Tin-containing Indane and Tetralin Derivatives

Elisabeth Zarl[a], Jörg H. Albering[b], Roland C. Fischer[a], Michaela Flock[a], Dominik Genser[a], Barbara Seibt[a], and Frank Uhlig[a]

[a] Institut für Anorganische Chemie, Technische Universität Graz, Stremayrgasse 16, A-8010 Graz, Austria
[b] Institut für Chemische Technologie von Materialien, Technische Universität Graz, Stremayrgasse 16, A-8010 Graz, Austria

Reprint requests to Prof. Dr. Frank Uhlig. Fax: +43 316 873 8701. E-mail: frank.uhlig@tugraz.at

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Dedicated to Professor Hubert Schmidbaur on the occasion of his 75th birthday

The preparation of tin-containing indane and tetralin derivatives *via* two different reaction pathways is reported. The first route is the reaction of dichlorostannanes or bis(fluoroalkylsulfonyl)stannanes with α,α'-di(chloromagnesium)xylene. The second reaction is the direct coupling of chlorostannanes and α,α'-dichloroxylene which always yields a mixture of tin-containing indanes and tetralins. The separation of these compounds can easily be achieved by fractional crystallization. By these simple and effective routes the first 2,3-distannatetralins were synthesized.

Key words: ^{119}Sn NMR Spectroscopy, Indane, Tetralin, Stannanes, Fluoroalkane Sulfonic Acids

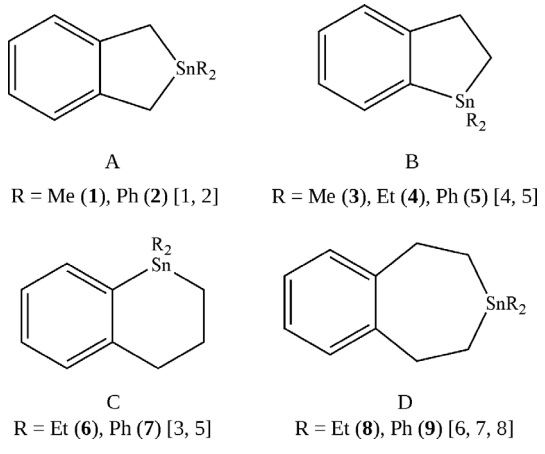
Introduction

Bicyclic structures with at least one tin atom in the backbone are not very common in the literature. The compounds known so far are described in Fig. 1. They comprise a limited number of indane derivatives (A and B), larger tetralin derivatives (C), and cycloheptanes (D). In these compounds the variety of the substituents at tin (methyl, ethyl, and phenyl groups) is rather limited as well.

In the literature different reaction pathways are described to obtain these compounds. Eisch [1] reported the formation of **1** through the reaction of α,α'-dilithio-*o*-xylene with dimethyldichlorostannane. The phenyl-substituted derivative **2** was prepared by reacting diphenyldichlorostannane with α,α'-di(chloromagnesium)-*o*-xylene [2]. Compound **7** was synthesized by the reaction of diphenyltindichloride with the di-Grignard reagent of 3-(*o*-bromophenyl)propylbromide [3] in very poor yield (9.4 %).

To the best of our knowledge indanes or tetralins containing a distanna unit in the backbone have not yet been published.

In this paper we present a novel route to indane and tetralin derivatives containing one tin atom in the saturated ring. Furthermore, we describe the reaction pathway for the formation of tetralins with a distanna moiety in the backbone (see Fig. 2).



A
R = Me (**1**), Ph (**2**) [1, 2]

B
R = Me (**3**), Et (**4**), Ph (**5**) [4, 5]

C
R = Et (**6**), Ph (**7**) [3, 5]

D
R = Et (**8**), Ph (**9**) [6, 7, 8]

Fig 1. Known tin-containing bicyclic compounds: indane derivatives (A and B), larger tetralin derivatives (C), and cycloheptanes (D).

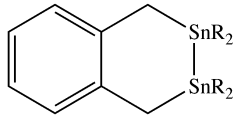


Fig. 2. 2,3-Distannatetralins.

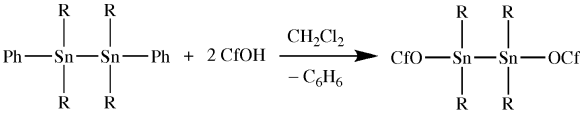
Results and Discussion

Synthesis

Recently, we were able to show that fluoroalkylsulfonic acids are useful reagents for the functionalization of stannanes and especially of distannanes [9] (Scheme 1). The sulfonyl group facilitates further derivatizations such as the reaction with Grignard reagents. Through this reaction pathway an almost unlimited variety of new distannanes is easily accessible.

