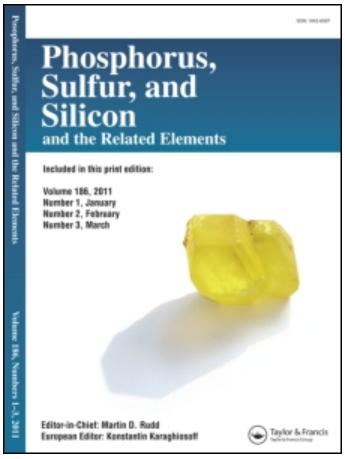

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Solvent Influence in Reactions of Fluoroalkyl Sulfonic Acids with Phenyldistannanes

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Solvent Influence in Reactions of Fluoroalkyl Sulfonic Acids with Phenyldistannanes

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The reaction of phenyl substituted distannanes and alkyl-bridged α,ω-distanna derivatives with trifluoromethyl or nonafluorobutyl sulfonic acid leads quantitatively to the corresponding bis(fluoroalkylsulfonyl) stanannes. Further derivatization of these sulfonyl tin compounds with Grignard reagents yields novel alkyl substituted distannanes. All compounds were characterized by NMR, MS and elemental analysis. The X-ray structure of compound ***13*** *is discussed.*

Keywords Distannanes; fluoroalkyl sulfonic acids; ^{119}Sn NMR

INTRODUCTION

Reactions of trifluoromethyl sulfonic acid with various silicon compounds are well investigated and in many cases connected with the name of Wolfram Uhlig. [1–5] Such reactions result in the formation of trifluoromethylsulfonyl substituted silanes, a class of compounds, which serve as starting materials for silica-element coupling reactions. Compounds containing silicon-silicon bonds can easily be functionalized using trifluoromethyl sulfonic acid without cleavage of Si-Si bonds.[2,3]

In contrast, very little is known about reactions of the higher homologues of silicon with fluoroalkane sulfonic acids. W. Sundermeyer et al. discuss the syntheses of sulfonic acid ester compounds of tin and germanium along with the synthesis of a broad range of silicon analogs.[4] In another publication the preparation and characterization of some

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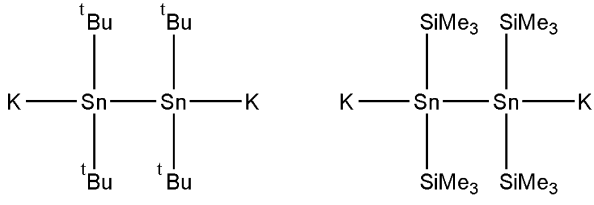


1 **2**

FIGURE 1 Dianionic distannanes.

methyl tin sulfonates is described.[5] It is known that the reaction of sulfonic acids with systems containing tin-tin bonds leads to the cleavage of these bonds.

In the last few years, we reported[6,7] on the synthesis of dianionic distannanes such as compounds **1** and **2** shown in Figure 1. In addition to this work, we were also interested in their synthetic counterparts such as distannanes with electrophilic tin centers. Since perfluoroalkylsulfonyl silicon derivatives have been shown to act as very useful reactive intermediates we wanted to investigate if analogous tin compounds can serve as building blocks with electrophilic tin centers.

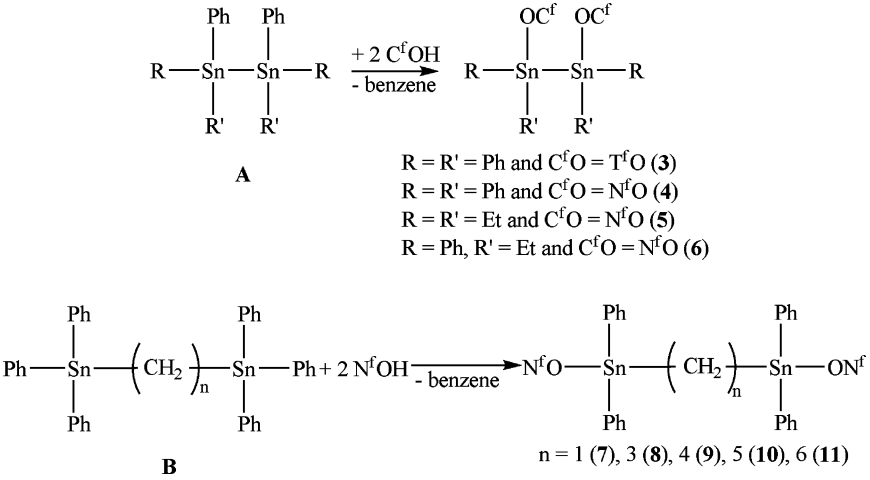
This paper deals with the reaction of phenyl-substituted distannanes (**A**) and alkyl bridged distanna compounds (**B**) with fluoroalkane sulfonic acids yielding compounds with electrophilic tin atoms. The reaction of the resulting derivatives with Grignard reagents yielding diastereomeric distannanes is also discussed. Although, some diastereomeric distannanes have already been published,[8–14] this novel reaction pathway allows an easy one-pot access to this class of compounds.

