of the $J(^{13}C4'–^{117}Sn)$ and observation of a relatively strong the ^{15}N NMR shielding increase in the case of compounds containing 'pyridine' type of nitrogen seem to be new and additionally support the Sn–N coordination in solution in the halides [27].

The increase of the ^{15}N shielding in case of halides **2–4** and **7–9** (Table 3) is about 25 ppm, when compared to that of phenyl-4-isopropyl-4,5-dihydro-oxazole **22** (−156.3 ppm), and is comparable with an effect observed in case of protonation or alkylation of the 'pyridine' nitrogen type [28,29]. Smaller and opposite ^{15}N NMR shielding effects were previously observed in the case of several organotin chelates containing 'amine' type of nitrogen described by Růžička et al. [6] They also measured the $^1J(^{15}N–^{117/119}Sn)$ couplings for (dimethylaminomethyl)-phenylalkylstannyl halides confirming the presence of strong Sn–N coordination in these molecules. In the case of **3** and **4**, in long accumulated ^{15}N NMR spectra we observed also the $^1J(^{15}N–^{117/119}Sn)$ couplings as small satellite lines (Fig. 4), the magnitude of which is ca. 110 Hz. The existence of such satellites clearly confirms the Sn–N coordination in the halides.

Structure in solution of the tetraorganotin compounds. Several tetraorganotin compounds have been reported as penta- or even hexacoordinate [30–34]. Such coordination favors the electron transfer from tetraalkylstannanes [35] or promotes the C–Sn cleavage [13,36]. From observations in solution it may be concluded that the ^{117}Sn NMR chemical shifts of tetraorganotin compounds are only influenced to a minor extent by additional coordination [27,37]. Therefore, it is not possible to correlate unambiguously these values with the coordination geometry at the tin. A reasonable way to get additional information concerning the Sn–N coordination could be a comparison of the NMR parameters of *o*- and *p*- substituted analogues with similar substituent patterns.

Table 3
The ^{15}N NMR data of compounds **1–11**, **17**, **18** and **22**

Compound	^{15}N (ppm)[a]	Compound	^{15}N (ppm)[a]
1	−155.7 (26)[b]	**8**	−181.0
2	−180.6	**9**	−181.6
3	−181.4 (122)[b]	**10**	−158.3(32)[b]
4	−182.8 (112)[b]	**11**	−156.0
5	−155.3 (34)[b]	**17**	−155.1
6	−156.1 (22)[b]	**18**	−156.3
7	−180.4	**22**	−156.3

[a] All values are in δ relative to $MeNO_2$ in $CDCl_3$ at 30 °C.
[b] The $J(^{15}N–^{117/119}Sn)$ couplings.

The ^{13}C and ^{117}Sn NMR data of the tetraorganotin compounds **1**, **6**, **11**, **14**, **17–20** is given in Tables 1 and 2, respectively. We noticed remarkable effect of shielding change in the ^{117}Sn NMR spectra (ca. 10–40 ppm) for pairs **1/11**, **6/14**, **17/19** and **18/20**. The upfield shifts of the ^{117}Sn nuclei may point to a higher coordination at the tin, but as compared to those from halides **2–4**, **7–9** (>150 ppm) they are considerably smaller. Next, we analyzed the $^1J(^{13}C–^{117/119}Sn)$ couplings, which are a sensitive measure of the state of hybridization at tin and increase with increasing coordination number in organotin compounds. Comparison of the $^1J(^{13}C–^{117/119}Sn)$ couplings for **1/6** and **17/18** with these for **11/14** and **19/20** (where the Sn–N interaction is not involved for obvious reasons) leads to an average increase of this parameter (ca. 50 Hz). The observed differences in the ^{117}Sn NMR chemical shifts and in the $^1J(^{13}C–^{117/119}Sn)$ couplings for the corresponding possibly coordinated and non-coordinated compounds support the Sn–N interaction in compounds **1**, **6**, **17** and **18**. Additionally, in the ^{15}N NMR spectra of **1** and **6** the $^{117/119}$Sn satellites were observed, which clearly prove the existence of such interaction. The values of $^1J(^{15}N–^{117/119}Sn)$ are considerably smaller (26 Hz for **1** and 22 Hz for **6**) than in the case of halides **2–4** and **7–9**, supposedly due to lower acidity of the tin atom in **1** and **6** (Table 3).

