Organotin Perfluorooctanesulfonates as Air-Stable Lewis Acid Catalysts: Synthesis, Characterization, and Catalysis

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Abstract: The reactions of 1,3-dichloro-1,1,3,3-tetrabutyldistannoxane and dialkyltin dihalides with silver perfluorooctanesulfonate provided the corresponding sulfonates as hydrates. The number of water molecules (n) of hydration was dependent on the conditions. The distannoxane derivative was identified as n from 0.5 to 6, while in the hydrated mononuclear species and DMSO complexes n varied widely from 4 to 13. ^{119}Sn NMR spectroscopy and conductivity measurements indicated the ionic dissociation of these compounds in solution. These compounds exhibited unusually high solubility in polar organic solvents. The ionic dissociation together with facile hydration probably causes the unusual solubility. The Lewis acidity of these compounds was found to be high among organotin derivatives on the basis of ESR spectra of superoxide/metal-ion complexes. In contrast to well-known organotin triflates, these compounds suffered no hydrolysis upon storage in open air. The high catalytic activity of the distannoxane **1** was exemplified for various carbon–carbon bond-forming reactions, such as Mukaiyama–aldol as well as -Michael reactions and allylation of aldehydes.

Keywords: EPR spectroscopy · homogeneous catalysts · Lewis acids · NMR spectroscopy · tin

Introduction

A number of organotin compounds serve as Lewis acid catalysts in organic synthesis.[1] Normally, their Lewis acidity is mild so that high chemoselectivity could be attained in various functional group transformations.[2] The mild Lewis acidity, on the other hand, often causes failure in the carbon–carbon bond formation. Hence, the increase of the Lewis acidity of organotin compounds is of prime importance to expand the scope of their synthetic utility. One method is to attach electron-withdrawing group(s) on tin. Guided by this postulate, we previously disclosed that organotin triflates served to catalyze carbon–carbon bond-forming reactions like Mukaiyama–aldol and –Michael reactions in a highly chemoselective manner.[3] However, their hygroscopic nature did not allow us to fully characterize these compounds despite strong demands for detailed information about such synthetically useful class of organotin compounds. Recently, we reported in a preliminary form that 1,3-bis(perfluorooctanesulfonato)-1,1,3,3-tertabutyldistannoxane (**1**) is air-stable and acidic enough to catalyze, for the first time for this class of compounds, various carbon–carbon bond-forming reactions with stannyl and silyl nucleophiles.[4] Hence, we have investigated relevant organotin perfluorooctanesulfonates. In this paper, we put forth a full account of synthesis and characterization of these compounds. Furthermore, their catalytic activities are assessed in carbon–carbon bond-forming reactions.

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Results and Discussion

Synthesis: The synthesis of **1** is straightforward (Scheme 1). Treatment of $(ClBu_2SnOSnBu_2Cl)_2$[5] with four equivalents of $AgOSO_2C_8F_{17}$ (AgOPf) in acetone afforded **1** in a hydrat-
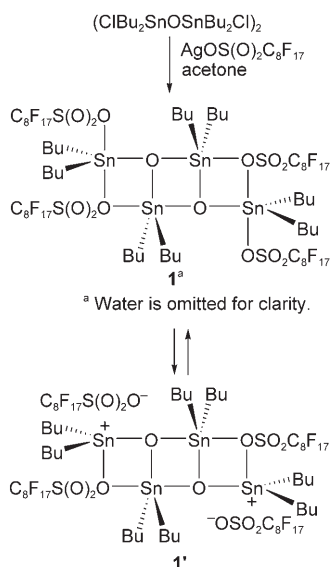
Scheme 1. Synthesis of perfluorooctanesulfonato distannoxane.

ed form $(PfOBu_2SnOSnBu_2OPf)_2 \cdot nH_2O$. This stands in strong contrast with the reaction with $AgOSO_2CF_3$ (AgOTf), which resulted in a skeletal change to furnish μ-hydroxo dimers **2** (Scheme 2).[6] Single-crystal X-ray analysis revealed a neutral structure for the butyl derivative **2a**, while a dicationic structure was found for the *tert*-butyl and 2-phenylbutyl derivatives, **2b** and **2c**, respectively. However, all compounds were found to dissociate into the ionic spe-
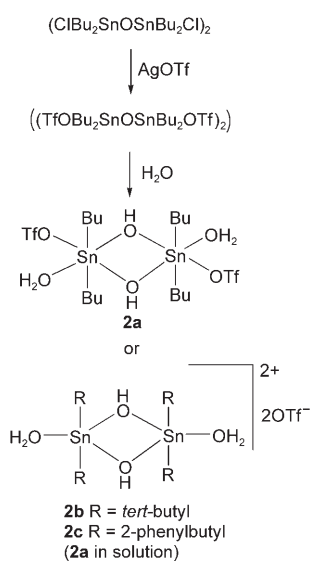
Scheme 2. Synthesis of cationic organotin compounds.

cies in CH_3CN on the basis of conductivity measurements. The hydration number of **1** is variable depending on the conditions. ^1H NMR spectroscopy (in dry CD_3CN) proved that the freshly prepared sample after recrystallization from EtOAc/hexane (1:3) contained approximately one H_2O molecule per each tin atom ($n = 4$); the water content increased up to $n = \approx 6$ (on the basis of ^1H NMR spectroscopy) upon standing in open air. Pumping in vacuo for two days at room temperature caused partial dehydration giving rise to $n \approx 0.5$. Elemental analysis of this sample was consistent with this composition.