RESULTS AND DISCUSSION

Synthesis

As expected, our first reactions of trifluoromethyl sulfonic acid with hexaphenyldistannane showed only tin-tin bond cleavage and the formation of Ph_3SnOT^f as the main product. Nevertheless, a careful and systematic investigation of the solvents used in these reactions opened a simple access to new distannanes. Usually diethylether or benzene is used as solvent in the reactions of phenylsilanes with trifluoromethyl sulfonic acid.

However, when methylene chloride is used as solvent instead of diethyl ether or benzene, hexaphenyldistannane reacts with the perfluoroalkyl sulfonic acids, CF_3SO_3H (T^fOH) and $C_4F_9SO_3H$ (N^fOH), without cleavage of the tin-tin-bond. In dichloromethane the reaction



SCHEME 1 Fluoroalkyl sulfonyl stannanes.

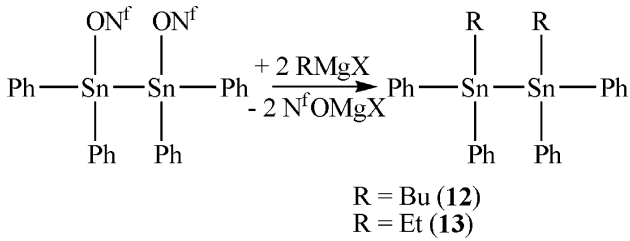
is very fast and highly selective, not only in the case of hexaphenyldistannane, but also for all investigated mixed alkyl-phenyl-distannanes (**A**) and phenyl-substituted alkyl bridged distanna compounds (**B**). The resulting products can always be used without further purification. Scheme 1 gives an overview of all prepared sulfonyl tin derivatives.

The reaction of these sulfonyl tin compounds with Grignard reagents is also strongly dependent on the solvent used. Surprisingly, dichloromethane turned out to be the best solvent for Grignard reactions resulting in very good yields without cleavage of the tin-tin bond, if the equimolar ratio between the Grignard reagent and the sulfonyl tin derivative is strictly maintained. In contrast solvents like diethylether or tetrahydrofurane, which are normally used for Grignard reactions, lead to partial cleavage of the tin-tin bond and hence to mixture of products.

The reaction of **4** with butyl and ethyl magnesium bromide results in the formation of compounds **12** and **13**, respectively (Scheme 2). This reaction can be extended to the alkyl bridged distanna compounds **7**–**11**.

All products from the reactions of the sulfonyl distannanes with Grignard reagents can be easily isolated by removing the solvent from the reaction mixture and extracting the product with hexane. Further purification can be achieved by recrystallization or fractional distillation depending on the physical properties of the product.

The reaction of **13** with $C_3F_9SO_3H$ (N^fOH) leads to the novel diastereomeric sulfonyl distannane **6** which can easily be converted into diastereomeric alkyl tin compounds by derivatization with Grignard



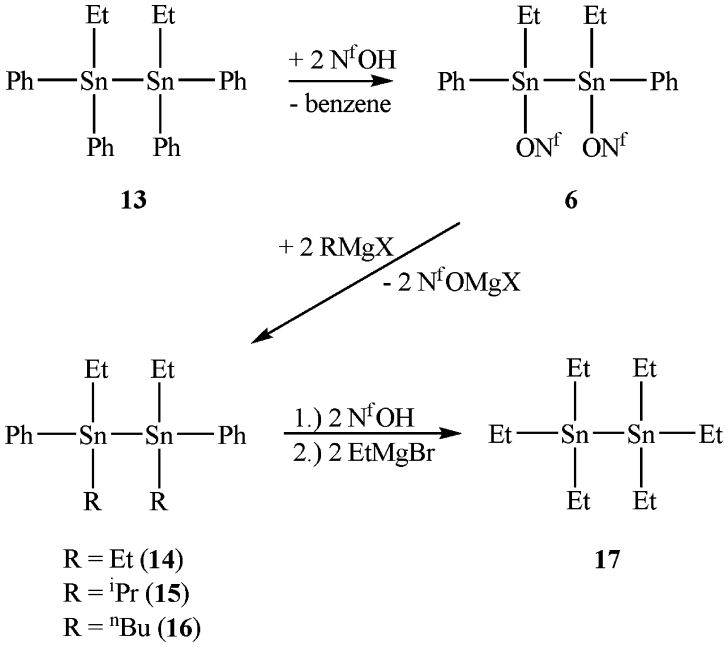
SCHEME 2 Reaction of sulfonyl stannanes with RMgX.

reagents. Finally all phenyl groups can be removed via this reaction pathway to form compound **17**[9] (Scheme 3).

