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

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Abstract

The *N*-coordinated tin hydrides containing the chiral 2-(4-isopropyl-2-oxazolinyl)-5-phenyl ligand in the presence of catalytic amounts of tetrakis(triphenylphosphine)palladium gave the corresponding distannanes in good yields. The distannanes have been fully characterized by means of the ^{1}H, ^{13}C, ^{15}N and ^{117}Sn NMR measurements. The $J(^{15}N–^{117/119}Sn)$, $J(^{117}Sn–^{119}Sn)$ couplings and single-crystal X-ray analysis of distannane **3** revealed a tendency towards penta-coordination at the tin center as a result of the Sn–N interaction.

Keywords: Distannanes; NMR spectroscopy; Palladium; Sn–N coordination; Tin hydrides

1. Introduction

There have been several reports concerning potentially intramolecularly coordinated tin hydrides in which the tin atom is coordinated to nitrogen from the ligand [1–8]. However, to the best of our knowledge the corresponding distannanes have not been reported yet. Such ditin compounds could serve as a source of stannyl radicals for atom transfer cyclizations [9]. We have recently described the synthesis and NMR study of tin hydrides **1** and **2** containing the chiral oxazoline moiety (Scheme 1) [10]. 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. We now describe the synthesis and NMR study of new distannanes containing the chiral 2-(4-isopropyl-2-oxazolinyl)-5-phenyl ligand.

2. Experimental

2.1. Methods and materials

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 178.208 MHz for ^{1}H, ^{13}C, ^{15}N and ^{117}Sn, respectively. 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 heteronuclear single quantum correlation (HSQC) and

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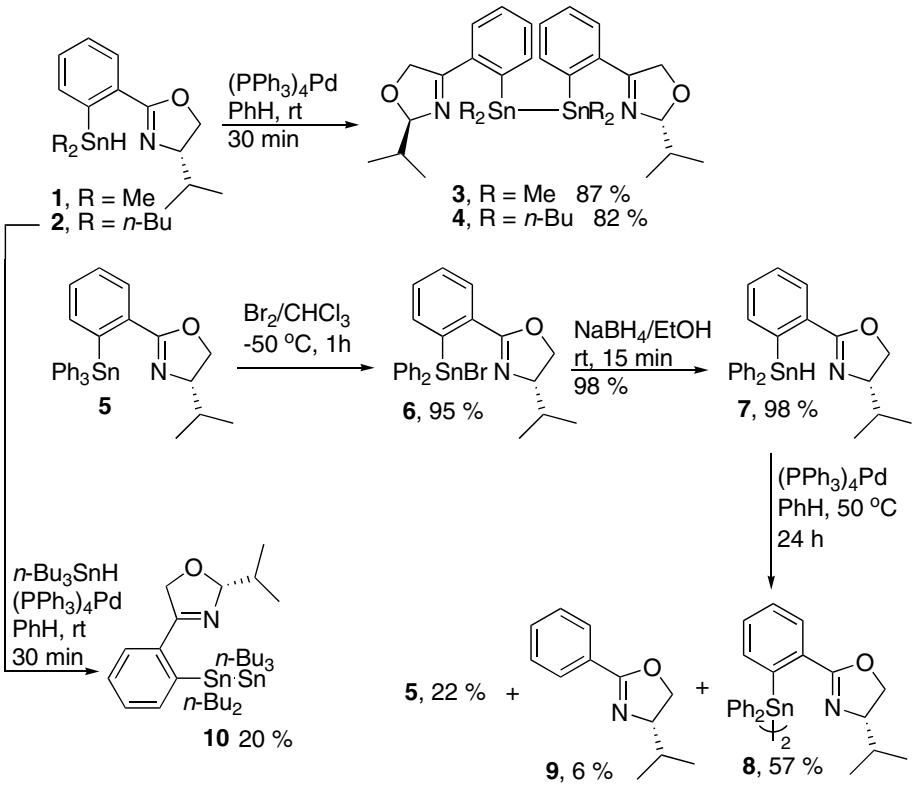


Scheme 1. The preparation of distannanes **3**, **4**, **8** and **10**.

heteronuclear multiple bond correlation (HMBC) spectroscopy taken for compounds **3** and **7**. 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 for compounds **3** and **5**–**7** and in other cases 2D $^{1}H–^{15}N$ NMR gradient selected HMBC method was applied. The ^{117}Sn NMR spectra were recorded using inverse gated decoupling sequence. During these experiments the $^{1}J(^{117}Sn–^{119}Sn)$ coupling constants were also measured as ^{119}Sn satellites of ^{117}Sn nucleus. 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 HR-MS spectra were determined on an ADM 604 Inectra GmbH spectometer. 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. (*S*)-2-(4-Bromo-phenyl)-4-isopropyl-4,5-dihydro-oxazole [11] and hydrides **1** and **2** [10] were prepared according to the published procedures. X-ray diffraction measurements of **3** (crystal of dimensions $0.77 \times 0.63 \times 0.6$ mm) were performed at rt at a Nonius BV MACH3 diffractometer. The best crystal used for data collection had ca. 3.5° mosaicity what made low-*T* experiments inaccessible. Monochromatized Cu Kα radiation ($\lambda = 1.54178$ Å) and ω–2θ scanning mode have been used. The intensities were corrected for Lorentz, polarization and ψ-scan based absorption. Structure of **3** was solved with direct methods using SHELXS-97 [12] and refinement with SHELXL-97 [13] programs included into WINGX [14] 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 **3** and details of refinement are shown in Table 1.