Mononuclear compounds **3**–**5** were prepared analogously by treatment of R_2SnCl_2 (R = Bu, Me, Ph) with two equivalents of AgOPf in acetone (Scheme 3). These compounds were also obtained as hydrates, but the hydration number varied widely from 4 to 13 depending on the conditions. Although the parent peaks corresponding to **3** and **4** were confirmed by ESI-MS, no reliable combustion analyses were attained for these compounds. We therefore transformed the hydrated species to DMSO adducts. Addition of four equivalents of DMSO to a solution of **3**–**5** in diethyl ether afforded $[R_2Sn(DMSO)_4]^{2+} \cdot 2OPf^-$, **6**–**8**, which gave correct analytical data.

As seen from Schemes 1 and 2, the perfluorooctanesulfonate anion reacts with $(ClBu_2SnOSnBu_2Cl)_2$ quite differently from the triflate anion. The skeletal change to **2** with the latter anion is induced by facile hydrolysis of the putative bis(triflato)distannoxane, while **1** can resist the hydrolysis though being hydrated. The analogous facile hydrolysis attacks mononuclear organotin triflates, $R_nSn(OTf)_{4-n}$, leading to unidentifiable products, yet the corresponding perfluorooctanesulfonates **3**–**5** survive the hydrolysis. As such, the organotin perfluorooctanesulfonates are storable in open air, offering a great advantage over the organotin triflates from the operational point of view.

Scheme 3. Synthesis of diorganotin perfluorooctanesulfonates.

Characterization: A ^{119}Sn NMR spectrum of **1** exhibited two signals at $\delta = -162.5$ and -203.0 ppm in $[D_6]$acetone, diagnostic of the dimeric formulation,[7] while a single peak was observed for **3**–**5** consistent with the mononuclear structure (Table 1). Upon complexation with DMSO, the δ values experienced low-frequency shifts. The dicationic character of **6** was supported by appearance of its ^{119}Sn NMR signal ($\delta =$

Table 1. The ^{119}Sn NMR spectra of organotin perfluorooctanesulfonates in $[D_6]$acetone.

Compound	δ [ppm]	Compound	δ [ppm]
1	−162.5, −203.0	**6**	−338.1
3	−348.9	**7**	−303.3
4	−324.4	**8**	−501.3
5	−524.1		

−338.1 ppm) in the same region as that found for [Me$_2$Sn-(DMSO)$_4$]$^{2+}$·2 Ph$_4$B$^{−[8]}$ in [D$_6$]DMSO ($\delta = -336.0$ ppm). The ^{119}Sn NMR chemical shift of a dibutyltin dicationic species, [Bu$_2$Sn(H$_2$O)$_4$]$^{2+}$·2 ClO$_4$$^−$, was estimated by use of Bu$_2$SnO in aqueous HClO$_4$.[9] The δ values were plotted against various tin concentrations and extrapolation to the infinite dilution gave rise to $\delta = -294.0$ ppm, which is close to $\delta = -303.2$ ppm of **7**, indicative of dicationic nature of this compound. No significant differences in δ values between **3–5** and **6–8** suggest that the hydrated compounds also are considerably dissociated into the dicationic species, for example, [R$_2$Sn(H$_2$O)$_m$]$^{2+}$·2 OPf$^−$·n H$_2$O.

The conductivity measurements are consistent with the ionic dissociation (Table 2). A substantially large conductivity was observed for **1** in CH$_3$CN, but the molar conductivity

Table 2. Conductivities of organotin perfluorooctanesulfonates.[a]

Compound	Conductivity [μS cm^{-1}][b]	Compound	Conductivity [μS cm^{-1}][b]
1	256.5 (64.1)	**6**	218.0 (218.0)
3	129.9 (129.9)	**7**	197.1 (197.1)
4	125.5 (125.5)	**8**	231.8 (231.8)
5	118.1 (118.1)	**2a**	165.5 (82.8)

[a] In CH$_3$CN (1.0 mmol L^{-1}) at 25 °C. [b] The value given in parentheses is the molar conductivity (Λ) (μS cm^2 mol^{-1}).

is somewhat smaller than that of well-defined dicationic μ-hydroxo dimer **2a**. It follows that **1** is not totally but partially dissociated into the dicationic species like **1′** (Scheme 1).[10] Mononuclear compounds **3–5** exhibited larger molar conductivities, the magnitudes of which, however, are not large enough to assume the dicationic formulation because the corresponding DMSO complexes gave much greater values. It is reasonably concluded as a whole that the DMSO complexes **6–8** are virtually dicationic, while the hydrates species **3–5** are involved in equilibrium between associated and dissociated forms.

Previously, we advanced that the binding energies (ΔE values) of Lewis acid metal atoms with O$_2$$^{•−}$ can be correlated with the Lewis acidity of the metals.[11] Thus, we measured the ΔE values of the organotin perfluorooctanesulfonates, which are shown in Table 3 together with those of relevant organotin compounds for comparison. As expected, compounds **1** and **3–5** exhibited relatively large ΔE values.

Table 3. g_{zz} and ΔE values of ESR spectra of O$_2$$^{•−}$/organotin complexes.