Through this synthesis aryl substituted tin compounds can now be easily modified and asymmetric tin centers are also accessible.

NMR Spectroscopy

Table I displays the ^{119}Sn NMR data of the synthesized compounds. Remarkable are the ^{119}Sn NMR shifts of compounds **6**, **15,** and **16**, which are distannanes containing chiral tin atoms. In all cases both, the *meso* and the *rac* isomer were formed. The difference in the ^{119}Sn



SCHEME 3 Reaction cascade leading to **17** starting from **13**.

TABLE I ^{119}Sn NMR Chemical Shifts and $^{1}J(^{119}Sn,^{117}Sn)$ coupling constants (in Hz) of the Distannanes RR′R″Sn–SnR″R′R Prepared

	R	R′	R″	δ^{119}Sn	$^{1}J(^{119}Sn,^{117}Sn)$
Ph_6Sn_2	Ph	Ph	Ph	−143.6	4470
3	Ph	Ph	T^fO	−100.2	8840
4	Ph	Ph	N^fO	−97.4	8870
5	Et	Et	N^fO	+102.7	4329
6	Ph	Et	N^fO	−3.7/−4.0	6120
12	Ph	Ph	Bu	−124.2	3620
13	Ph	Ph	Et	−117.1	3525
14	Ph	Et	Et	−89.7	2960
15	Ph	Et	^{i}Pr	−77.5/−77.8	2400
16	Ph	Et	^{n}Bu	−98.5	3040
17	Et	Et	Et	−60.9	2545

NMR chemical shifts of the two isomers strongly depends on the sterical demand of the substituents. In the case of **6** and **15** (R = *i*Pr) distinct ^{119}Sn NMR signals are displayed for the *meso* and the *rac* isomer, while in the case of **16** (R = *n*Bu) only one signal is observed in the ^{119}Sn NMR spectrum.

In the series of distannanes **12–17** the ^{119}Sn NMR signal shifts to lower field and the $^{1}J(^{119}Sn,^{117}Sn)$ coupling constant decreases with decreasing number of phenyl substituents at the tin atom. Introduction of the nonafluorobutyl sulfonyl substituent in compounds **3–6** (C^fO = $C_4F_9SO_3$) causes generally a strong low-field shift of the ^{119}Sn-NMR signal and a remarkably large $^{1}J(^{119}Sn,^{117}Sn)$ coupling constant (Table I).

A similar situation is found for the alkyl bridged sulfonyl substituted tin derivatives **7–11** as shown in Table II. Again, the sulfonyl substituent causes a shift of the ^{119}Sn NMR signal to low field; the influence is not as strong as in the case of the distannanes discussed above, however.

Molecular and Crystal Structure of 1,2-Diethyl-1,1,2,2-tetraphenyldistannane (13)

All solid distannanes prepared are crystalline. Single crystals of **13** suitable for X-ray diffraction and were obtained via recrystallization from *n*-hexane. The molecular structure of 1,2-diethyl-1,1,2,2-tetraphenyldistannane (**13**) in the crystal is depicted in Figure 2.

The distannane **13** crystallizes in the monoclinic space group $P2_1/c$. The tin-tin bond length is 2.769(2) Å; the sum of the Sn-Sn-C angles is with 332.96° close to the value of 329.13° suggesting a regular tetrahedral environment of the tin atoms.

TABLE II ^{119}Sn NMR Chemical Shifts and $J(^{119}Sn,^{117}Sn)$ Coupling Constants (in Hz) of $Ph_2(N^fO)Sn(CH_2)_nSn(ON^f)Ph_2$ (4, 7–11) and $Ph_3Sn(CH_2)_nSnPh_3$

	$Ph_2(N^fO)Sn(CH_2)_nSn(ON^f)Ph_2$			$Ph_3Sn(CH_2)_nSnPh_3$	
N	compound	δ^{119}Sn	$J(^{119}Sn,^{117}Sn)$	δ^{119}Sn	$J(^{119}Sn,^{117}Sn)$
0	**4**	−97.4	8870	−143.6	4470
1	**7**	−54.8	337	−77.7	243
3	**8**	−66.6	—	−104.6	—
4	**9**	−64.1	—	−102.0	—
5	**10**	−96.4	—	−101.1	—
6	**11**	−95.6	—	−101.2	—

CONCLUSION

The reaction of phenyl substituted distannanes and alkyl bridged α,ω-distanna derivatives with trifluoromethyl or nonafluorobutyl sulfonic acid leads quantitatively to the corresponding bis(fluoroalkylsulfonyl) stannanes. Further derivatization of these sulfonyl tin compounds with Grignard reagents yields novel alkyl substituted distannanes.