Following this synthetic approach [9] 1,2-bis(triphenylstannylmethyl)benzene (**10**) was reacted with nonafluorobutylsulfonic acid in dichloromethane. The conversion and selectivity of this reaction is 100 %. Consequently, the solution can be used without further purification in subsequent reactions. Scheme 2 depicts the reaction pathway.

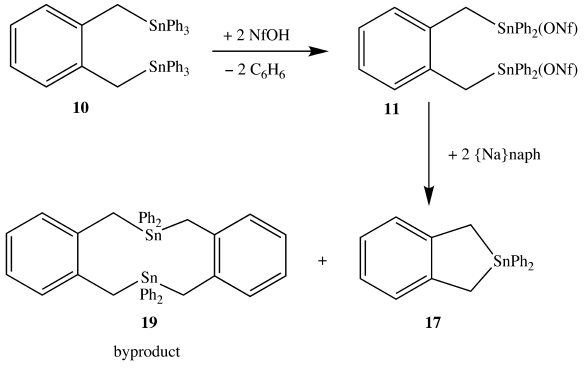
For the ring closure reaction sodium naphthalene, Na{naph}, was used as it is a common reagent for the formation of tin–tin bonds [10]. Unfortunately, the reaction of the sulfonyl-substituted derivative with Na{naph} did not yield the expected result (Scheme 2). Besides the indane derivative as the main product, the reaction solution contained a plethora of tin-containing byproducts. In the case of the diphenyltin derivative one of these byproducts was isolated by fractional



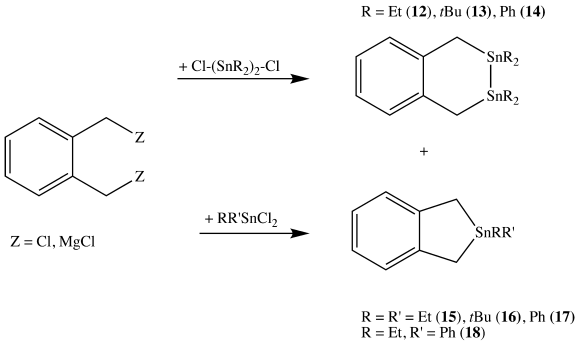
CfO = TfO (CF_3SO_3), NfO ($C_4F_9SO_3$)

R = Alkyl, Aryl

Scheme 1. Functionalization of distannanes with fluoralkylsulfonic acids.



Scheme 2. Reaction of 1,2-bis(triphenylstannylmethyl)benzene with nonafluorobutylsulfonic acid (NfOH).



Scheme 3. Grignard (*Z* = MgCl) and Wurtz (*Z* = Cl) routes towards tin-substituted indane and tetralin derivatives.

crystallization from hexane. The colorless solid was identified as the dibenzoditin derivative **19** *via* crystal structure determination (see Fig. 4a, b). Attempts to increase the yield of **19** by altering concentration and temperature failed so far.

As an alternative route 1,2-dihalo-substituted distannanes, 1,2-disulfonyl-substituted distannanes, or simply dihalostannanes were reacted with a di-Grignard reagent of α,α'-dichloro-*o*-xylene (Scheme 3).

This reaction works well for both mono- and distannanes resulting in stanna-substituted indane and distanna-substituted tetralin derivatives. However, the di-Grignard reagent is highly sensitive towards the reaction conditions (concentration and temperature). As this could be a source for problems, we tried to find a more reliable alternative route.

Direct coupling in a Wurtz reaction, as shown in Scheme 3, proved to be a simple alternative. However, regardless of the kind of stannane educts, a mixture of the corresponding tetralin and indane derivative was formed. The outcome of this reaction is independent of the concentration, the temperature, and the substituents at the tin atoms. Only the choice of the solvent has some marked impact: no reaction was observed in diethyl ether, whereas THF and DME turned out to be suitable solvents, and the best results were obtained in THF (see Table 1). The reaction products can easily be separated by fractional crystallization from hexane solution.

Discussion of the NMR spectra

The ^{119}Sn NMR data of the indane and tetralin derivatives are collected in Tables 2 and 3. The influence of the tin substituents on the ^{119}Sn NMR chemical shift becomes obvious by comparing compounds **17**, **18**, and **15**. The resonance of compound **17**

Table 1. Variation of the reaction conditions for the Wurtz reaction.