Compound	g_{zz}	ΔE
1	2.0336	0.90
3	2.0333	0.90
4	2.0338	0.90
5	2.0343	0.88
6	2.0335	0.90
7	2.0342	0.88
8	2.0346	0.87
2a	2.0595	0.49
Bu$_2$Sn(OTf)$_2$[a]	2.0327	0.92
(C$_6$F$_5$)$_2$SnBr$_2$[a]	2.0336	0.89

[a] Reference [11].

Rather unexpectedly, however, the DMSO complexes **6–8** did not give rise to the significant decrease in the ΔE values. For example, the ΔE value of Sc(OTf)$_3$ changed from 1.00 to 0.72 upon complexation with hexamethyl phosphoramide (HMPA).[11] This may be reminiscent of weaker coordination of DMSO on the tin than that of HMPA on the scandium.

Another notable feature is unusual solubility of **1** and **3–5**. As given in Table 4, the solubility of these compounds in acetone, THF, EtOAc, CH$_3$CN, and MeOH is extraordinarily high amounting up to 3251 g L^{-1}; it is better to say that

Table 4. Solubility of organotin perfluorooctanesulfonates in organic solvents at 25 °C.

	Solubility [g L^{-1}]						
	1	**3**	**4**	**5**	**6**	**7**	**8**
acetone	3018	2447	1745	1973	2123	1646	98
THF	2908	2239	517	1323	22	81	0
EtOAc	1594	2569	2417	1155	17	33	0
MeOH	2643	3251	1878	2317	2114	2036	1137
CH$_3$CN	1245	3018	42	119	1971	1438	54
Et$_2$O	108	192	88	351	0	0	0
CH$_2$Cl$_2$	0	0	0	0	152	21	0
toluene	0	0	0	0	0	0	0
hexane	0	0	0	0	0	0	0

they are miscible with each other to form a slightly viscous liquid. They exhibit normal solubility in less polar Et$_2$O, but are not soluble in CH$_2$Cl$_2$, a quite surprising behavior because this solvent is usually the best solvent for similar organotin compounds. Consistently, they are not soluble in much less polar toluene and nonpolar hexane. Nevertheless, these compounds are also hydrophobic as is apparent from their insolubility in water. The long fluoroalkyl chain in the sulfonate ligand must be responsible for the hydrophobicity. Presumably, such amphiphilic nature is reflected on the unusual solubility in the polar organic solvents. Upon dissolving the organotin compounds in polar solvents, the solvent molecules can approach the coordination sphere of the tin to replace the hydrated water on account of the compatibility between them, and the resulting solvated species are highly soluble in the same polar solvents. By contrast, CH$_2$Cl$_2$ as well as hydrocarbons cannot have access to the tin atoms because of interference by the water against these hydrophobic solvents. It is concluded therefore that the organotin perfluorooctanesulfonates are neither hydrophilic nor lipophilic in their hydrated form, and accordingly they are not soluble in both strongly hydrophobic organic solvents and water. However, the water molecules are readily replaced by the polar organic solvents to generate the highly soluble solvated species.

It is reasonable to assume that the solubility decreases by formation of the highly cationic DMSO complexes. In fact, the solubility of the hydrated mononuclear species basically decreases upon formation of the DMSO complexes **6–8**. In particular, conversion of **5** to **8** induced a drastic decrease in solubility except in MeOH. By contrast, dibutyltin and di-

methyltin derivatives **4** and **5**, respectively, exhibited different behaviors. The solubility was greatly decreased in THF, EtOAc, and Et$_2$O, whereas only slightly in acetone, MeOH, and CH$_3$CN, or even increased occasionally. These compounds became slightly soluble in CH$_2$Cl$_2$ upon complex formation in contrast to the insoluble parent hydrates. The high solubility of these DMSO complexes might result from replacement of DMSO with polar solvent molecules. However, in ^{1}H NMR spectra in [D$_6$]acetone, the *S*-methyl proton signals of **6** and **7** experienced strong upfield shifts ($\Delta\delta$ relative to pure DMSO: -0.38 ppm for **6** and -0.52 ppm for **7**). As shown in Table 1, ^{119}Sn NMR spectra also gave rise to appreciable shifts upon complexation. These outcomes support the retention of the DMSO coordination in acetone.

Catalysis: The catalytic activities of **1** and **3** together with μ-hydroxo dimer **2a** as a control cationic species were assessed for various carbon–carbon bond-forming reactions. First, reactions of benzaldehyde (**9**) with nucleophiles, such as tetraallyltin (**10**), enol silyl ethers **11** and **12**, and ketene silyl acetals **13** and **14**, were scrutinized (Scheme 4). All reactions
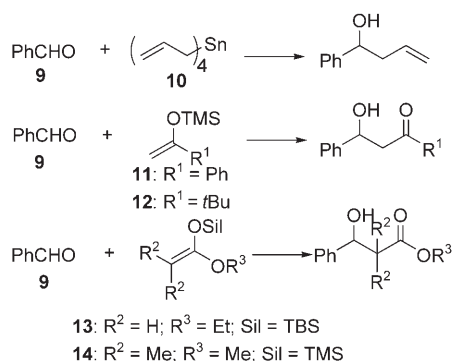
Scheme 4. Reaction of benzaldehyde with various nucleophiles catalyzed by **1**.

were carried out in the presence of **1** (0.5 mol%) or **3** and **2a** (1 mol%), and the yields of the respective reactions are compiled in Table 5. High yields were constantly attained with **1**, while the other catalysts resulted in much lower yields. Notably, the solvent, that is, CH$_3$CN, in these reactions was used as received. No dry solvent is needed, because of tolerance of **1** toward hydrolysis.[12,13] The low activity of **2a** is reasonable in terms of the criterion which we put forth previously: efficient carbon–carbon bond-forming reactions are effected by Lewis acid catalysts with the ΔE values lager than 0.88.[11] By contrast, rather low activity of **3** cannot be accommodated by this notion. We have no explicit explanation for this anomaly at present.