This synthetic route can be used as a simple access to novel distanna derivatives. In an upcoming paper, we will discuss the use of

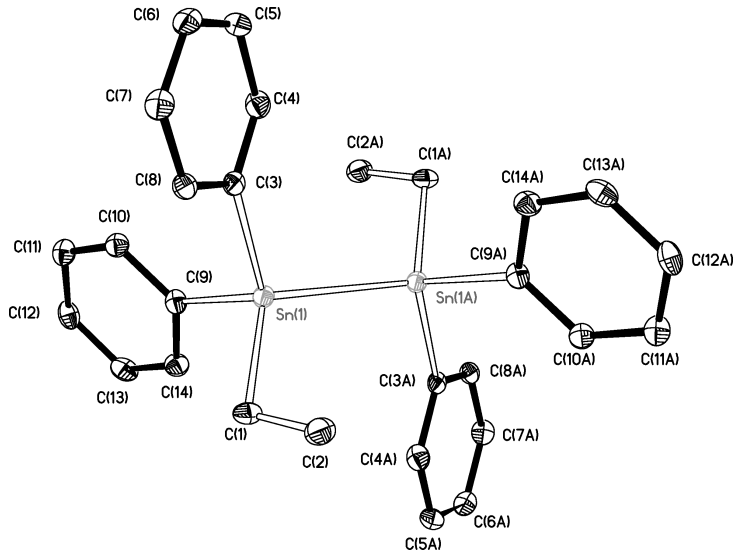


FIGURE 2 Molecular structure of **13** in the crystal. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity.

TABLE III Crystallographic Data for Compound 13

Empirical formula	$C_{28}H_{30}Sn_2$
Formula weight	603.96
T (K)	100
Crystal size (mm)	0.30 × 0.22 × 0.16
Crystal system	Monoclinic
Space group	P21/c
a (Å)	8.0451(16)
b (Å)	20.519(4)
c (Å)	7.6696(15)
α(°)	90
β(°)	98.55(3)
γ(°)	90
V (Å^3)	1252.0(4)
Z	2
D_{calc} (g cm^{-1})	1.602
Abs. coeff. (mm^{-1})	2.007
F (0 0 0)	596
θ range (°)	1.99 to 26.38
Reflections collected/unique (R_{int})	9815/2558 [R(int) = 0.1212]
Completeness to theta (%)	26.38 [99.9]
Absorption correction	SADABS
Data/restraints/parameters	2558/0/137
Goodness-of-fit on F^2	1.010
Final R indices [I > 2 σ(I)]	R1 = 0.0442, wR2 = 0.1111
R indices (all data)	R1 = 0.0534, wR2 = 0.1158
Largest diff. peak and hole [e$^-$/Å^3]	2.801 and −1.153

such compounds for the formation of ring systems containing at least one distannane unit.

EXPERIMENTAL

General Methods

All reactions were carried out under inert atmosphere (N_2) using standard Schlenk techniques. All solvents were dried by standard methods and freshly distilled prior to use. Nonafluorobutyl sulfonic acid was dried over molecular sieve (4 Å) and distilled; Trifluoromethyl sulfonic acid was distilled from fresh concentrated sulfuric acid before use.

All alkyl-bridged stannanes were prepared following literature procedures.[10] All other chemicals used as starting materials were obtained commercially. All NMR spectra were recorded using a Varian Mercury 300 MHz or a Varian Inova 300 MHz instrument. Chemical shifts are referred to TMS (^{1}H, ^{13}C) and $Sn(CH_3)_4$ (^{119}Sn) as external standards.

Preparation of the Trifluoromethyl Sulfonyl and Nonafluorobutyl Sulfonyl Distannanes—General Procedure

0.6 mmol of the corresponding distannane were dissolved in 10 mL of CH_2Cl_2 and cooled to 0°C using an ice/water bath. 1.2 mmol of the fluoroalkylsulfonic acid were added dropwise via a syringe and the resulting reaction mixture was stirred for another 2 h at 0°C. The yield and the purity of the resulting product were determined by ^{119}Sn NMR spectroscopy. The solution thus obtained was used without further purification.

1,2-Bis(trifluoromethylsulfonyl)-1,1,2,2-tetraphenyldistannane (3)

Compound **3** was prepared from hexaphenyldistannane (425 mg, 0.6 mmol) and trifluoromethyl sulfonic acid (0.1 mL, 1.2 mmol). $^{119}Sn\{^1H\}$ NMR (111.82 MHz, D_2O-capillary): $\delta = -100.2$ [$^1J(^{119}Sn,^{117}Sn) = 8810$ Hz, $^1J(^{119}Sn\text{-}^{13}C) = 559$ Hz].