Variation	Stannane (mg/mmol)	Magnesium (eq./mg/mmol)	Xylene[a] (mol L^{-1})	Solvent	T (°C)	Indane : tetralin (%)
Conc.	tBu$_2$SnCl$_2$ 1000 / 3.3	2 / 160 / 6.6	0.039	THF	20	90 : 10
	tBu$_2$SnCl$_2$ 1000 / 3.3	2 / 160 / 6.6	0.155	THF	20	94 : 6
	tBu$_2$SnCl$_2$ 1000 / 3.3	2 / 160 / 6.6	0.772	THF	20	91 : 9
Solvent	tBu$_2$SnCl$_2$ 1000 / 3.3	2 / 160 / 6.6	0.150	DME	20	94 : 6
	tBu$_2$SnCl$_2$ 1000 / 3.3	2 / 160 / 6.6	0.150	Et$_2$O	20	–
Temp.	tBu$_2$SnCl$_2$ 1000 / 3.3	2 / 160 / 6.6	0.150	THF	0	93 : 7
	tBu$_2$SnCl$_2$ 1000 / 3.3	2 / 160 / 6.6	0.150	THF	65	79 : 16
Stannane	Ph$_2$SnCl$_2$ 1135 / 3.3	2 / 160 / 6.6	0.150	THF	20	80 : 20
	Et$_2$SnCl$_2$ 820 / 3.3	2 / 160 / 6.6	0.150	THF	20	90 : 10
	PhEtSnCl$_2$ 980 / 3.3	2 / 160 / 6.6	0.150	THF	20	95 : 5
	(CltBu$_2$Sn)$_2$ 1770 / 3.3	2 / 160 / 6.6	0.150	THF	20	20 : 80
Stoich.	tBu$_2$SnCl$_2$ 1000 / 3.3	3 / 240 / 9.9	0.150	THF	20	90 : 10
	tBu$_2$SnCl$_2$ 1000 / 3.3	12 / 1925 / 79	0.150	THF	20	90 : 10

[a] α,α'-Dichloroxylene.

Table 2. NMR chemical shifts of the indane derivatives.

Compound	R	R′	δ^{119}Sn (ppm)
16	tBu	tBu	+89.4
15	Et	Et	+82.0
18	Et	Ph	+39.8
17	Ph	Ph	+2.0

Table 3. NMR chemical shifts of the tetralin derivatives.

Compound	R = R′	δ^{119}Sn (ppm)	^1J (^{117}Sn-^{119}Sn) (Hz)
13	tBu	−55.9	800
12	Et	−9.5	826
14	Ph	−102.7	1413

with two phenyl substituents at the tin atom appears at +2.2 ppm. Upon substitution of one phenyl group by an ethyl group, as in compound **18**, the NMR signal is shifted downfield to +39.8 ppm. In compound **15** both tin substituents are ethyl groups, and the δ^{119}Sn is shifted by another 40 ppm to +82.0.

Going from the indane to the tetralin derivatives the ^{119}Sn NMR signal is moved at least 90 ppm upfield (compound **15/12** and **17/14**). The ^1J (^{117}Sn-^{119}Sn) coupling constants of the ditin unit of the tetralin derivatives are within the expected range (800 Hz for alkyl groups, 1400 Hz for phenyl groups).

*Molecular structure of 2,2,3,3-tetra-tert-butyl-2,3-distannatetralin (**13**)*

All solid distannanes are obtained as crystalline materials. The bicyclic distannane **13** crystallizes in the triclinic space group $P\bar{1}$ with $Z = 2$. Figs. 3a, b depict the molecular structure of **13** in the crystal.

Being part of a six-membered ring the Sn–Sn bond length at 2.8070(3) Å is slightly shorter than the Sn–Sn bond in, *e. g.*, hexa-*tert*-butyldistannane (2.894 Å) [11]. The sum of the Sn–Sn–C angles at 328.1° is close to 329.1°, suggesting a regular tetrahedral environment of the tin atoms. However, upon closer inspection severe distortions become apparent. Due to the rigid cyclic environment the Sn(2)–Sn(1)–C(1) bond angle is dramatically reduced to 93.2(8)°, and the angles enclosed by the sterically demanding *tert*-butyl substituents and the tin-tin axis are widened and close to 120°.

Due to the steric effects caused by the *tert*-butyl groups the saturated tin-containing cycle is forced into a boat conformation. Fig. 3 shows the structure of compound **13** together with selected bond lengths, angles, and dihedral angles.