Then, the reactions of other substrates, such as acetophenone (**15**), bezaldehyde dimethyl acetal (**16**), and cyclohexenone (**17**), were examined under catalysis of **1** and **3** (Scheme 5, Table 6). As expected, acetophenone is less reactive than benzaldehyde and thus no reaction occurred with

Table 5. Yields [%] in reactions of benzaldehyde with stannyl and silyl nucleophiles catalyzed by organotin perfluorooctanesulfonates and **2a**.

| Nucleophile | Product | Catalyst | | |
		1[a]	**3**[g]	**2a**[g]
10	**18**	98[b]	59[h]	90[i]
11	**19**	81[c]	30	–
12	**20**	85[d]	27	75
13	**21**	91[e]	27	64
14	**22**	95[f]	25	67

[a] Reaction conditions: substrate (1.0 mmol); nucleophile (1.3 mmol); catalyst (0.05 mmol); solvent (3.0 mL); RT; 24 h. [b] **10** (0.3 mmol), **1** (0.005 mmol), THF, 12 h. [c] THF, 12 h. [d] THF, 6 h. [e] **1** (0.01 mmol), MeCN, 2 h. [f] **1** (0.01 mmol), MeCN, 3 h. [g] Reaction conditions: substrate (1.0 mmol); nucleophile (1.3 mmol); Catalyst (0.01 mmol); MeCN (3 mL); RT; 24 h. [h] **10** (0.3 mmol). [i] **10** (0.3 mmol), 4 h.
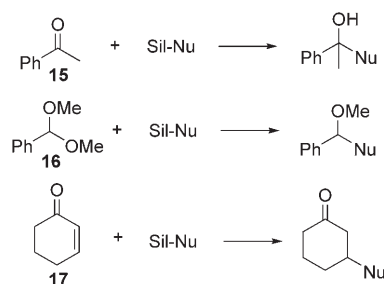
Scheme 5. Reaction of acetophenone, benzaldehyde, and cyclohexenone with silyl nucleophiles catalyzed by **1**.

Table 6. Yields [%] in reaction of **15**, **16**, and **17** with stannyl and silyl nucleophiles catalyzed by organotin perfluorooctanesulfonates.[a]

| Substrate | Nucleophile | Product | Catalyst[b] | |
			1	**3**
15	**10**	**23**	87[c]	19[k]
	11		nr	nr
	12		nr	nr
	13	**24**	87[d]	21
	14	**25**	90[e]	20
16	**10**		nr	nr
	11	**25**	91[f]	37
	12	**27**	93[f]	34
	13	**28**	50[g]	21
	14	**29**	93[h]	35
17	**10**		nr	nr
	11	**30**	71[i]	29
	13	**31**	–	25
	14	**32**	95[j]	43

[a] Reaction conditions: substrate (1.0 mmol); nucleophile (1.3 mmol); catalyst (0.01 mmol); CH$_3$CN (3.0 mL); RT; 24 h. [b] nr=no reaction. [c] **10** (0.4 mmol); **1** (0.05 mmol); THF (3.0 mL). [d] 14 h. [e] **1** (0.02 mmol); 10 h. [f] 13 h. [g] 0°C, 16 h. [h] **1** (0.02 mmol); 0°C; 8 h. [i] **1** (0.02 mmol); 0°C; 16 h. [j] 6 h. [k] **10** (0.4 mmol).

the enol silyl ethers **11** and **12**; however, the other reactions exhibited the similar tendency of the catalytic activity to the reaction with **9**. Probably, the nucleophilicity of the enol silyl ethers is very strong. Finally, reactions of the acetal and cyclohexenone substrates **16** and **17** were carried out. No reactions occurred with tetraallyltin, which usually exhibits highest reactivity, whereas high yields were obtained in the

other reactions catalyzed by **1**, except the reaction of **16** with **13**.

Conclusion

The reactions of 1,3-dichloro-1,1,3,3-tetrabutyldistannoxane and dialkyltin dihalides with silver perfluorooctanesulfonate provided the corresponding sulfonates as hydrates. The hydrated mononuclear species could be converted to DMSO complexes. ^{119}Sn NMR spectroscopy and conductivity measurements indicated the ionic dissociation of these compounds in solution. The ionic dissociation together with facile hydration probably causes the unusual solubility. The Lewis acidity of these compounds was found to be high among organotin derivatives. In contrast to well-known organotin triflates, these compounds suffered no hydrolysis when stored in open air. The high catalytic activity of the distannoxane **1** was exemplified for various carbon–carbon bond-forming reactions. The stability and catalytic activity of organotin perfluorooctanesulfonates will find a wide range of applications.

Experimental Section

General: All reactions were carried out under an atmosphere of nitrogen with freshly distilled solvents, unless otherwise noted. Tetrahydrofuran (THF) was distilled from sodium/benzophenone. Acetonitrile was distilled from CaH$_2$. Silica gel (Daiso gel IR-60) was used for column chromatography. NMR spectra were recorded at 25 °C on JEOL Lambda 300 and JEOL Lambda 500 instruments and calibrated with tetramethylsilane (TMS) as an internal reference and tetramethylstannane (Me$_4$Sn) as an external reference. Mass spectra were recorded on Platform II single quadrupole mass spectrometer (Micromass, Altrinchan, UK). Elemental analyses were performed by the Perkin–Elmer PE 2400. Conductivity was measured on HORIBA conductivity meter DS-12.