1,2-Bis(nonafluorobutylsulfonyl)-1,1,2,2-tetraphenyldistannane (4)

Compound **4** was prepared from hexaphenyldistannane (425 mg, 0.6 mmol) and nonafluorobutyl sulfonic acid (0.2 mL, 1.2 mmol). $^{119}Sn\{^1H\}$ NMR (111.82 MHz, D_2O-capillary): $\delta = -97.4$ [$^1J(^{119}Sn,^{117}Sn) = 8710$ Hz, $^1J(^{119}Sn,^{13}C) = 552$ Hz].

1,2-Bis(nonafluorobutylsulfonyl)-1,1,2,2-tetraethyldistannane (5)

Compound **5** was prepared from 1,1,2,2-tetraethyl-1,2-diphenyldistannane (650 mg, 1.28 mmol) and nonafluorobutyl sulfonic acid (0.42 mL, 2.5 mmol). $^{119}Sn\{^1H\}$ NMR (111.82 MHz, D_2O-capillary): $\delta = +102.7$ [$^1J(^{119}Sn,^{117}Sn) = 4329$ Hz].

1,2-Diethyl-1,2-diphenyl-1,2-bis(nonafluorobutylsulfonyl) distannane (6)

Compound **6** was prepared from 1,2-diethyl-1,1,2,2-tetraphenyldistannane (366 mg, 0.6 mmol) and nonafluorobutyl sulfonic acid (0.2 mL, 1.2 mmol). $^{119}Sn\{^1H\}$ NMR (111.82 MHz, D_2O-capillary): $\delta = -3.7, -4.0$ [$^1J(^{119}Sn,^{117}Sn) = 6120$ Hz].

Bis(nonafluorobutylsulfonyl-diphenylstannyl)methane (7)

Compound **7** was prepared from bis(triphenylstannyl) methane (866 mg, 1.2 mmol) and nonafluorobutyl sulfonic acid (0.4 mL,

2.4 mmol). $^{119}Sn\{^1H\}$ NMR (111.82 MHz, D_2O-capillary): $\delta = -54.8$ [$^2J(^{119}Sn,^{117}Sn) = 337$ Hz].

1,3-Bis(nonafluorobutylsulfonyl-diphenylstannyl)propane (8)

Compound **8** was prepared from 1,3-bis(triphenylstannyl) propane (900 mg, 1.2 mmol) and nonafluorobutyl sulfonic acid (0.4 mL, 2.4 mmol). $^{119}Sn\{^1H\}$ NMR (111.82 MHz, D_2O-capillary): $\delta = -66.6$.

1,4-Bis(nonafluorobutylsulfonyl-diphenylstannyl)butane (9)

Compound **9** was prepared from 1,4-bis(triphenylstannyl) butane (918 mg, 1.2 mmol) and nonafluorobutyl sulfonic acid (0.4 mL, 2.4 mmol). $^{119}Sn\{^1H\}$ NMR (111.82 MHz, D_2O-capillary): $\delta = -64.1$.

1,5-Bis(nonafluorobutylsulfonyl-diphenylstannyl)pentane (10)

Compound **10** was prepared from 1,5-bis(triphenylstannyl)pentane (924 mg, 1.2 mmol) and nonafluorobutane sulfonic acid (0.4 mL, 2.4 mmol). $^{119}Sn\{^1H\}$ NMR (111.82 MHz, D_2O-capillary): $\delta = -96.4$.

1,6-Bis(nonafluorobutylsulfonyl-diphenylstannyl)hexane (11)

Compound **11** was prepared from 1,6-bis(triphenylstannyl)hexane (941 mg, 1.2 mmol) and nonafluorobutyl sulfonic acid (0.4 mL, 2.4 mmol). $^{119}Sn\{^1H\}$ NMR (111.82 MHz, D_2O-capillary): $\delta = -95.6$.

Reaction of the Fluoroalkyl Sulfonic Tin Derivatives with Grignard Reagents—General Procedure

0.6 mmol of the corresponding tetraorganyl bis(perfluoroalkylsulfonyl) distannane was dissolved in 10 mL of CH_2Cl_2 and the solution was cooled to 0°C using an ice/water bath. 1.2 mmol of the Grignard reagent was added dropwise via a syringe and the resulting reaction mixture was stirred for another hour at 0°C. The solvent was removed under reduced pressure and the remaining residue was extracted with *n*-hexane. After filtration, the distannane was obtained by removing the *n*-hexane under reduced pressure. All solid distannanes were recrystallized from *n*-hexane.