Structure in solution of the organotin hydrides. There are only a limited number of reports on the Sn–N coordination in hydrides containing potentially bonding ligands (Fig. 3). For example, Schumann et al. found a small Sn–N intramolecular interaction for tin hydride **A**, however, such interaction did not alter significantly the ^{117}Sn NMR chemical shift in this hydride [38]. Dakternieks et al. stated that nitrogen appeared to be coordinated to the tin centre in hydride **B** [39]. Larger $^1J(^1H–^{117/119}Sn)$ couplings compared to non-coordinated tin hydrides with similar substituent patterns were reported by Metzger et al. for hydride **C** [40].

The tin center in hydrides **5** and **10** has a lower Lewis acidity in comparison with the corresponding halides. However, taking into account that tetraorganotin compounds **1** and **6** are pentavalent, the corresponding hydrides

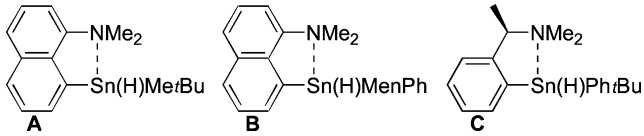


Fig. 3. Examples of hydrides with the postulated Sn–N coordination.

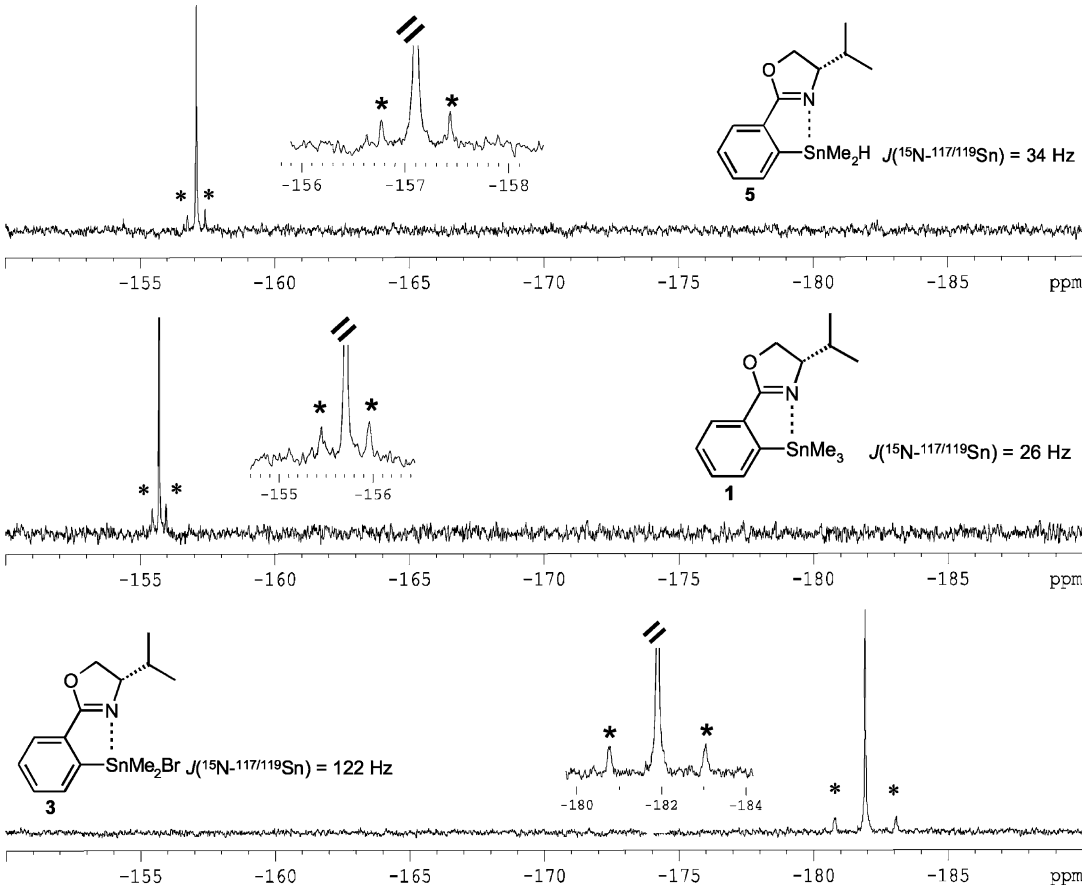


Fig. 4. The ^{15}N NMR spectra of compounds **1**, **3** and **5** recorded by inverse gated pulse sequence in C_6D_6. Result of 22,000–42,000 transients (repetition delay 2.5–3.0 s, acquisition time 1.3 s). The $^{117/119}Sn$ satellites are marked by asterisks.