2.2. Synthesis

2.2.1. General procedure for the preparation of distannanes *3*, *4*, *8* and *10*

To a stirred solution of hydride **1**, **2** or **7** (1.0 mmol) in dry benzene (5 mL) under an atmosphere of argon was added $Pd(PPh_3)_4$ (77 mg, 0.1 mmol) and the mixture was stirred 2 h at rt (**7**, at 50 °C for 24 h). In the case of distannane **10** an equimolar mixture of hydride **2** and *n*-Bu_3SnH was used. Then the solvent was removed, and the residue was subjected to column chromatography on silica gel (hexanes/ethyl acetate) to give the corresponding distannanes.

2.2.2. Distannane *3*

White crystals, 132–134 °C, 87%. $[\alpha]_D = +89.3$ ($CHCl_3$, $c = 1$). IR cm^{-1} (KBr): 3053, 2954, 2904, 2868, 1641, 1465, 1357, 1249, 1081, 1043, 964. ^{1}H NMR (C_6D_6) ppm:

Table 1
Crystal data and structure refinement for compound **3**

Empirical formula	$C_{28}H_{40}N_2O_2Sn_2$
Formula weight	674.00
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	
a (Å)	12.256(3)
b (Å)	15.099(2)
c (Å)	16.575(2)
V (Å^3)	3067.3(9)
Z	4
D_{calc} (Mg m^{-3})	1.460
Absorption coefficient (mm^{-1})	13.132
$F(000)$	1352
Theta range for data collection (°)	3.96 to 74.23
Reflections collected/unique (R_{int})	3476/3473 (0.0953)
Completeness to $2\theta = 74.23$ (%)	99.3
Absorption correction	Psi-scan
Maximum and minimum transmission	0.9981 and 0.6910
Data/restraints/parameters	3473/0/298
Goodness-of-fit on F^2	0.969
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0798$, $wR_2 = 0.1782$
Absolute structure parameter	−0.08(5)
Largest difference in peak and hole (e Å^3)	1.408 and −1.841

7.84–7.81 (1H, dd, J = 7.6 and 1.3 Hz), 7.70–7.67 (1H, dd, J = 7.2 and 1.4 Hz), 7.41–7.38 (1H, dt, J = 7.3 and 1.3 Hz), 7.35–7.31 (1H, dt, J = 7.6 and 1.2 Hz), 3.82–3.78 (1H, t, J = 8.0 Hz), 3.64–3.60 (1H, dd, J = 18.3 and 9.8 Hz), 3.42–3.37 (1H, ddd, J = 9.8 and 7.7 and 5.6 Hz), 1.71–1.64 (1H, m), 0.84 (3H, d, J = 6.8 Hz), 0.74 (3H, d, J = 6.8 Hz), 0.38 [3H, *s*, $^2J(^1H–^{117/119}Sn)$ = 51.0 Hz, $^3J(^1H–^{117/119}Sn)$ = 15.1 Hz], 0.29 [3H, *s*, $^2J(^1H–^{117/119}Sn)$ = 38.5 Hz, $^3J(^1H–^{117/119}Sn)$ = 15.7 Hz]. ^{13}C NMR (C_6D_6) ppm: 164.9 [$J(^{13}C–^{117/119}Sn)$ = 1.2 and 6.1Hz], 147.0 [$J(^{13}C–^{117/119}Sn)$ = 369/386 and 41.7/43.3 Hz], 136.6 [$J(^{13}C–^{117/119}Sn)$ = 14.9 and 31.1 Hz], 134.0 [$J(^{13}C–^{117/119}Sn)$ = 21.5 Hz], 130.1 [$J(^{13}C–^{117/119}Sn)$ = 4.3 and 41.3 Hz], 128.5, 128.3, 71.9, 69.3, 32.2, 18.7, 17.3, −5.2 [$J(^{13}C–^{117/119}Sn)$ = 294/308 and 58.7/60.7 Hz], −6.5 [$J(^{13}C–^{117/119}Sn)$ = 174/182 and 100/105 Hz]. ^{15}N NMR (C_6D_6) ppm: −154.2 [$J(^{15}N–^{117/119}Sn)$ = 20.0 Hz]. ^{117}Sn NMR (C_6D_6) ppm: −120.5 [$^1J(^{117}Sn–^{119}Sn)$ = 7928 Hz]. MS (EI) *m/z*: 661 (M^+ − Me, 1), 511 (6), 338 (100), 308 (44), 252 (33), 222 (36). Anal. Calc. for $C_{28}H_{40}N_2O_2Sn_2$: C, 49.90; H, 5.98; N, 4.16. Found: C, 49.90; H, 5.83; N, 4.02%.