1,2-Dibutyl-1,1,2,2-tetraphenyldistannane (12)

Compound **12** was prepared from 1,1,2,2-tetraphenyl-1,2-bis(nonafluorobutylsulfonyl) distannane (1.39 g, 1.2 mmol) in 15 mL of CH_2Cl_2 and BuMgCl (2.4 mmol) in THF. ^1H NMR (300.22 MHz, $CDCl_3$): $\delta = 7.5$ (m, 8H, *o*-H); 7.3 (m, 12H, *m*-, *p*-H); 1.60 (m, 4H, CH_2); 1.35 (m, 4H, CH_2); 0.92 [m, $^3J_{HH} = 7.3$ Hz, 4H, CH_2); 0.85 (t, $^3J_{HH} = 7.2$ Hz, 6H, CH_3). $^{13}C\{^1H\}$ NMR (75.50 MHz, $CDCl_3$): $\delta = 140.6$ (C-*i*);

137.5 ($^2J(^{119/117}Sn,^{13}C) = 37$ Hz, $^3J(^{119/117}Sn,^{13}C) = 8$ Hz C-*o*); 128.67 ($^3J(^{119/117}Sn,^{13}C) = 44$ Hz, C-*m*); 128.67 (C-*p*); 30.3 ($^3J(^{119/117}Sn,^{13}C) = 35$ Hz, $^4J(^{119/117}Sn,^{13}C) = 18$ Hz, CH_2); 27.6 ($^2J(^{119/117}Sn,^{13}C) = 64$ Hz, $^3J(^{119/117}Sn,^{13}C) = 15$ Hz, CH_2); 13.8 ($^4J(^{119/117}Sn,^{13}C) = 12$ Hz,CH_3); 13.2 ($^1J(^{119}Sn,^{13}C) = 269$ Hz, $^1J(^{117}Sn,^{13}C) = 259$ Hz, $^2J(^{119/117}Sn,^{13}C) = 21$ Hz, CH_2]. $^{119}Sn\{^1H\}$ NMR (111.92 MHz, $CDCl_3$): $\delta = -124.4$ ($^1J(^{119}Sn,^{117}Sn) = 3616$ Hz). Anal. calcd. for $C_{28}H_{30}Sn_2$ (660.06): C, 58.23; H, 5.80%. Found: C, 55.80; H, 5.75%.

1,2-Diethyl-1,1,2,2-tetraphenyldistannane (13)

Compound **13** was prepared from 1,1,2,2-tetraphenyl-1,2-bis(nonafluorobutylsulfonyl) distannane (10.4 g, 9.1 mmol) in 100 mL of CH_2Cl_2 and EtMgBr (18.2 mmol) in THF. Yield: 2.3 g (42%) after recrystallization from *n*-hexane; m.p. 91°C. ^1H NMR (300.22 MHz, $CDCl_3$): $\delta = 7.43$ (m, $^3J_{HH} = 3.2$ Hz, 8H, *o*-H); 7.23 (m, 12H, *m*-, *p*-H]; 1.44 (q, $^3J_{HH} = 7.5$ Hz, 4H, CH_2); 1.26 (t, $^3J_{HH} = 7.2$ Hz, 6H, CH_3). $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): $\delta = 140.3$ ($^1J(^{119}Sn,^{13}C) = 360$ Hz, $^1J(^{117}Sn,^{13}C) = 344$ Hz, $^2J(^{119}Sn,^{13}C) = 54$ Hz, $^2J(^{117}Sn,^{13}C) = 52$ Hz, C-*i*); 137.5 ($^2J(^{119}Sn,^{13}C) = 38$ Hz, $^2J(^{117}Sn,^{13}C) = 36$ Hz, $^3J(^{119/117}Sn,^{13}C) = 8$ Hz, C-*o*); 128.69 ($^3J(^{119}Sn,^{13}C) = 44$ Hz, $^3J(^{117}Sn,^{13}C) = 43$ Hz, C-*m*), 128.67 ($^4J(^{119/117}Sn,^{13}C) = 11$ Hz, C-*p*), 12.4 ($^2J(^{119/117}Sn,^{13}C) = 21$ Hz, $^3J(^{119/117}Sn,^{13}C) = 7$ Hz,CH_3); 5.3 ($^1J(^{119}Sn,^{13}C) = 302$ Hz, $^1J(^{117}Sn,^{13}C) = 289$ Hz, $^2J(^{119}Sn,^{13}C) = 53$ Hz, $^2J(^{117}Sn,^{13}C) = 50$ Hz,CH_2). $^{119}Sn\{^1H\}$ NMR (111.92 MHz, $CDCl_3$): $\delta = -117.1$ [$^1J(^{119}Sn,^{117}Sn) = 3525$ Hz]. Anal. calcd.. for $C_{28}H_{30}Sn_2$ (603.96): C, 55.68; H, 5.01%. Found: C, 55.62; H, 5.11%.