ESR measurements: A quartz ESR tube (4.5 mm i.d.) containing an oxygen-saturated solution of dimeric 1-benzyl-1,4-dihydronicotinamide [(BNA)$_2$] in MeCN (1.0×10^{-3} M) and a Lewis acid (1.0×10^{-3} M) was irradiated in the cavity of the ESR spectrometer with the focused light of a 1000 W high-pressure Hg lamp through an aqueous filter. Dimeric (BNA)$_2$, which used as an electron donor to reduce oxygen, was prepared according to the literature.[14–16] The ESR spectra of O$_2$·$^-$ Lewis acid complexes in frozen MeCN were measured at 143 K with a JEOL X-band spectrometer (JES-RE1XE) using an attached VT (variable temperature) apparatus under nonsaturating microwave power conditions. The g values were calibrated precisely with an Mn^{2+} marker, which was used as a reference.

Preparation of C$_8$F$_{17}$SO$_3$Ag:[17] Commercially available C$_8$F$_{17}$SO$_3$H was not pure, but used as received. A suspension of C$_8$F$_{17}$SO$_3$H (1.00 g; assuming it was pure, it corresponded to 2.0 mmol) and Ag$_2$CO$_3$ (331 mg, 1.2 mmol) in water (15 mL) was stirred in the dark at 100 °C for 1 h, and then at RT for 1 h. After filtration, the solids obtained were washed with ice-water till the filtrate turned neutral. The solids were dissolved in acetone and filtered. After the filtrate had been evaporated, the crude solids were subjected to recrystallization from THF (1.5 mL) and Et$_2$O (4 mL) to afford C$_8$F$_{17}$SO$_3$Ag in a pure form (484 mg, 40 %). ^{19}F NMR (282 MHz, [D$_6$]acetone): $\delta = -79.20$ (m, 3F), -112.29 (m, 2F), -118.59 (m, 2F), -119.72 to -120.00 (m, 6F), -120.85 (m, 2F), -124.25 to -124.38 ppm (m, 2F).

Preparation of (PfOBu$_2$SnOSnBu$_2$OPf)$_2$ (1): A solution of (ClBu$_2$SnOSnBu$_2$Cl)$_2$[5] (553 mg, 0.5 mmol) and silver perfluorooctanesulfonate

(1.214 g, 2.0 mmol) in acetone (10 mL) was stirred at RT for 3 h in the dark. After filtration, the filtrate was evaporated. The crude products were dissolved in acetone (2 mL), and the solution was added dropwise to CH$_2$Cl$_2$ (50 mL). Precipitates were separated by filtration and dried in vacuo. Recrystallization of the solids from AcOEt (4 mL)/hexane (10 mL) afforded **1** as a hydrate (1.05 g, 71 %). ^{1}H NMR (300 MHz, [D$_6$]acetone): $\delta = 0.93$ (t, 24H), 1.37–1.41 (m, 16H), 1.63–1.78 (m, 32H), 4.64 ppm (s, 9.8H); ^{19}F NMR (282 MHz, [D$_6$]acetone): $\delta = -79.21$ (m, 24F), -112.21 (m, 16F), -118.59 (m, 16F), -119.74 to -119.99 (m, 48F), -120.85 (m, 16F), -124.27 to -124.37 ppm (m, 16F); ^{119}Sn NMR (111 MHz, acetone-d_6): $\delta = -162.54$, -202.95 ppm; IR (Nujol mull): $\tilde{v} = 3389$, 2959, 2925, 2854, 1634, 1329, 1240, 1153, 1074, 1037, 940, 747, 687 cm^{-1}; elemental analysis calcd (%) for C$_{64}$H$_{76}$F$_{68}$O$_{16}$S$_4$Sn$_4$ (as dihydrate): C 25.65, H 2.56; found: C 25.63, H 2.51 (after pumping for 2 days).

Preparation of Bu$_2$Sn(OSO$_2$C$_8$F$_{17}$)$_2$ (3): An solution of Bu$_2$SnCl$_2$ (304 mg, 1.0 mmol) and silver perfluorooctanesulfonate (1.214 g, 2.0 mmol) in acetone (10 mL) was stirred at RT for 3 h in the dark. After filtration, the filtrate was evaporated. The crude products were dissolved in acetone (2 mL) and the solution was added dropwise to CH$_2$Cl$_2$ (50 mL). Precipitates were separated by filtration and dried in vacuo. Recrystallization of the solids from AcOEt (8 mL)/hexane (1 mL) afforded **3** as a hydrate (850 mg, 69 %). ^{1}H NMR (300 MHz, [D$_6$]acetone): $\delta = 0.94$ (t, 6H), 1.37–1.41 (m, 4H), 1.69–1.80 (m, 8H), 3.52 ppm (s, 6.1H); ^{19}F NMR (282 MHz, [D$_6$]acetone): $\delta = -79.20$ (m, 6F), -112.27 (m, 4F), -118.61 (m, 4F), -119.74 to -119.99 (m, 12F), -120.85 (m, 4F), -124.27 to -124.37 ppm (m, 4F); ^{119}Sn NMR (111 MHz, [D$_6$]acetone): $\delta = -348.89$ ppm: IR (Nujol mull): $\tilde{v} = 3357$, 2955, 2924, 2853, 1650, 1331, 1203, 1152, 1075, 1038, 942, 706 cm^{-1}; ESI-MS: m/z calcd for C$_{24}$H$_{18}$F$_{34}$NaO$_6$S$_2$Sn [M+Na]$^+$: 1254.89; found: 1254.42.