might also share this feature. To test such a possibility we measured the ^{117}Sn NMR chemical shifts, the $^{1}J(^{1}H–^{117/119}Sn)$, $J(^{13}C–^{117/119}Sn)$ and $J(^{15}N–^{117/119}Sn)$ couplings in hydrides **5** and **10**, as well as, in their non-coordinated analogues **13** and **16**. The ^{117}Sn NMR signal shift to lower frequency by ca. 8 ppm is observed when **5** is compared with its analogue **13**, whereas an opposite effect (20 ppm) is found for hydrides **10** and **16**. Again, from the ^{117}Sn NMR data it cannot be concluded much about the postulated coordinative interaction. The $J(^{13}C–^{117/119}Sn)$ values of **5** and **10** are lager than in **13** and **16** indicating the Sn–N interaction in the first pair of hydrides. Surprisingly, the $^{1}J(^{1}H–^{117/119}Sn)$ couplings for **5** (1676, 1753 Hz) and **10** (1434, 1503 Hz) are smaller than these in **13** (1746, 1827 Hz) and **16** (1634, 1706 Hz) [41]. This finding was in contradiction with the data reported by Metzger et al. who observed larger $^{1}J(^{1}H–^{117/119}Sn)$ couplings in coordinated tin hydrides containing the chiral 2-(1-dimethylamino-alkyl)phenyl ligands [40]. Similarly like in tetraorganotins **1** and **6** the ^{15}N NMR chemical shifts of hydrides **5** and **10** are not diagnostic. On the other hand the $J(^{15}N–^{117/119}Sn)$ couplings measured for **5** and **10** again appeared to be very useful (Fig. 4). To the best of our knowledge such interactions have not been yet measured in so-called ‘coordinated hydrides’. Their values (34 and 32 Hz, respectively) point to even stronger Sn–N coordination than in tetraorganotin compounds **1** and **6** (26 and 22 Hz, respectively).

4. Conclusions

A number of arguments based on the ^{13}C, ^{15}N and ^{117}Sn NMR studies supported the hypothesis that in solution, in non-polar solvents, compounds **1**–**10**, **17** and **18** occur in the form of molecular complexes with a more or less strong intramolecular Sn–N interaction. The ^{117}Sn NMR chemical shifts and $^{1}J(^{13}C–^{117/119}Sn)$ couplings reported here are of the expected magnitude and are comparable with these from the related systems. In the case of the tetraorganotin compounds the existence of the Sn–N coordination was additionally supported by the $^{15}N/^{117}Sn$ NMR and X-ray studies. The Sn–N distances observed in solid state correlate well with the NMR data. For the first time the $J(^{15}N–^{117/119}Sn)$ couplings in coordinated hydrides have been detected. The results of synthesis and radical studies of new tin hydrides containing the oxazole moiety will be reported at a later date.