2.2.3. Distannane **4**

Yellowish oil, 82%. $[\alpha]_D$ = +49.3 ($CHCl_3$, c = 1). IR cm^{-1} (film): 3054, 2956, 2921, 2871, 2853, 1642, 1463, 1358, 1251, 1082, 1043, 963. ^1H NMR (C_6D_6) ppm: 8.04–8.02 (1H, dd, J = 7.7 and 1.2 Hz), 7.84–7.82 (1H, dd, J = 7.2 and 1.2 Hz), 7.19–7.15 (1H, dt, J = 7.3 and 1.3 Hz), 7.11–7.07 (1H, dt, J = 7.6 and 1.3 Hz), 3.63–3.59 (1H, m), 3.38–3.29 (2H, m), 1.92–1.35 (13H, m), 1.07–1.04 (3H, t, J = 7.3 Hz), 0.86–0.84 (3H, t, J = 7.3 Hz), 0.78 (3H, d, J = 6.9 Hz), 0.71 (3H, d, J = 6.9 Hz). ^{13}C NMR (C_6D_6) ppm: 164.8 [$J(^{13}C–^{117/119}Sn)$ = 4.8 Hz], 147.6 [$J(^{13}C–^{117/119}Sn)$ = 318/333 and 26.5 Hz], 136.9 [$J(^{13}C–^{117/119}Sn)$ = 13.4 and 27.5 Hz], 134.1 [$J(^{13}C–^{117/119}Sn)$ = 18.0 Hz], 129.7 [$J(^{13}C–^{117/119}Sn)$ = 37.7 Hz], 128.5 [$J(^{13}C–^{117/119}Sn)$ = 26.1 Hz], 128.1, 72.1, 69.2, 32.3, 30.9, 30.3 [$J(^{13}C–^{117/119}Sn)$ = 15.1 and 24.5 Hz], 28.4 [$J(^{13}C–^{117/119}Sn)$ = 55.6/58.1 and 3.4 Hz], 27.6 [$J(^{13}C–^{117/119}Sn)$ = 62.2/65.0 and 9.4 Hz], 19.0, 17.3, 15.0 [$J(^{13}C–^{117/119}Sn)$ = 300/314 and 49.3/51.1 Hz], 13.8, 13.6, 13.4 [$J(^{13}C–^{117/119}Sn)$ = 185/194 and 85.6/89.6 Hz]. ^{15}N NMR (C_6D_6) ppm: −152.2. ^{117}Sn NMR (C_6D_6) ppm: −101.9 [$^1J(^{117}Sn–^{119}Sn)$ = 6016 Hz]. MS (EI) *m/z*: 787 (M^+ − Bu, 1), 553 (48), 422 (100), 308 (55), 222 (49). Anal. Calc. for $C_{40}H_{64}N_2O_2Sn_2$: C, 57.04; H, 7.66; N, 3.33. Found: C, 57.08; H, 7.53; N, 3.17%.

2.2.4. Distannane **10**

Yellowish oil, 20%. $[\alpha]_D$ = +19.2 ($CHCl_3$ *c*s 1). IR cm^{-1} (film): 3056, 2956, 2922, 2871, 2853, 1642, 1463, 1375, 1080, 1043. ^1H NMR (C_6D_6) ppm: 8.27–8.24 (1H, dd, J = 7.7 and 1.3 Hz), 7.95–7.93 (1H, dd, J = 7.3 and 1.3 Hz), 7.31–7.27 (1H, dt, J = 7.3 and 1.3 Hz), 7.22–7.18 (1H, dt, J = 7.6 and 1.3 Hz), 4.13–4.03 (2H, m), 3.94–3.90 (1H, m), 2.01–1.20 (31 H, m), 1.12–1.08 (3H, t, J = 7.3 Hz), 1.03–1.00 (3H, t, J = 7.3 Hz), 1.02–0.99 (9H, t, J = 7.3 Hz), 0.96 (3H, d, J = 6.8 Hz), 0.85 (3H, d, J = 6.8 Hz). ^{13}C NMR (C_6D_6) ppm: 165.4, 145.8, 137.5, 134.0, 130.3, 128.9, 128.1, 72.6, 68.9, 32.1, 30.6, 30.5, 30.4, 28.3, 27.8, 27.7, 19.3, 16.9, 14.5, 13.8 (2×), 13.7 (2×), 10.6. ^{117}Sn NMR (C_6D_6) ppm: −79.3 [$^1J(^{117}Sn–^{119}Sn)$ = 3629 Hz], −104.8 [$^1J(^{117}Sn–^{119}Sn)$ = 3629 Hz]. MS (EI) *m/z*: 710 (M^+, 2), 654 (40), 422 (100), 308 (72), 222 (30). Anal. Calc. for $C_{32}H_{59}N_1O_1Sn_2$: C, 54.04; H, 8.36; N, 1.97. Found: C, 53.99; H, 8.29; N, 1.95%.