1,1,2,2-Tetraethyl-1,2-diphenyldistannane (14)

Compound **14** was prepared from 1,2-diethyl-1,2-diphenyl-1,2-bis(nonafluorobutylsulfonyl) distannane (1.9 g, 1.82 mmol) in 15 mL of CH_2Cl_2 and EtMgBr (3.64 mmol) in THF. After extraction with *n*-hexane 760 mg (82%) of a colorless oil were obtained. B.p. 90°C ($p = 0.1$ mbar). ^1H-NMR (300.22 MHz, $CDCl_3$): $\delta = 7.66$ (m, 6H, *m*-, *p*-H); 7.45 (m, 4H, *o*-H); 1.46 [m, 20H, CH_2CH_3). $^{13}C\{^1H\}$ NMR (75.50 MHz, $CDCl_3$): $\delta = 141.7$ ($^1J(^{119/117}Sn,^{13}C) = 348$ Hz, C-*i*); 137.4 ($^3J(^{119/117}Sn,^{13}C) = 34$ Hz, $^4J(^{119/117}Sn,^{13}C) = 8$ Hz, C-*m*); 128.6 ($^2J(^{119/117}Sn,^{13}C) = 46$ Hz, $^3J(^{119/117}Sn,^{13}C) = 28$ Hz, C-*o*); 128.3 ($^4J(^{119/117}Sn,^{13}C) = 10$ Hz, C-*p*); 12.7 ($^2J(^{119/117}Sn,^{13}C) = 20$ Hz, $^3J(^{119/117}Sn,^{13}C) = 7$ Hz, CH_3); 3.6 ($^1J(^{119}Sn,^{13}C) = 275$ Hz, $^1J(^{117}Sn,^{13}C) = 262$ Hz, $^2J(^{119/117}Sn,^{13}C) = 48$ Hz, CH_2). $^{119}Sn\{^1H\}$ NMR (111.92 MHz, $CDCl_3$): $\delta = -89.7$ ($^1J(^{119}Sn,^{117}Sn) = 2960$ Hz). Anal. calcd. for $C_{28}H_{30}Sn_2$ (507.87): C, 47.30; H, 5.95%. Found: C, 47.31; H, 5.64%.

1,2-Diethyl-1,2-diisopropyl-1,2-diphenyldistannane (15)

Compound **15** was prepared from 1,2-diethyl-1,2-diphenyl-1,2-bis(nonafluorobutylsulfonyl) distannane (635 mg, 0.6 mmol) in 10 mL of CH_2Cl_2 and ^{i}PrMgCl (1.2 mmol) in Et_2O. ^{1}H NMR (300.22 MHz, $CDCl_3$): δ = 7.5 (m, 6H, *m*-, *p*-H); 7.3 (m, 4H, *o*-H); 1.82 [septett, $^3J_{HH}$ = 8.0 Hz, 2H, C*H*$(CH_3)_2$); 1.37 (t, $^3J_{HH}$ = 6.0 Hz, 6H, CH_2CH_3); 1.36 (d, $^3J_{HH}$ = 8.0 Hz, 12H, CH(CH_3)$_2$); 1.34 (q, $^3J_{HH}$ = 6.0 Hz, 4H, CH_2CH$_3$). ^{13}C{^{1}H} NMR (75.50 MHz, $CDCl_3$): δ = 141.77 (C-*i*); 141.75 (C-*i*); 137.5 ($^2J(^{119/117}Sn,^{13}C)$ = 33 Hz, $^3J(^{119/117}Sn,^{13}C)$ = 8 Hz, C-*o*); 128.4 (C-*m*); 128.1 ($^4J(^{119/117}Sn,^{13}C)$ = 9 Hz, C-*p*); 30.0 ($^2J(^{119/117}Sn,^{13}C)$ = 50 Hz, CH(*C*H$_3$)$_2$); 16.8 ($^1J(^{119}Sn,^{13}C)$ = 309 Hz, $^1J(^{117}Sn,^{13}C)$ = 295 Hz, $^2J(^{119/117}Sn,^{13}C)$ = 43 Hz, *C*H(CH$_3$)$_2$); 12.7 ($^2J(^{119/117}Sn,^{13}C)$ = 16 Hz, CH$_2$*C*H$_3$), 3.3 ($^1J(^{119}Sn,^{13}C)$ = 256 Hz, $^1J(^{117}Sn,^{13}C)$ = 245 Hz, $^2J(^{119/117}Sn,^{13}C)$ = 40 Hz,*C*H$_2$CH$_3$). ^{119}Sn{^{1}H} NMR (111.92 MHz, $CDCl_3$): δ = −77.54, -77.56 ($^1J(^{119}Sn,^{117}Sn)$ = 2396 Hz). Anal. calcd. for $C_{28}H_{30}Sn_2$ (535.93): C, 49.30; H, 6.39%. Found: C, 49.08; H, 6.48%.