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References

[1] J.T.B.T. Jastrzebski, G. van Koten, Adv. Organomet. Chem. 35 (1993) 241.
[2] S.J. Blunden, P.A. Cusack, R. Hill, The Industrial Uses of Tin Chemicals, Royal Society of Chemistry, London, 1985.
[3] M. Gielen, R. Willem, J. Holeček, A. Lyčka, Main Group Met. Chem. 16 (1993) 29 and references therein.
[4] B. Wrackmeyer, Annu. Reports NMR Spectrosc. 38 (1999) 203.
[5] B. Wrackmeyer, M. Vosteen, W. Storch, J. Mol. Struct. 602-603 (2002) 177.
[6] A. Růžička, R. Jambor, J. Brus, I. Císařová, J. Holeček, Inorg. Chim. Acta 323 (2001) 163 and references cited therein.
[7] J.T.B.H. Jastrzebski, E. Wehman, J. Boersma, G. van Koten, K. Goubitz, D. Heijdenrijk, J. Organomet. Chem. 409 (1991) 157.
[8] D. Dakternieks, K. Dunn, C.H. Schiesser, E.R.T. Tiekink, J. Chem. Soc. Dalton Trans. (2000) 3693.
[9] G.M. Sheldrick, Acta Crystallogr. A46 (1990) 467.
[10] G.M. Sheldrick, SHELXL97, Program for Crystal Structure Refinement, University of Göttingen, Germany, 1997.
[11] 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.
[12] G. Koch, G.C. Lloyd-Jones, O. Loiseleur, A. Pfaltz, R. Prétôt, S. Schaffner, P. Schnider, P. von Matt, Recl. Trav. Chim. Pays-Bas 114 (1995) 206.
[13] M.J. Brown, K.V. Baker, N. Hughs, A.J. Skarnulis, A. Sexton, J. Org. Chem. 56 (1991) 698.
[14] S.D. Rosenberg, E. Debreczeni, E.L. Weinberg, J. Am. Chem. Soc. 81 (1959) 972.
[15] B. Jousseaume, P.J. Villeneuve, J. Chem. Soc., Chem. Commun. (1987) 513.
[16] Another way involves preparation of the copper derivatives, see: Ref. [7] and E. Wehman, G. van Koten, J.T.B.H. Jastrzebski, M.A. Rotteveel, C.H. Stam, Organometallics 7 (1988) 1477.
[17] A.E. Finholt, A.C. Bond Jr., K.E. Wilzbach, H.I. Schlesinger, J. Am. Chem. Soc. 69 (1947) 2692.
[18] W.P. Neumann, H. Niermann, Liebigs Ann. Chem. 653 (1962) 164.
[19] D.L.J. Clive, J. Wang, J. Org. Chem. 67 (2002) 1192.
[20] D.P. Curran, G. Gualtieri, SynLetters (2001) 1038.
[21] T.N. Mitchell, B.S. Bronk, Organometallics 19 (1991) 936.
[22] The hydrides reported by Dakternieks appeared to be less stable, see Ref. [8].
[23] D. Cunningham, T. Higgins, P. McArdle, J. Chem. Soc., Chem. Commun. (1984) 833.
[24] Thereplacement of alkyl by phenyl groups has an influence on the tin chemical shift values. An increasing low-frequency chemical shift is observed, see: B. Wrackmeyer, Annu. Reports NMR Spectrosc. 16 (1995) 73.
[25] U. Kolb, M. Dräger, B. Jousseaume, Organometallics 10 (1991) 2737.
[26] It could be explained in terms of unresolved Sn–X scalar interactions, see: Ref. [4].
[27] In order to examine a possibility of intermolecular coordination we measured the ^{1}H and ^{117}Sn spectra of an equimolar mixture of (−)-(*S*)-phenyl-4-isopropyl-4,5-dihydro-oxazole and *n*-Bu_3SnCl in $CDCl_3$ at 30 °C. From the NMR results it was clear that the coordination of it with *n*-Bu_3SnCl did not take place or it was too week to be manifested in the ^{117}Sn NMR.
[28] P. Cmoch, H. Korczak, L. Stefaniak, G.A. Webb, J. Phys. Org. Chem. 12 (1999) 470.
[29] P. Cmoch, J.W. Wiench, L. Stefaniak, J. Sitkowski, J. Mol. Struct. 477 (1999) 119.
[30] F. Fu, H. Li, D. Zhu, Q. Fang, H. Pan, E.R.T. Tiekink, F. Kayser, M. Biesemans, I. Verbruggen, R. Willem, M. Gielen, J. Organomet. Chem. 490 (1995) 163 and references cited therein.
[31] R. Willem, A. Delmotte, I. De Borger, M. Biesemans, M. Gielen, F. Kayser, E.R.T. Tiekink, J. Organomet. Chem. 480 (1994) 255.
[32] F. Kayser, M. Biesemans, A. Delmotte, I. Verbruggen, I. De Borger, M. Gielen, R. Willem, Organometallics 13 (1994) 4026.
[33] F. Kayser, M. Biesemans, H. Pan, M. Gielen, R. Willem, J. Chem. Soc., Perkin Trans. 2 (1994) 297.
[34] F. Kayser, M. Biesemans, A. Delmotte, R. Hendrix, P. Malschaert, I. Verbruggen, B. Mahieu, R. Willem, M. Gielen, Bull. Soc. Chim. Belg. 103 (1994) 273.
[35] J. Yoshida, M. Izawa, J. Am. Chem. Soc. 119 (1997) 9361.
[36] E. Vedejs, A.R. Haight, W.O. Moss, J. Am. Chem. Soc. 114 (1992) 6556.
[37] J.T.B.H. Jastrzebski, D.M. Grove, J. Boersma, G. van Koten, J.-M. Ernsting, Magn. Reson. Chem. 29 (1991) 25.
[38] H. Schumann, B.C. Wassermann, F.E. Hahn, Organometallics 11 (1992) 2803.
[39] D. Dakternieks, K. Dunn, C.H. Schiesser, E.R.T. Tiekink, J. Organomet. Chem. 605 (2000) 209.
[40] K. Schwarzkopf, J.O. Metzger, W. Saak, S. Pohl, Chem. Ber./Recueil 130 (1997) 1539.
[41] A similar effect has been described, see: M. Biesemans, R. Willem, S. Damoun, P. Geerlings, M. Lahcini, P. Jaumier, B. Jousseaume, Organometallics 15 (1996) 2237.