2.2.5. Distannane **8**

Colorless oil, 57%. $[\alpha]_D$ = +56.4 ($CHCl_3$, c = 1). IR cm^{-1} (film): 3060, 1643, 1577, 1561, 1479, 1427, 1362, 1255, 1083, 1042, 726, 699. ^1H NMR ($CDCl_3$) ppm: 7.87–7.82 (1H, dd, J = 7.0 and 1.0 Hz), 7.57–7.12 (13H, m), 3.72–3.69 (1H, dd, J = 8.2 and 5.8 Hz), 3.27–3.22 (1H, m), 2.95–2.91 (1H, dd, J = 9.8 and 8.3 Hz), 1.39–1.32 (1H, m), 0.52 (3H, d, J = 6.8 Hz), 0.36 (3H, d, J = 6.8 Hz). ^{13}C NMR ($CDCl_3$) ppm: 164.5 [$J(^{13}C–^{117/119}Sn)$ = 4.4/7.6/Hz], 146.4 [$J(^{13}C–^{117/119}Sn)$ = 260/272 and 120/125 Hz], 145.0 [$J(^{13}C–^{117/119}Sn)$ = 421/440 and 47.7 Hz], 143.6 [$J(^{13}C–^{117/119}Sn)$ = 487/509 and 56.9 Hz], 137.9 [$J(^{13}C–^{117/119}Sn)$ = 9.6 and 36.0 Hz], 137.5 [$J(^{13}C–^{117/119}Sn)$ = 9.4 and 41.6 Hz], 133.7 [$J(^{13}C–^{117/119}Sn)$ = 22.9 Hz], 130.3 [$J(^{13}C–^{117/119}Sn)$ = 5.9 and

46.4 Hz], 128.3 [$J(^{13}C–^{117/119}Sn)$ = 9.7 Hz], 127.9 [$J(^{13}C–^{117/119}Sn)$ = 31.2 Hz], 127.7 [$J(^{13}C–^{117/119}Sn)$ = 12.0 Hz], 127.6 [$J(^{13}C–^{117/119}Sn)$ = 52.4 Hz], 127.5 [$J(^{13}C–^{117/119}Sn)$ = 8.7 Hz], 70.7 [$J(^{13}C–^{117/119}Sn)$ = 5.6 Hz], 68.6, 31.1, 18.6, 15.7. ^{15}N NMR ($CDCl_3$) ppm: −152.8. ^{117}Sn NMR ($CDCl_3$) ppm: −152.2 [$^1J(^{117}Sn–^{119}Sn)$ = 8531 Hz]. MS (EI) *m/z*: 847 (M^+ − Ph, 1), 573 (2), 462 (100), 376 (17), 308 (14), 222 (9). MS (ESI) 847 (M^+ − Ph), HR-MS (ESI): calcd for $C_{42}H_{43}N_2O_2{}^{120}Sn_2$: 847.1363. Found: 847.1353. Anal. Calc. for $C_{48}H_{48}N_2O_2Sn_2$: C, 62.51; H, 5.25; N, 3.04. Found: C, 62.32; H, 5.21; N, 3.02%.

2.3. Synthesis of hydride 7

To activated by 'dry stirring' magnesium (106 mg, 4.4 mmol) in THF (50 mL) was added (*S*)-2-(4-bromo-phenyl)-4-isopropyl-4,5-dihydro-oxazole (1.072 g, 4.0 mmol) and a small amount of 1,2-dibromoethane. The mixture was stirred at reflux until the magnesium was consumed. Subsequently, a solution of Ph_3SnCl (1.542 g, 4.0 mmol) in THF (10 mL) was added. After 30 min the mixture was diluted with Et_2O (50 mL) and filtered over a short silica gel pad. The solvents were removed in vacuo and the residue was purified by flash chromatography (hexanes) to give tetraorganotin **8** (1.593 g, 74%) as white crystals.

2.3.1. (*S*)-4-Isopropyl-2-(2-triphenylstannanyl-phenyl)-4,5-dihydro-oxazole (**5**)

White crystals, mp 127–129 °C, 74%. $[\alpha]_D$ = +4.3 ($CHCl_3$, *c* = 1). IR cm^{-1} (film): 3062, 1648, 1480, 1428, 1361, 1086, 728, 699. ^1H NMR ($CDCl_3$) ppm: 8.20–8.14 (1H, dd, *J* = 7.7 and 1.0 Hz), 7.78–7.44 (13H, m), 4.37–4.32 (1H, dd, *J* = 9.7 and 8.5 Hz), 4.09–4.04 (1H, t, *J* = 8.8 Hz), 3.68–3.61 (1H, dt, *J* = 9.5 Hz), 1.54–1.45 (1H, m), 0.65 (3H, d, *J* = 6.8 Hz), 0.62 (3H, d, *J* = 6.8 Hz). ^{13}C NMR ($CDCl_3$) ppm: 165.3 [$J(^{13}C–^{117/119}Sn)$ = 14.0 Hz], 142.8 [$J(^{13}C–^{117/119}Sn)$ = 545/570 Hz], 141.8 [$J(^{13}C–^{117/119}Sn)$ = 559/585 Hz], 138.7 [$J(^{13}C–^{117/119}Sn)$ = 42.6 Hz], 137.3 [$J(^{13}C–^{117/119}Sn)$ = 37.0 Hz], 133.7 [$J(^{13}C–^{117/119}Sn)$ = 21.7 Hz], 131.3 [$J(^{13}C–^{117/119}Sn)$ = 55.0 Hz], 129.2 [$J(^{13}C–^{117/119}Sn)$ = 10.3 Hz], 128.3 [$J(^{13}C–^{117/119}Sn)$ = 11.2 Hz], 128.2 [$J(^{13}C–^{117/119}Sn)$ = 52.5 Hz], 128.0 [$J(^{13}C–^{117/119}Sn)$ = 37.2 Hz], 71.9, 70.8, 31.8, 19.2, 17.7. ^{15}N NMR ($CDCl_3$) ppm: −156.6 [$J(^{15}N–^{117/119}Sn)$ = 41 Hz]. ^{117}Sn NMR ($CDCl_3$) ppm: −155.5. MS (EI) *m/z*: 462 (M^+ − Ph, 100), 376 (25), 222 (11). Anal. Calc. for $C_{30}H_{29}N_1O_1Sn_1$: C, 66.94; H, 5.43; N, 2.60. Found: C, 66.80; H, 5.38; N, 2.59%.