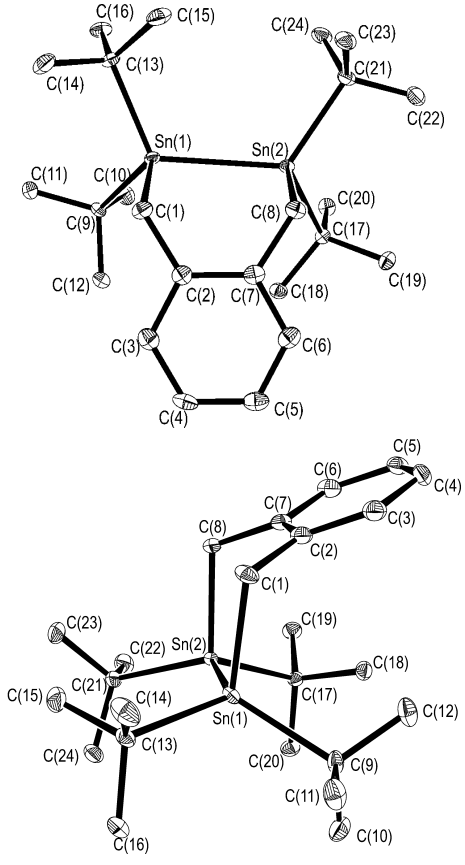


Fig. 3. Molecular structure of **13** in the crystal in two different orientations (displacement ellipsoids at the 30 % probability level; H atoms omitted for clarity). Selected distances (Å) and angles (deg): Sn(1)–Sn(2) 2.8070(3); Sn(2)–Sn(1)–C(1) 93.2(8), Sn(2)–Sn(1)–C(9) 120.0(1), Sn(2)–Sn(1)–C(13) 116.1(2), C(13)–Sn(1)–C(9) 110.8(1); C(1)–Sn(1)–Sn(2)–C(8) −5.5(1).

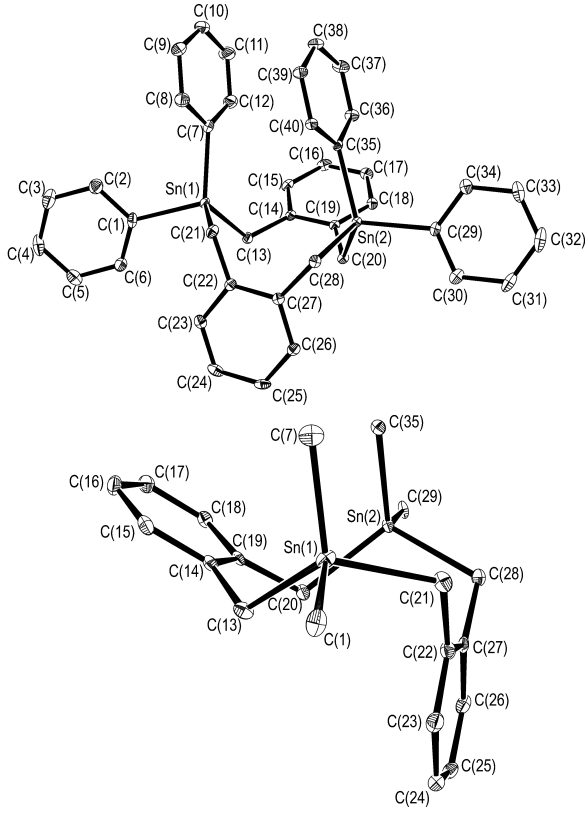


Fig. 4. Molecular structure of one of the crystallographically independent heterocycles of **19** in the crystal in two different orientations (displacement ellipsoids 30 %; H atoms omitted for clarity). Selected distances (Å) and angles (deg): Sn(1)–C(1) 2.160(4), Sn(1)–C(13) 2.148(4); C(1)–Sn(1)–C(7) 106.3(1), C(1)–Sn(1)–C(13) 106.2(1), C(1)–Sn(1)–C(21) 102.8(1), C(13)–Sn(1)–C(21) 113.8(1), C(7)–Sn(1)–C(13) 116.7(1), C(7)–Sn(1)–C(21) 133.5(1).

*Molecular structure of the dibenzoditin derivative **19***

Derivative **19** crystallizes in the triclinic space group $P\bar{1}$ with four crystallographically independent tin macrocycles (Z = 8) and three molecules of chloroform in the asymmetric unit (Z' = 2 for $(C_{40}H_{36}Sn_2)_4(CHCl_3)_3$). Two of the chloroform molecules were found disordered over two positions. The central ten-membered ring adopts a puckered conformation in all molecules present in the asymmetric unit. Sn–C and C–C distances fall in the range of expectations. In contrast to **13**, where a C(1)–Sn(1)–Sn(2) angle of only 93.27(8)° was found, the geometry around the tin atoms in **19** is much closer to an ideal tetrahedral arrangement, as the geometry is less constrained.

The major structural differences concerning the conformations of the crystallographically independent molecules arise from different packing modes of the phenyl groups attached to the tin centers leading to eight dibenzodistanna molecules and six molecules of chloroform in the unit cell. Apart from the varying twisting of the phenyl groups along the Sn–$C_{1Phenyl}$ bonds the structural similarities in all the conformers present in the crystal structure of **19** prevail, so that only one of the independent molecules is depicted in Fig. 4.