Preparation of compounds Ph$_2$Sn(OSO$_2$C$_8$F$_{17}$)$_2$ (5) and Me$_2$Sn-(OSO$_2$C$_8$F$_{17}$)$_2$ (4): Compounds **4** and **5** were obtained by using a similar procedure described above for compound **3**.

Data for Ph$_2$Sn(OSO$_2$C$_8$F$_{17}$)$_2$ (5): Yield: 61 %; ^{1}H NMR (300 MHz, [D$_6$]acetone): $\delta = 6.30$ (s, 10.8H), 7.51 (m, 6H), 8.02 ppm (m, 4H); ^{19}F NMR (282 MHz, [D$_6$]acetone): $\delta = -79.20$ (m, 6F), -112.38 (m, 4F), -118.62 (m, 4F), -119.75 to -119.99 (m, 12F), -120.84 (m, 4F), -124.25 to -124.35 ppm (m, 4F); ^{119}Sn NMR (111 MHz, [D$_6$]acetone): $\delta = -524.07$ ppm; IR (Nujol mull): $\tilde{v} = 3411$, 1650, 1332, 1268, 1235, 1204, 1151, 1075, 1037, 939, 695 cm^{-1}.

Data for Me$_2$Sn(OSO$_2$C$_8$F$_{17}$)$_2$ (4): Yield: 66 %; ^{1}H NMR (300 MHz, [D$_6$]acetone): $\delta = 1.32$ (s, 6H), 5.91 ppm (s, 5.4H); ^{19}F NMR (282 MHz, [D$_6$]acetone): $\delta = -79.21$ (m, 6F), -112.44 (m, 4F), -118.66 (m, 4F), -119.75 to -120.00 (m, 12F), -120.86 (m, 4F), -124.27 to -124.39 ppm (m, 4F); ^{119}Sn NMR (111 MHz, [D$_6$]acetone): $\delta = -324.43$ ppm; IR (Nujol mull): $\tilde{v} = 3252$, 1650, 1328, 1241, 1205, 1152, 1076, 1041, 940, 742 cm^{-1}; ESI-MS: m/z calcd for C$_{18}$H$_6$F$_{34}$NaO$_6$S$_2$Sn [M+Na]$^+$: 1170.79; found: 1170.26.

Preparation of Bu$_2$Sn(OSO$_2$C$_8$F$_{17}$)$_2$(DMSO)$_4$ (6): A solution of **3** (1.231 mg, 1.0 mmol) and DMSO (313 mg, 4.0 mmol) in Et$_2$O (10 mL) was stirred at RT for 1 h in the dark. After filtration, the solids were washed with AcOEt. Recrystallization of the solids from CH$_2$Cl$_2$/AcOEt afforded **6** in a pure form (1.36 g, 88 %). ^{1}H NMR (300 MHz, [D$_6$]acetone): $\delta = 0.91$ (t, 6H), 1.36–1.42 (m, 4H), 1.72–1.84 (m, 8H), 2.91 ppm (s, 24H); ^{19}F NMR (282 MHz, [D$_6$]acetone): $\delta = -79.19$ (m, 6F), -112.52 (m, 4F), -118.57 (m, 4F), -119.70 to -119.97 (m, 12F), -120.82 (m, 4F), -124.26 to -124.35 ppm (m, 4F); ^{119}Sn NMR (111 MHz, [D$_6$]acetone): $\delta = -338.05$ ppm; IR (Nujol mull): $\tilde{v} = 2954$, 2923, 2854, 1329, 1258, 1204, 1150, 986, 931 cm^{-1}; elemental analysis calcd (%) for C$_{32}$H$_{42}$F$_{34}$O$_{10}$S$_6$Sn: C 24.90, H 2.74; found: C 24.65, H 2.61.

Preparation of compounds Ph$_2$Sn(OSO$_2$C$_8$F$_{17}$)$_2$(DMSO)$_4$ (8) and Me$_2$Sn(OSO$_2$C$_8$F$_{17}$)$_2$(DMSO)$_4$ (7): Compounds **7** and **8** were obtained by using a similar procedure described above for compound **6**.

Data for Ph$_2$Sn(OSO$_2$C$_8$F$_{17}$)$_2$(DMSO)$_4$ (8): Yield: 80 %; ^{1}H NMR (300 MHz, [D$_6$]acetone): $\delta = 2.98$ (s, 24H), 7.51 (m 6H), 7.99 ppm (m, 4H); ^{19}F NMR (282 MHz, [D$_6$]acetone): $\delta = -79.19$ (m, 6F), -112.77 (m, 4F), -118.58 (m, 4F), -119.69 to -119.99 (m, 12F), -120.84 (m, 4F), -124.25 to -124.37 ppm (m, 4F); ^{119}Sn NMR (111 MHz, [D$_6$]acetone):

$\delta = -501.30$ ppm; IR (Nujol mull): $\tilde{v} = 1329$, 1243, 1216, 1152, 1023, 942 cm^{-1}; elemental analysis calcd (%) for $C_{36}H_{34}F_{34}O_{10}S_6Sn$: C 27.30, H 2.16; found: C 27.43, H 2.23.