A solution of tetraorganotin **5** (1.345 g, 2.5 mmol) and Br_2 (mg, 2.5 mmol) in $CHCl_3$ (20 mL) was stirred at −50 °C. The mixture was then evaporated and the crude product was recrystalized from hexane/CH_2Cl_2 to give the bromide **6** (1.285 g, 95%) as white crystals.

2.3.2. (*S*)-2-[(2-Bromo-diphenylstannanyl)-phenyl]-4-isopropyl-4,5-dihydro-oxazole (**6**)

White crystals, mp 195–200 °C, 95%. $[\alpha]_D$ = +54.4 ($CHCl_3$, *c* = 1). IR cm^{-1} (KBr): 3066, 3047, 1635, 1578, 1559, 1482, 1431, 1386, 1261, 1103, 947, 733, 698. ^1H NMR ($CDCl_3$) ppm: 8.70–8.55 (1H, dd, *J* = 7.4 and 1.0 Hz), 7.94–7.88 (1H, dd, *J* = 7.6 and 1.1 Hz), 7.83–7.30 (12H, m), 4.58–4.53 (1H, dd, *J* = 9.8 and 9.0 Hz), 4.39–4.35 (1H, t, *J* = 8.6 Hz), 3.89–3.84 (1H, ddd, *J* = 9.9, 8.3 and 4.8 Hz), 1.52–1.45 (1H, m), 0.57 (3H, d, *J* = 6.8 Hz), 0.38 (3H, d, *J* = 6.8 Hz). ^{13}C NMR ($CDCl_3$) ppm: 170.5 [$J(^{13}C–^{117/119}Sn)$ = 21.6 Hz], 143.5 [$J(^{13}C–^{117/119}Sn)$ = 776/812 Hz], 142.8 [$J(^{13}C–^{117/119}Sn)$ = 727/761 Hz], 141.9 [$J(^{13}C–^{117/119}Sn)$ = 803/840 Hz], 138.6 [$J(^{13}C–^{117/119}Sn)$ = 43.0 Hz], 135.7 [$J(^{13}C–^{117/119}Sn)$ = 48.7 Hz], 135.0 [$J(^{13}C–^{117/119}Sn)$ = 49.1 Hz], 133.2 [$J(^{13}C–^{117/119}Sn)$ = 69.0 Hz], 130.0 [$J(^{13}C–^{117/119}Sn)$ = 32.2 Hz], 129.9 [$J(^{13}C–^{117/119}Sn)$ = 12.5 Hz], 129.1 [$J(^{13}C–^{117/119}Sn)$ = 7.5 Hz], 129.0 [$J(^{13}C–^{117/119}Sn)$ = 7.9 Hz], 128.5 [$J(^{13}C–^{117/119}Sn)$ = 72.4/75.5 Hz], 128.3 [$J(^{13}C–^{117/119}Sn)$ = 71.8/74.8 Hz], 126.6 [$J(^{13}C–^{117/119}Sn)$ = 47.7 Hz], 72.1, 69.1 [$J(^{13}C–^{117/119}Sn)$ = 11.2 Hz], 30.2, 19.3, 15.4. ^{15}N NMR ($CDCl_3$) ppm: −180.7 [$J(^{15}N–^{117/119}Sn)$ = 119 Hz]. ^{117}Sn NMR ($CDCl_3$) ppm: −222.1. MS (EI) *m/z*: 462 (M^+ − Br, 100), 376 (17), 308 (7), 222 (10). Anal. Calc. for $C_{24}H_{24}Br_1N_1O_1Sn_1$: C, 53.28; H, 4.47; Br, 14.77; N, 2.59. Found: C, 53.15; H, 4.39; Br, 14.68; N, 2.52%.

A solution of $NaBH_4$ (567 mg, 15.0 mmol) in ethanol (5 mL) was added to a solution of the tin bromide **6** (812 mg, 1.5 mmol) in ethanol (10 mL) and stirred at room temperature for 15 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 hydride **7** (679 mg, 98%) as colorless oil.