Conclusion

Monotin-containing indanes and distannatetralin derivatives are accessible from trifluoromethyl- or nonafluorobutyl sulfonic acid-derivatized stannanes and

distannanes. For the ring closure reaction two pathways have been shown to be successful. However, the reaction with a di-Grignard reagent turned out to be highly sensitive towards the reaction conditions and thus was less reliable. The alternative route of a Wurtz coupling reaction results in a product mixture of indanes and tetralins, but both types of compounds can easily be separated by fractional crystallization. In this way we succeeded to synthesize the first distanna unit-containing tetralin.

Experimental Section

All reactions were carried out under inert nitrogen atmosphere using standard Schlenk techniques. All solvents were dried by standard methods and freshly distilled prior to use. Nonafluorobutansulfonic acid was dried over molecular sieve (4 Å) and distilled.

Di-*tert*-butyldichlorostannane and tetra-*tert*-butyldichlorodistannane were prepared as described in the literature [12]. All other starting materials were obtained commercially. The NMR spectra were recorded using a Varian Mercury 300 MHz or a Varian Inova 300 MHz NMR spectrometer.

General procedure for the preparation of trifluoromethylsulfonyl- and nonafluorobutylsulfonyl compounds

0.6 mmol of the stannane was dissolved in 10 mL of dichloromethane and cooled to 0 °C by using an ice/water bath. 1.2 mmol of fluoroalkylsulfonic acid was added dropwise *via* a syringe, and the mixture was stirred for 2 h at 0 °C. The reaction was monitored by ^{119}Sn NMR spectroscopy. The solution was used without further purification, but the solvent was replaced by THF directly before the second reaction step.

*1,2-Bis(diphenyl(nonafluorobutylsulfonyl)stannyl)xylene (**11**)*

Compound **11** was prepared following the general procedure described above. Starting materials: 931 mg 1,2-bis(triphenylstannylmethyl)benzene (1.2 mmol); 0.40 mL nonafluorobutane sulfonic acid (2.4 mmol). – ^{119}Sn{^{1}H} NMR (111.817 MHz, D_2O capillary): $\delta = -105.6$.

General procedure for the reaction of fluoroalkylsulfonyltin derivatives or chlorostannanes with α,α′-bis(magnesiumchloro)xylene

1.2 mmol of a bis(fluoroalkylsulfonyl)distannane, 1,2-dichlorodistannane, or a dichlorostannane was dissolved in 10 mL of THF and cooled to 0 °C using an ice/water bath. 1.2 mmol of the Grignard reagent was added dropwise *via* a syringe, and the mixture was stirred for 1 h at 0 °C. Then the solvent was removed under reduced pressure and the product extracted with hexane from the remaining residue. After filtration the product was obtained by removing the hexane under reduced pressure. All solid derivatives were recrystallized from hexane. The resulting products were characterized by ^{1}H, ^{13}C, and ^{119}Sn NMR spectroscopy.

General procedure for the Wurtz reaction of dichlorodialkyltin, magnesium and α,α′-dichloromethylxylene

5.0 mmol of dichlorodialkylstannane and 5.0 mmol (875 mg) of α,α′-dichloroxylene were dissolved in 20 mL THF. Then 10 mmol (243 mg) magnesium was added. The reaction started after 15 min as indicated by a change in color. The mixture was stirred over night and the solvent then removed under reduced pressure. The product was extracted with hexane from the remaining residue. After filtration the product was obtained by removing the hexane under reduced pressure. All solid derivatives were recrystallized from hexane. The resulting products were characterized by ^{1}H, ^{13}C, and ^{119}Sn NMR spectroscopy.

*2,2,3,3-Tetraethyl-2,3-distannatetralin (**12**)*

Starting material: 0.82 g (3.3 mmol) Et_2SnCl_2; colorless liquid; not isolated. Yield determined by ^{119}Sn-NMR spectroscopy: 30 % **12** and 70 % **15**. – ^{1}H NMR (300.224 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.17 (m, 2H), 6.96 (m, 2H), 2.81 (s, 4H, CH_2, $^2J(^1H\text{-}^{119}Sn)$ = 61 Hz), 1.12 (t, 12H, CH_2-CH_3, $^3J(^1H\text{-}^1H)$ = 7.89 Hz), 0.82 (q, 8H, CH_2-CH_3, $^3J(^1H\text{-}^1H)$ = 7.44 Hz). – ^{13}C{^{1}H} NMR (75.500 MHz, $CDCl_3$): δ = 138.36 (C-4a and C-8a), 129.02 (C-4 and C-7, $^3J(^{13}C\text{-}^{117/119}Sn)$ = 16 Hz), 124.11 (C-6 and C-7), 19.04 (C-1 and C-4, $^1J(^{13}C\text{-}^{117/119}Sn)$ = 434/418 Hz, $^2J(^{13}C\text{-}^{117/119}Sn)$ = 85 Hz), 11.14 (CH_2-CH_3, $^2J(^{13}C\text{-}^{117/119}Sn)$ = 24 Hz); 2.83 (CH_2-CH_3, $^1J(^{13}C\text{-}^{117/119}Sn)$ = 312/305 Hz, $^2J(^{13}C\text{-}^{117/119}Sn)$ = 50 Hz). – ^{119}Sn{^{1}H} NMR (111.817 MHz, $CDCl_3$): δ = −9.5 ($^1J(^{117}Sn\text{-}^{119}Sn)$ = 826 Hz, $^1J(^{13}C\text{-}^{119}Sn)$ = 434 Hz).