1,2-Diethyl-1,2-di-n-butyl-1,2-diphenyldistannane (16)

Compound **16** was prepared from 1,2-diethyl-1,2-diphenyl-1,2-bis(nonafluorobutylsulfonyl) distannane (635 mg, 0.6 mmol) in 10 mL of $CH_2Cl_2$and BuMgCl (1.2 mmol) in THF. ^{1}H NMR (300.22 MHz, $CDCl_3$): δ = 7.5 (m, 6H, *m*-, *p*-H); 7.3 (m, 4H, *o*-H); 1.56 (sextett, 4H, CH_2); 1.35 (t, $^3J_{HH}$ = 10.9 Hz, 6H, CH_3); 1.26 (q, $^3J_{HH}$ = 8.2 Hz, 4H, CH_2CH$_3$); 1.26 (t, $^3J_{HH}$ = 8.2 Hz, 6H, CH$_2$CH_3); 0.90 (quintet, $^3J_{HH}$ = 8.5 Hz, 4H, CH_2); 0.86 [t, $^3J_{HH}$ = 8.5 Hz, 4H, CH_2). ^{13}C{^{1}H} NMR (75.50 MHz, $CDCl_3$): δ = 141.9 ($^1J(^{119}Sn,^{13}C)$ = 312 Hz, $^1J(^{117}Sn,^{13}C)$ = 298 Hz, $^2J(^{119/117}Sn,^{13}C)$ = 42 Hz, C-*i*); 137.3 ($^2J(^{119/117}Sn,^{13}C)$ = 34 Hz, $^3J(^{119/117}Sn,^{13}C)$ = 8 Hz, C-*o*); 128.4 ($^3J(^{119/117}Sn,^{13}C)$ = 18 Hz, C-*m*); 128.1 ($^4J(^{119/117}Sn,^{13}C)$ = 10 Hz, C-*p*); 30.6 ($^3J(^{119/117}Sn,^{13}C)$ = 34 Hz, $^4J(^{119/117}Sn,^{13}C)$ = 16 Hz, CH_2); 27.7 ($^2J(^{119/117}Sn,^{13}C)$ = 58 Hz, $^3J(^{119/117}Sn,^{13}C)$ = 12 Hz, CH_2); 13.9 ($^4J(^{119/117}Sn,^{13}C)$ = 22 Hz, $^5J(^{119/117}Sn,^{13}C)$ = 8 Hz, CH_3); 12.5 ($^2J(^{119/117}Sn,^{13}C)$ = 20 Hz, $^3J(^{119/117}Sn,^{13}C)$ = 8 Hz, CH_3); 11.4 ($^1J(^{119}Sn,^{13}C)$ = 268 Hz, $^1J(^{117}Sn,^{13}C)$ = 258 Hz, $^2J(^{119/117}Sn,^{13}C)$ = 43 Hz, CH_2); 3.9 ($^1J(^{119}Sn,^{13}C)$ = 272 Hz, $^1J(^{117}Sn,^{13}C)$ = 260 Hz, $^2J(^{119/117}Sn,^{13}C)$ = 46 Hz, CH_2). ^{119}Sn{^{1}H} NMR (111.92 MHz, $CDCl_3$): δ = −97.5 ($^1J(^{119}Sn,^{117}Sn)$ = 2960 Hz). Anal. calcd. for $C_{28}H_{30}Sn_2$ (563.98): C, 51.11; H, 6.79%. Found: C, 48.40; H, 6.68%.

Hexaethyldistannane (17)

Compound **17** was prepared from 1,2-bis(nonafluorobutylsulfonyl)-1,1,2,2-tetraethyl-distannane (571 mg, 0.6 mmol) in 10 mL of CH_2Cl_2

and EtMgBr (1.2 mmol) in THF. All analytical data of **17** were consistent with the published data.[19]

X-ray Structure Analysis of 1,2-Diethyl-1,1,2,2-tetraphenyldistannane (13)

A suitable single crystal of **13** was obtained from *n*-hexane by cooling the solution to –30°C. For data collection the crystal was mounted onto the tip of glass fiber. Data collection was performed with a Bruker-AXS SMART APEX CCD diffractometer using graphite monochromated Mo-K_α radiation (0.71073 Å). The data were corrected for absorption effects with SADABS.[11]

Supplementary Material

Crystallographic data for the structure investigation of compound **13** have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 607158. Copies of this information may be obtained free of charge by quoting the above CCDC number from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44–1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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