2.3.3. [2-(4-(*S*)-Isopropyl-2-oxazoline)-5-phenyl] diphenyltin hydride (**7**)

Oil, 98%. IR cm^{-1} (film): 3061, 1849, 1647, 1479, 1428, 1362, 1259, 1087, 728, 699. ^1H NMR (C_6D_6) ppm: 8.21–8.15 (1H, d, *J* = 8.1 Hz), 7.85–7.16 (13H, m), 7.62 [1H, *s*, $^1J(^1H–^{117/119}Sn)$ = 2070/2167 Hz], 3.98–3.94 (1H, t, *J* = 9.0 Hz), 3.80–3.75 (1H, t, *J* = 8.6 Hz), 3.69–3.63 (1H, dt, *J* = 9.2 Hz), 1.54–1.47 (1H, m), 0.83 (3H, d, *J* = 6.8 Hz), 0.68 (3H, d, *J* = 6.8 Hz). ^{13}C NMR (C_6D_6) ppm: 166.1 [$J(^{13}C–^{117/119}Sn)$ = 12.7 Hz], 143.3 [$J(^{13}C–^{117/119}Sn)$ = 470/492 Hz], 142.5 [$J(^{13}C–^{117/119}Sn)$ = 567/593 Hz], 142.1 [$J(^{13}C–^{117/119}Sn)$ = 521/591 Hz], 138.7 [$J(^{13}C–^{117/119}Sn)$ = 43.8 Hz], 137.8 [$J(^{13}C–^{117/119}Sn)$ = 38.6 Hz], 137.4 [$J(^{13}C–^{117/119}Sn)$ = 40.6], 133.5 [$J(^{13}C–^{117/119}Sn)$ = 21.3 Hz], 131.5 [$J(^{13}C–^{117/119}Sn)$ = 56.8 Hz], 129.3 [$J(^{13}C–^{117/119}Sn)$ = 10.5 Hz], 128.4, 128.3 (2×), 128.2, 127.8, 71.9, 71.4, 32.4, 19.0, 18.4. ^{15}N NMR (C_6D_6) ppm: −158.5

[$J(^{15}N–^{117/119}Sn) = 49$ Hz]. ^{117}Sn NMR (C_6D_6) ppm: −187.5. MS (EI) *m/z*: 462 ($M^+ - H$, 100), 376 (24), 351 (19), 308 (27), 222 (28). HR-MS (EI): calcd for $C_{24}H_{24}N_1O_1Sn_1$: 462.0880. Found: 462.0841.

2.4. Reaction of distannanes 3 and 4 with iodine

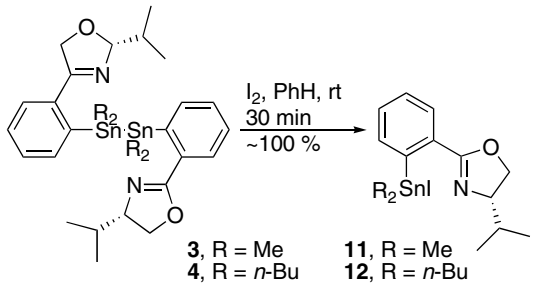
A solution of distannane **3** (192 mg, 0.285 mmol) or **4** (240 mg, 0.285 mmol) and I_2 (74 mg, 0.29 mmol) in benzene was stirred in the dark at rt. The mixture was then evaporated and the crude product was purified by filtering-column chromatography on silica gel to give compound **11** (264 mg, ~100%) or **12** (312 mg, ~100%) (NMR data, see [10]).

3. Results and discussion

3.1. Synthesis of the distannanes

Ditin reagents can be prepared from the corresponding hydrides using different reagents, such as: acetic acid [15], pyridine [16,17], dimethylformamide [18], diborane [19], sodium borohydride in ethanol [20], transition-metal salts [21–23]. The transition-metal salts appeared to be particularly useful for the preparation of distannanes from the corresponding hydrides on a large scale. Preliminary experiments revealed that treatment of the hydrides **1** and **2** in CCl_4 and $CHCl_3$ with $Pd(PPh_3)_2Cl_2$ or $Pd(PPh_3)_4$ lead exclusively to the corresponding chlorides (Scheme 1). Replacement of the solvent for benzene in the presence of quantitative amount of $Pd(PPh_3)_2Cl_2$ gave again the corresponding chlorides. It could mean that the internally coordinated hydrides **1** and **2** exhibit increased nucleophilic hydride reactivity [2]. In view of these results the reported distannanes (**3** and **4**) were prepared via addition of catalytic amount of $Pd(PPh_3)_4$ to hydrides **1** and **2** in benzene at ambient temperatures (Scheme 1). In the case of hydride **7**, which was prepared in two steps from tetraorganostannane **5** the reaction had to be conducted at higher temperature (50 °C) to obtain good yields. However, a longer reaction time and heating of the reaction mixture resulted in the formation, besides distannane **8** two other products (**5** and **9**). The mechanism for the formation of compounds **5** and **9** does not appear to have been studied and we decided not to pursue this avenue. Additionally, we prepared distannane **10**. All four distannanes (**3**, **4**, **8** and **10**) were stable to decomposition at room temperature. They could be purified on silica gel to give satisfactory elemental analyses.