Data for $Me_2Sn(OSO_2C_8F_{17})_2(DMSO)_4$ *(7)*: Yield: 92%; ^1H NMR (300 MHz, [D$_6$]acetone): $\delta = 1.19$ (s, 6H), 3.04 ppm (s, 24H); ^{19}F NMR (282 MHz, [D$_6$]acetone): $\delta = -79.19$ (m, 6F), -112.56 (m, 4F), -118.58 (m, 4F), -119.70 to -119.99 (m, 12F), -120.84 (m, 4F), -124.25 to -124.37 (m, 4F); ^{119}Sn NMR (111 MHz, [D$_6$]acetone): $\delta = -303.29$ ppm; IR (Nujol mull): $\tilde{v} = 1329$, 1283, 1242, 1202, 1151, 1073, 1040, 993, 941 cm^{-1}; elemental analysis calcd (%) for $C_{26}H_{30}F_{34}O_{10}S_6Sn$: C 21.40, H 2.07; found: C 21.37, H 1.70.

Determination of a hydration number of 1 (representative): Molecular sieves (4 Å, 11 g, dried at 190 °C for 0.5 h under reduced pressure) were added to [D$_3$]acetonitrile (25 g), and the mixture was kept under argon overnight. In this [D$_3$]acetonitrile, water was not detected by ^1H NMR spectroscopy. The dehydrated [D$_3$]acetonitrile (0.6 mL) was added to a freshly prepared **1** (10 mg, recrystallized from AcOEt/hexane followed by drying under reduced pressure for 2 h), and the solution was analyzed by ^1H NMR spectroscopy. Based on integrations of CH$_3$ of butyl ($\delta = 0.93$ ppm (t, 24H)) and H$_2$O ($\delta = 3.66$ ppm (s, 8.08H)), a hydration number was determined to be about 1.01 per each Sn atom.

According the same procedure, hydration numbers were determined for the following organotin compounds which had been dried under reduced pressure overnight and kept in the air (Table 7).

Table 7. Hydration numbers for compounds **1** and **3–5**.

	Hydration number per Sn atom[a]		
	5 min	1 day	3 days
(PfOBu$_2$SnOSnBu$_2$OPf)$_2$ (**1**)	0.13	1.28	1.30
Bu$_2$Sn(OSO$_2C_8F_{17}$)$_2$ (**3**)	0.24	3.06	3.20
Ph$_2$Sn(OSO$_2C_8F_{17}$)$_2$ (**5**)	1.46	11.0	12.7
Me$_2$Sn(OSO$_2C_8F_{17}$)$_2$ (**4**)	1.12	6.70	6.90

[a] After keeping in the air.

Solubility determination of 1 (representative): AcOEt (0.5 mL) was placed in a test tube; compound **1** was added gradually at RT. When the amount of added **1** exceeded 797.2 mg, insoluble **1** appeared. Based on this data, solubility of $(C_8F_{17}SO_3)Bu_2SnOSnBu_2(OSO_2C_8F_{17})$ was determined to be 1594 g L^{-1}. According to the same procedure, other solubilities were determined.

Allylation of benzaldehyde with 10 catalyzed by 1 (representative): PhCHO (106 mg, 1.0 mmol) and **10** (85 mg, 0.3 mmol) were added to a solution of **1** (74 mg, 0.05 mmol) in THF (3 mL), and the mixture was stirred at RT for 12 h. After water (2 mL) was added, the mixture was stirred at RT for 1 h. After usual workup with AcOEt/water, the combined organic layer was evaporated. The crude product was subjected to GC analysis to determine a GC yield (98%).

Mukaiyama–aldol reaction of benzaldehyde with 11 catalyzed by 1 (representative): PhCHO (106 mg, 1.0 mmol) and **11** (250 mg, 1.3 mmol) were added to a solution of **1** (74 mg, 0.05 mmol) in THF (3 mL), and the mixture was stirred at RT for 12 h. After water (2 mL) had been added, the mixture was stirred at RT for 1 h. After usual workup with AcOEt/water, the combined organic layer was evaporated. The crude product was subjected to column chromatography on silica gel (5:1 hexane/AcOEt) to afford the desired compound in a pure form (81% yield).

Aldehydes such as benzaldehyde, **15–17** and nucleophiles **10–14** are commercially available. All products have been reported: **18**,[18] **19**,[19] **20**,[20] **21**,[21] **22**,[22] **23**,[23] **24**,[20] **25**,[24] **26**,[25] **27**,[26] **28**,[27] **29**,[28] **30**,[29] **31**,[30] and **32**.[31]

[1] a) A. Orita, J. Otera, in *Main Group Metals in Organic Synthesis Vol. 2* (Eds.: H. Yamamoto, K. Oshima), Wiley-VCH, Weinheim, **2004**, p. 621; b) M. Pereyre, J.-P. Quintard, A. Rahm, *Tin in Organic Synthesis*, Butterworths, London, **1987**.

[2] a) J. Otera, in *Advances in Detailed Reaction Mechanisms, Vol. 3* (Ed.: J. M. Coxon), JAI, London, **1994**, p. 167; b) J. Otera, in *Encyclopedia of Reagents for Organic Synthesis, Vol. 2* (Ed.: L. A. Paquette), Wiley, Chichester, **1995**, p. 1140; c) O. A. Mascaretti, R. L. E. Furlán, *Aldrichimica Acta* **1997**, *30*, 55; d) J. Otera, *Acc. Chem. Res.* **2004**, *37*, 288.