*2,2,3,3-Tetra-tert-butyl-2,3-distannatetralin (**13**)*

Starting material A: 1.77 g (3.3 mmol) Cl*t*Bu_2Sn-Sn*t*Bu_2Cl; Yield: 1.03 g (55 %) of colorless needles consisting of pure **13**. Starting material B: 1.0 g (3.3 mmol) Cl_2tBu_2Sn; Yield: 0.19 g (10 %) of colorless needles consisting of pure **13**. – ^{1}H NMR (300.224 MHz, $CDCl_3$): δ = 7.06 (m, 2H), 6.87 (m, 2H), 2.31 (s, 4H, CH_2, $^2J(^1H\text{-}^{119/117}Sn)$ = 41/21 Hz), 1.25 (s, 36H, CH_3, $^3J(^1H\text{-}^{119/117}Sn)$ = 67/64 Hz). – ^{13}C{^{1}H} NMR (75.500 MHz, $CDCl_3$): δ = 139.5 (C-4a and C-8a, $^2J(^{13}C\text{-}^{117/119}Sn)$ = 28 Hz), 129.0 (C-5 and C-8, $^3J(^{13}C\text{-}^{117/119}Sn)$ = 20 Hz), 123.78 (C-6 and C-7, $^4J(^{13}C\text{-}^{117/119}Sn)$ = 8 Hz), 33.03 ($C(CH_3)_3$, $^2J(^{13}C\text{-}^{117/119}Sn)$ = 6 Hz), 31.38 ($C(CH_3)_3$, $^1J(^{13}C\text{-}^{117/119}Sn)$ =

280/270 Hz, $^2J(^{13}C\text{-}^{117/119}Sn)$ = 40 Hz), 19.42 (C-4 and C-1, $^1J(^{13}C\text{-}^{117/119}Sn)$ = 100/90 Hz, $^2J(^{13}C\text{-}^{117/119}Sn)$ = 20 Hz). – $^{119}Sn\{^1H\}$ NMR (111.817 MHz, $CDCl_3$): δ = −55.9 ($^1J(^{117}Sn\text{-}^{119}Sn)$ = 800 Hz, $^1J(^{13}C\text{-}^{119}Sn)$ = 100 Hz, $^1J(^{13}C\text{-}^{119}Sn)$ = 280 Hz). – $C_{24}H_{44}Sn_2$ (570.026): calcd. C 50.57, H 7.78; found C 50.37, H 7.80.

*2,2,3,3-Tetraphenyl-2,3-distannatetralin (**14**)*

Starting material A: 3.3 mmol $NfOPh_2Sn\text{-}Ph_2SnONf$; colorless liquid; not isolated. Yield determined by ^{119}Sn-NMR spectroscopy: 40 % **14** and 60 % **17**. Starting material B: 1.13 g (3.3 mmol) Ph_2SnCl_2; colorless liquid; not isolated. Yield determined by ^{119}Sn-NMR spectroscopy: 20 % **14** and 80 % **17**. – ^1H NMR (300.224 MHz, $CDCl_3$): δ = 8.11 (s, 4H, $^2J(^1H\text{-}^{119}Sn)$ = 50 Hz), 7.91 (s, 2H), 7.83 (s, 4H), 7.84 (s, 2H), 7.60 (s, 2H), 3.24 (s, 4H, CH_2, $^2J(^1H\text{-}^{117/119}Sn)$ = 43 Hz). – $^{13}C\{^1H\}$ NMR (75.500 MHz, $CDCl_3$): δ = 142.86 (C-4a and C-8a), 140.20 (*i*-Ph, $^1J(^{13}C\text{-}^{117/119}Sn)$ = 450/430 Hz), 136.91 (*m*-Ph), 131.39 (C-5 and C-8), 128.77 (*o*-Ph), 126.44 (*p*-Ph), 124.95 (C-6 and C-7), 18.26 (C-1 and C-4, $^1J(^{13}C\text{-}^{117/119}Sn)$ = 350/343 Hz). – $^{119}Sn\{^1H\}$ NMR (111.817 MHz, $CDCl_3$): δ = −102.7 ($^1J(^{117}Sn\text{-}^{119}Sn)$ = 1413 Hz, $^1J(^{13}C\text{-}^{119}Sn)$ = 450 Hz).