Treatment of both the distannanes with iodine resulted in the quantitative formation of the corresponding iodides **11** and **12** (Scheme 2). The iodides are expected to be formed from the distannanes **3** and **4** in the iodine atom transfer reactions. After reduction with $NaBH_4$ and subsequent reaction with $Pd(PPh_3)_4$ the starting distannanes were recovered in 80% yields.



Scheme 2. Breaking of the Sn–Sn bond in distannanes **3** and **4**.

3.2. Crystal structure of distannane 3

Compound **3** was obtained as white crystalline solid and an X-ray structure determination of it was carried out. The molecular structure of distannane **3** is shown in Fig. 1. and selected interatomic parameters are collected in Table 2. The molecule adopts a *syn*-orientation with eclipsed groups. The Sn–Sn bond is short in comparison with similar *syn*-oriented molecules [tetra-*t*-butyl-1,2-bis(2,4,6-triisopropylphenyl)distannane, 3.034 Å] [24]. The Sn–N distance is very long, almost the same as the longest one found in Ph_2SnCl_2–pyrazine (2.965 Å) [25]. The orientation of N11(N28) towards Sn1(Sn2) suggests apical positions of the nitrogen atoms. C2 and C18 seem to be other apical atoms.

3.3. Structure in solution of the organotin compounds

We have recently described that the tin atom in tetraorganotin compounds containing the chiral oxazoline was in fact pentacoordinated [10] due to the Sn–N coordination. Newly synthesized compounds **5**–**7**, which

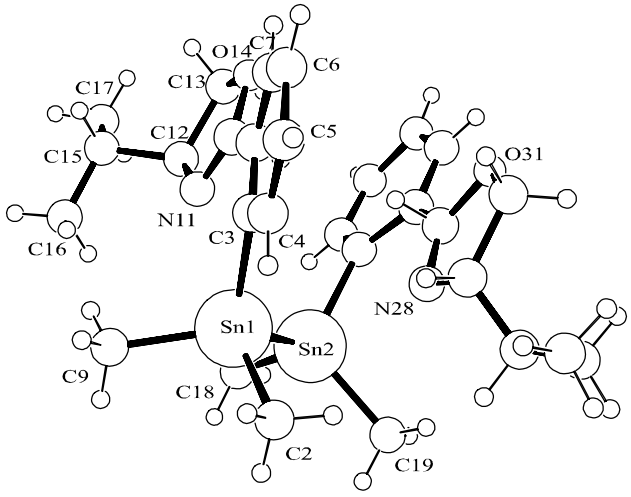


Fig. 1. Molecular structure and atomic numbering scheme for distannane **3**.

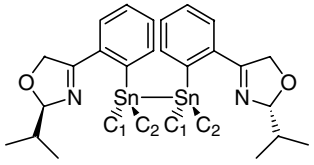
Table 2
Selected bond lengths and angles for **3**

Bond lengths (Å)		Bond angles (°)	
Sn1–Sn2	2.741(3)	C2–Sn1–C3	103(1)
N11–Sn1	3.04(2)	C2–Sn1–C9	104(1)
N28–Sn2	2.94(2)	C2–Sn1–Sn2	109(1)
C2–Sn1	2.16(3)	C3–Sn1–C9	107(1)
C3–Sn1	2.21(3)	C3–Sn1–Sn2	116(1)
C9–Sn1	2.13(3)	C9–Sn1–Sn2	114(1)
C18–Sn2	2.11(3)	C18–Sn2–Sn1	110(1)
C19–Sn2	2.13(4)	C19–Sn2–Sn1	113(1)
C20–Sn2	2.18(3)	C20–Sn2–Sn1	116(1)
		N11–Sn1–C2	168(1)
		N11–Sn1–C9	83(1)
		N11–Sn1–Sn2	75(1)
		N28–Sn2–C18	170(1)
		N28–Sn2–C19	79(1)
		N28–Sn2–Sn1	55(1)