[3] a) T. Sato, J. Otera, H. Nozaki, *J. Am. Chem. Soc.* **1990**, *112*, 901; b) T. Sato, Y. Wakahara, J. Otera, H. Nozaki, *Tetrahedron Lett.* **1990**, *31*, 1581; c) T. Sato, Y. Wakahara, J. Otera, H. Nozaki, S. Fukuzumi, *J. Am. Chem. Soc.* **1991**, *113*, 4028; d) T. Sato, Y. Wakahara, J. Otera, H. Nozaki, *Tetrahedron* **1991**, *47*, 9773; e) T. Sato, J. Otera, H. Nozaki, *J. Org. Chem.* **1993**, *58*, 4971.

[4] X. Li, A. Kurita, S. Man-e, A. Orita, J. Otera, *Organometallics* **2005**, *24*, 2567.

[5] Commercially available from Aldrich Chemical Co. Inc.

[6] a) K. Sakamoto, Y. Hamada, H. Akashi, A. Orita, J. Otera, *Organometallics* **1999**, *18*, 3555; b) K. Sakamoto, H. Ikeda, H. Akashi, T. Fukuyama, A. Orita, J. Otera, *Organometallics* **2000**, *19*, 3242.

[7] a) J. Otera, T. Yano, K. Nakashima, R. Okawara, *Chem. Lett.* **1984**, 2109; b) T. Yano, K. Nakashima, J. Otera, R. Okawara, *Organometallics* **1985**, *4*, 1501.

[8] V. G. Kumar Das, W. Kitching, *J. Organomet. Chem.* **1967**, *10*, 59.

[9] H. N. Farrer, M. M. McGrady, R. S. Tobias, *J. Am. Chem. Soc.* **1965**, *87*, 5019.

[10] It is not likely that all PfO ligands are dissociated to give highly positive species, and thus the structure **1′** represents merely one possible ionic species.

[11] K. Ohkubo, S. C. Manson, A. Orita, J. Otera, S. Fukuzumi, *J. Org. Chem.* **2003**, *68*, 4720.

[12] The allylation with **10** catalyzed by HCl in H$_2$O/THF: a) A. Yanagisawa, H. Inoue, M. Morodome, H. Yamamoto, *J. Am. Chem. Soc.* **1993**, *115*, 10356; b) A. Yanagisawa, M. Morodome, H. Nakashima, H. Yamamoto, *Synlett* **1997**, 1309.

[13] Mukaiyama–aldol reactions in water: a) S. Kobayashi, K. Manabe, *Acc. Chem. Res.* **2002**, *35*, 209; b) K. Manabe, S. Kobayashi, *Chem. Eur. J.* **2002**, *8*, 4095, and references therein.

[14] K. Wallenfels, M. Gellerich, *Chem. Ber.* **1959**, *92*, 1406.

[15] M. Patz, Y. Kuwahara, T. Suenobu, S. Fukuzumi, *Chem. Lett.* **1997**, 567.

[16] S. Fukuzumi, T. Suenobu, M. Patz, T. Hirasaka, S. Itoh, M. Fujitsuka, O. Ito, *J. Am. Chem. Soc.* **1998**, *120*, 8060.

[17] G. M. Whitesides, F. D. Gutowski, *J. Org. Chem.* **1976**, *41*, 2882.

[18] Y.-Z. Jin, N. Yasuda, H. Furuno, J. Inanaga, *Tetrahedron Lett.* **2003**, *44*, 8765.

[19] T. Nakagawa, H. Fujisawa, T. Mukaiyama, *Chem. Lett.* **2003**, *32*, 462.

[20] J. Chen, K. Sakamoto, A. Orita, J. Otera, *Synlett* **1996**, 877.

[21] J.-X. Chen, J. Otera, *Tetrahedron* **1997**, *53*, 14275.

[22] S.-L. Chen, S.-J. Ji, T.-P. Loh, *Tetrahedron Lett.* **2004**, *45*, 375.

[23] R. Hamasaki, Y. Chounan, H. Horino, Y. Yamamoto, *Tetrahedron Lett.* **2000**, *41*, 9883.

[24] G. Wenke, E. N. Jacobsen, G. E. Totten, A. C. Karydas, Y. E. Rhodes, *Synth. Commun.* **1983**, *13*, 449.

[25] H. Ishitani, M. Iwamoto, *Tetrahedron Lett.* **2003**, *44*, 299.

[26] J.-X. Chen, K. Sakamoto, A. Orita, J. Otera, *Tetrahedron* **1998**, *54*, 8411.

[27] K. Saigo, M. Osaki, T. Mukaiyama, *Chem. Lett.* **1976**, 769.

[28] W.-D. Z. Li, X.-X. Zhang, *Org. Lett.* **2002**, *4*, 3485.

[29] T.-P. Loh, L.-L. Wei, *Tetrahedron* **1998**, *54*, 7615.

[30] T. Inokuchi, Y. Kurokawa, M. Kusumoto, S. Tanigawa, S. Takagishi, S. Torii, *Bull. Chem. Soc. Jpn.* **1989**, *62*, 3739.

[31] T. Mukaiyama, T. Nakagawa, H. Fujisawa, *Chem. Lett.* **2003**, *32*, 56.