*2,2-Diethyl-2-stanna-indane (**15**)*

Starting material: 0.82 g (3.3 mmol) Et_2SnCl_2; Yield: 0.23 g (25 %) of a colorless liquid consisting of pure **15**. – ^1H NMR (300.224 MHz, $CDCl_3$): δ = 7.09 (m, 2H), 6.91 (m, 2H), 2.34 (s, 4H, CH_2, $^2J(^1H\text{-}^{119}Sn)$ = 37.89 Hz), 1.82 (q, 4H, $^3J(^1H\text{-}^1H)$ = 7.81 Hz), 1.59 (t, 6H, $^3J(^1H\text{-}^1H)$ = 7.63 Hz). – $^{13}C\{^1H\}$ NMR (75.500 MHz, $CDCl_3$): δ = 144.24 (C-3a and C-7a), 131.28 (C-4 and C-7), 125.18 (C-5 and C-6), 15.87 (C-1 and C-3, $^1J(^{13}C\text{-}^{117/119}Sn)$ = 280/268 Hz), 11.66 (CH_2-CH_3, $^2J(^{13}C\text{-}^{117/119}Sn)$ = 26 Hz), 2.46 (CH_2-CH_3, $^1J(^{13}C\text{-}^{117/119}Sn)$ = 336/322 Hz). – $^{119}Sn\{^1H\}$ NMR (111.817 MHz, $CDCl_3$): δ = 82.0 ($^1J(^{13}C\text{-}^{119}Sn)$ = 67 Hz). – $C_{12}H_{18}Sn$ (280.981): calcd. C 51.29, H 6.45; found C 52.49, H 6.54.

*2,2-Di-tert-butyl-2-stanna-indane (**16**)*

Starting material: 1.0 g (3.3 mmol) Cl_2tBu_2Sn; Yield: 0.56 g (50 %) of a colorless liquid consisting of pure **16**. – ^1H NMR (300.224 MHz, $CDCl_3$): δ = 7.28 – 7.01 (m, 4H, Ph), 2.25 (s, 4H, CH_2, $^2J(^1H\text{-}^{117/119}Sn)$ = 32.27 Hz), 1.25 (s, 18H, CH_3, $^2J(^1H\text{-}^{117/119}Sn)$ = 65/63 Hz). – $^{13}C\{^1H\}$ NMR (75.500 MHz, $CDCl_3$): δ = 144.17 (C-3a and C-7a), 131.21 (C-4 and C-7), 125.16 (C-5 and C-6), 31.84 ($C(CH_3)_3$, $^2J(^{13}C\text{-}^{117/119}Sn)$ = 65 Hz), 28.55 ($C(CH_3)_3$, $^1J(^{13}C\text{-}^{117/119}Sn)$ = 360/340 Hz), 15.48 (C-1 and C-3, $^1J(^{13}C\text{-}^{117/119}Sn)$ = 230/220 Hz). – $^{119}Sn\{^1H\}$ NMR (111.817 MHz, $CDCl_3$): δ = 89.4 ($^1J(^{13}C\text{-}^{119}Sn)$ = 360 Hz, $^1J(^{13}C\text{-}^{119}Sn)$ = 230 Hz). – $C_{16}H_{26}Sn$ (337.088): calcd. C 57.01, H 7.77; found C 56.11, H 7.77.

Table 4. Crystallographic data for **13** and **19**.

Compound	**13**	**19**
Formula	$C_{24}H_{44}Sn_2$	$(C_{40}H_{36}Sn_2)_4$-$(CHCl_3)_3$
M_r	569.97	3373.36
T, K	100(2)	100(2)
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a, Å	9.3629(4)	18.7025(5)
b, Å	9.7655(4)	19.7436(5)
c, Å	14.9263(6)	22.6789(6)
α, deg	103.750(2)	106.652(1)
β, deg	100.886(2)	90.014(1)
γ, deg	98.135(2)	116.721(1)
V, Å^3	1276.70(9)	7084.3(3)
Z	2	2
d_{calc}, g cm^{-3}	1.48	1.58
$\mu(MoK_\alpha)$, mm^{-1}	2.0	1.6
$F(000)$, e	576	3354
Crystal size, mm^3	0.198×0.173 ×0.162	0.254×0.221 ×0.158
$\theta_{min/max}$, deg	2.19 / 25.99	1.22 / 27.00
Index ranges *hkl*	±11, ±12, ±18	±23, −24/+25, ±28
Reflections collected	65379	140091
Completeness to θ, %	98.7	98.9
Independent refls / R_{int}	4964 / 0.0252	30603 / 0.0356
Data / restraints / params	4964 / 0 / 247	30603 / 0 / 1639
Final $R1/wR2$ [$I \geq 2\sigma(I)$]	0.0236 / 0.0552	0.0364 / 0.0969
Final $R1/wR2$ (all data)	0.0249 / 0.0567	0.0494 / 0.1095
Goodness-of-fit on $F2$	1.026	1.024
Largest diff. peak / hole, e Å^{-3}	1.82 / −1.52	2.87 / −1.70