are substrates in two-step reaction leading to distannane **8** also share this feature. The NMR data for these compounds have not been reported yet and that is why we decided to present them in the experimental section of this paper. The presence of the $^{1}J(^{15}N–^{117/119}Sn)$ couplings observed in long accumulated ^{15}N NMR spectra taken for **5**–**7** (41, 119 and 49 Hz, respectively) supports the existence of the Sn–N interaction in these compounds. The hydride **7** appears to be another example of hydrides in which nitrogen is intermolecularly coordinated to the tin atom. In this case the Sn–N interaction is even stronger than in the earlier reported hydrides [10]. It was of interest to test whether the tin atom in the corresponding distannanes shared the same feature. For distannane **3** in a long accumulated ^{15}N NMR spectrum, we were able to detect the $^{117/119}Sn$ satellites. Based on the $J(^{15}N–^{117/119}Sn)$ coupling of 20 Hz we concluded that the tin atom in **3** is also coordinated to the nitrogen from the ligand. However, the Sn–N interaction seems to be weaker than in the previously reported tetratorganotin compounds and triorganotin hydrides [10]. The ^{13}C NMR parameters, especially the $J(^{13}C–^{117/119}Sn)$ couplings are useful tool in the study of organotin compounds. In the ^{13}C NMR spectra of **3**, **4** and **8** we found rather surprising changes in the $J(^{13}C–^{117/119}Sn)$ couplings (Table 3) at carbon atoms directly bounded to the tin. The differences observed between the two $^{1}J(^{13}C_{1\ \text{or}\ 2}–^{117/119}Sn)$ as well as $^{2}J(^{13}C_{1\ \text{or}\ 2}–^{117/119}Sn)$ couplings for the distannanes were not temperature-dependent and could be explained on the basis of the intermolecular Sn–N interaction that forces a different arrangement of substituents (Me, *n*-Bu, Ph) at the tin atom. To the best of our knowledge such observation has not been reported yet and further studies are required before a conclusion can be drawn. Additionally, after comparison of the $^{1}J(^{13}C–^{117/119}Sn)$ couplings at *ipso*-carbons of the phenyl rings between **3**, **4**, **8** and the corresponding trimethyl/tri-*n*-butyl/triphenylstannanes [10] we noticed remarkable changes in those values. Decrease of the $^{1}J(^{13}C–^{117/119}Sn)$ couplings in the case of **3**, **4** and **8** by ca. 100 Hz suggests that the Sn–N interaction is weaker in distannanes studied, what additionally supports the $^{1}J(^{15}N–^{117/119}Sn)$ value of **3**.

Taking into account that configuration of the tin atom in distannanes **3**, **4** and **8** could be described as slightly distorted trigonal-bipyramidal one, the N–Sn coordination should be also reflected in the $J(^{117}Sn–^{119}Sn)$ values. Based on the relation between giromagnetic ratios for the ^{117}Sn and ^{119}Sn nuclei we recalculated the measured $^{1}J(^{117}Sn–^{119}Sn)$ to $^{1}J(^{119}Sn–^{119}Sn)$ couplings (Table 3). It is generally accepted that the values of J(Sn–Sn) couplings increase with an increase of the coordination number at the Sn atom. When compared with alkyl/aryl-substituted ditins the $^{1}J(^{119}Sn–^{119}Sn)$ couplings for distannanes **3**, **4**, **8** and **10** the changes are distinctly visible [26]. In our cases, replacement of one *n*-butyl group in $n\text{-}Bu_6Sn_2$ by 2-(4-isopropyl-2-oxazolinyl)-5-phenyl ligand leading to compound **10** results in an increase of $^{1}J(^{119}Sn–^{119}Sn)$ from 2748 to 3796 Hz. Additionally, replacement of two *n*-butyl groups in hexa-*n*-butylditin

Table 3
The ^{117}Sn NMR data of distannanes **3**, **4** and **8**[a]



Distannane	$^{1}J(^{119}Sn–^{119}Sn)$[a]	$^{1}J(^{117/119}Sn–C_1)$	$^{2}J(^{117/119}Sn–C_2)$	$^{1}J(^{7/119}Sn–C_2)$	$^{2}J(^{117/119}Sn–C_2)$
3[b]	8294	294/308	58.7/60.7	174/182	100/105
4[c]	6294	300/314	49.3/51.1	185/194	85.6/89.6
8[d]	8925	421/440	47.7[e]	260/272	120/125

[a] Coupling constant values in Hz calculated from measured values of $^{1}J(^{119}Sn–^{119}Sn)$.
[b] ^{117}Sn NMR = −120.5 ppm.
[c] ^{117}Sn NMR = −101.9 ppm.
[d] ^{117}Sn NMR = −152.2 ppm.
[e] The ^{117}Sn and ^{119}Sn satellites were not resolvable.

by the above-mentioned ligand leads to an increase of the $^1J(^{119}Sn–^{119}Sn)$ by ca. 3500 Hz. A more spectacular observation was reported when two *n*-butyl groups in *n*-Bu_6Sn_2 were replaced by two electronegative acetoxy groups [26]. Such a change of substituents leads to a remarkable increase of the $^1J(^{119}Sn–^{119}Sn)$ from 2748 to 11 272 Hz and it is related to the Sn–O interactions in *n*-$Bu_4Sn_2(OAc)_2$. A comparison of the $^1J(^{119}Sn–^{119}Sn)$ couplings for our distannanes and hexaalkyl/aryl ditins, which are as follows: Me_6Sn_2 4004 Hz/compound **3** 8294 Hz, Ph_6Sn_2 4470 Hz/compound **8** 8925 Hz leads to the conclusion that two-fold increase of the $J(^{119}Sn–^{119}Sn)$ couplings can be related to the changes of electron density and coordination number at the tin atoms in the distannanes.

In conclusion, the synthesized coordinated distannanes are stable and easy to handle. They could be useful in the iodine atom transfer or Pd-catalyzed reactions. Further investigations on the properties of the distannanes with the chiral oxazoline ligand and additional chirality on the tin are in progress.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structure **3** in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication No. CCDC 258408. Copies of the data can be obtained free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033 or e-mail: deposit@ccdc.cam.ac.uk).

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