*2,2-Diphenyl-2-stanna-indane (**17**)*

Starting material: 1.13 g (3.3 mmol) Ph_2SnCl_2; Yield: 0.44 g (40 %) of a colorless solid consisting of pure **17**. – ^1H NMR (300.224 MHz, $CDCl_3$): δ = 8.11 (s, 4H, $^1J(^1H\text{-}^{117/119}Sn)$ = 50 Hz), 7.91 (m, 2H), 7.84 (m, 2H), 7.83 (m, 4H), 7.60 (m, 2H), 3.24 (s, 4H, CH_2, $^2J(^1H\text{-}^{117/119}Sn)$ = 43 Hz). – $^{119}Sn\{^1H\}$ NMR (111.817 MHz, $CDCl_3$): δ = 2.0 ($^1J(^{13}C\text{-}^{119}Sn)$ = 55.77 Hz). – $C_{20}H_{18}Sn$ (337.067): calcd. C 63.71, H 4.81; found C 64.24, H 5.21.

*2-Ethyl-2-phenyl-2-stanna-indane (**18**)*

Starting material: 0.98 g (3.3 mmol) $Ph(Et)SnCl_2$; Yield: 0.7 g (65 %) of a colorless liquid consisting of pure **18**. – ^1H NMR (300.224 MHz, $CDCl_3$): δ = 7.5 (m, 2H), 7.3 (m, 4H), 7.26 (m, 1H), 7.00 (m, 2H), 2.50 (s, 4H, CH_2, $^2J(^1H\text{-}^{117/119}Sn)$ = 40.45 Hz), 1.36 (t, 3H, CH_2-CH_3, $^3J(^1H\text{-}^1H)$ = 4.5 Hz), 1.34 (q, 2H, CH_2-CH_3, $^3J(^1H\text{-}^1H)$ = 4.8 Hz). – $^{13}C\{^1H\}$ NMR (75.500 MHz, $CDCl_3$): δ = 143.78 (C-3a and C-7a, $^2J(^{13}C\text{-}^{117/119}Sn)$ = 16 Hz), 140.42 (*i*-Ph, $^1J(^{13}C\text{-}^{117/119}Sn)$ = 433/415 Hz), 137.07 (C-4 and C-7, $^3J(^{13}C\text{-}^{117/119}Sn)$ = 35 Hz), 131.71 (*m*-Ph, $^3J(^{13}C\text{-}^{117/119}Sn)$ = 62 Hz), 129.45 (*p*-Ph, $^4J(^{13}C\text{-}$

$^{117/119}$Sn) = 11 Hz), 129.08 (C-4 and C-7), 125.92 (*o*-Ph, $^2J(^{13}C\text{-}^{117/119}Sn)$ = 145/126 Hz), 17.49 (C-1 and C-3, $^1J(^{13}C\text{-}^{117/119}Sn)$ = 308/295 Hz), 12.07 (CH_2-CH_3, $^2J(^{13}C\text{-}^{117/119}Sn)$ = 26 Hz), 3.20 (CH_2-CH_3, $^1J(^{13}C\text{-}^{117/119}Sn)$ = 374/357 Hz). – $^{119}Sn\{^1H\}$ NMR (111.817 MHz, $CDCl_3$): δ = 39.8 ($^1J(^{13}C\text{-}^{119}Sn)$ = 430 Hz, $^1J(^{13}C\text{-}^{119}Sn)$ = 374 Hz, $^1J(^{13}C\text{-}^{119}Sn)$ = 308 Hz, $^2J(^{13}C\text{-}^{119}Sn)$ = 140 Hz). – $C_{16}H_{18}Sn$ (329.024): calcd. C 58.41, H 5.51; found C 55.30, H 5.25.

Crystal structure determinations

A suitable crystal of **13** was grown from hexane by cooling the solution to −30 °C. Single crystals of **19** were also obtained from hexane. Data collections were performed on a Bruker-AXS KAPPA8 APEX II CCD diffractometer using graphite-monochromatized MoK_α radiation (λ = 0.71073 Å). Absorption corrections were performed using SADABS [13, 14]. The structures were solved with Direct Methods, and the non-hydrogen atoms were refined anisotropically (full-matrix least squares on F^2) with the SHELX suite of programs [15, 16]. All non-hydrogen atoms were refined employing anisotropic displacement parameters. Hydrogen atoms were located in calculated positions to correspond to standard bond lengths and angles. Crystallographic data for **13** and **19** are given in Table 4.

CCDC 751622 and 751623 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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