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Synthesis and characterization of fluoroalkyldistannoxanes

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Abstract

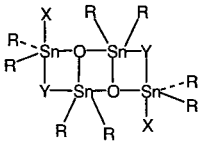
1,3-Disubstituted tetrakis(fluoroalkyl)distannoxanes ($XRf_2SnOSnRf_2Y)_2$ ($Rf = C_6F_{13}C_2H_4$, $C_4F_9C_2H_4$; X, Y = Cl, Br, NCS) were synthesized from readily available dibenzyltin dibromide. The dimeric formulation of these compounds that was confirmed by ^{119}Sn-NMR spectra gave rise to a structure in which the metalloxane core is covered by the surface fluorophilic alkyl groups. Thus, these compounds exhibited high solubility in fluorocarbon solvents and large partition coefficients for FC-72 against common organic solvent.

Keywords: Fluoroalkyldistannoxanes; Partition coefficients; Alkyl groups

1. Introduction

Fluorous biphase technology has received extensive attention from the viewpoint of environmentally-benign chemical process [1]. A variety of reagents and catalysts workable under fluorous biphasic conditions have been developed. In this context, Curran and his coworkers proved fluoroalkyltin hydrides [2], aryls [3], allyl [4], and oxides [5] to be highly useful.

1,3-Disubsituted tetraalkyldistannoxanes (**1**) (R = alkyl) are unique in that they are soluble in most organic solvents despite involving a large metalloxane core [6]. Such high solubility is attributable to a ladder structure resulting from dimerization as shown below. The inorganic core is surrounded by eight alkyl groups which render the molecule hydrophobic [7]. This led us to postulate that the compound would become soluble in fluorocarbon solvents if the surface alkyl groups were replaced by fluoroalkyl groups. Endowment of fluorophilic character to the distannoxanes seemed to us of great promise for exploring novel Lewis acid catalysts useful in the fluorous biphase technology. In fact, we disclosed preliminarily that $[Cl(C_6F_{13}C_2H_4)_2SnOSn(C_2H_4C_6F_{13})_2Cl]_2$ (**1a**, $R = C_6F_{13}C_2H_4$) was highly soluble in fluorocarbons and served as an excellent catalyst for fluorous biphasic transesterification (Fig. 1) [8]. Accordingly, further exploitation of relevant compounds in this category is expected to expand the synthetic scope of this technology. Herein, is described the full account on the synthesis and characterization of 1,3-disubstituted tetrakis(fluoroalkyl)-distannoxanes.



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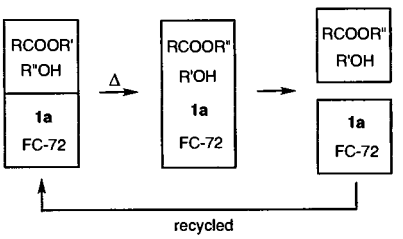

Fig. 1. Fluorous biphasic transesterification with fluoroalkyldistannoxaenes.

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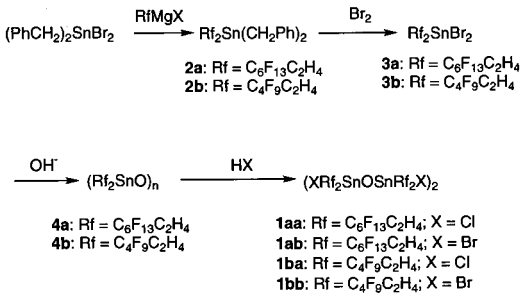
2. Results and discussion

The synthetic route for the fluoroalkyldistannoxanes is shown in Scheme 1. Treatment of dibenzyltin dibromide that can be readily obtained from benzyl bromide and tin powder [9] with RfMgX ($Rf = C_6F_{13}C_2H_4$ or $C_4F_9C_2H_4$) furnished tetraalkyltins **2** in 80–99% yield. Bromination of **2** (94–95% yield) followed by alkaline hydrolysis (92–93% yield) provided oxides **4**. These compounds were amorphous solids like other organotin oxides and difficult to obtain in analytically pure form. Previously, **4a** had been prepared by Curran et al. according to Eq. (1)[5]. They suggested this

$$(C_6F_{13}C_2H_4)_2SnPh_2 \rightarrow (C_6F_{13}C_2H_4)_2Sn(OCOCH_2Cl)_2 \rightarrow \mathbf{4a} \quad (1)$$

compound to be oligomeric, yet a single ^{119}Sn resonance (δ −59.1 in $CDCl_3$) was observed. Our compound, on the other hand, exhibited many (ca. 15) signals in the region between −168 and −233 ppm. Probably, the different preparative methods had resulted in different degree and mode of oligomerization. The ^{119}Sn-NMR of **4b** exhibited a similar pattern as **4a**. With the assumption that the desired oxides had been formed, we treated **4** with a slightly excess of aqueous HCl in acetone. 1,3-Dichlorodistanoxanes **1aa** and **1ba** were obtained in 85 and 84% yields, respectively. Treatment of dialkyltin oxide and dialkyltin dihalide in a 1:1 ratio, a very common procedure to arrive at 1,3-dichlorodistannoxanes [10], did not work in the present cases. The use of aqueous HBr in stead of HCl afforded the 1,3-dibromo derivatives **1ab** and **1bb** in 78–84% yields.

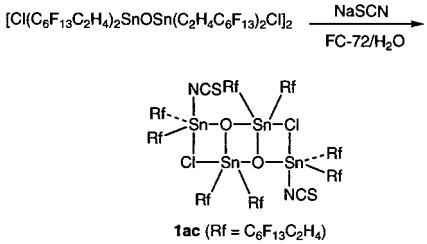


Scheme 1.

Table 1
Partition coefficients (PC) of **1aa** in the binary FC-72/organic solvent system at room temperature

Solvent	Distribution		PC
	FC-72	Organic solvent	
$C_6H_5CH_3$	100	0	>100
C_6H_6	100	0	>100
CH_2Cl_2	99	1	99
CH_3OH	98	2	49
C_3H_6O	97	3	32
THF	96	4	24

An FC-72 (perfluorohexanes, 3 M) solution of **1aa** was combined with aqueous solution of NaSCN, and the mixture was stirred at room temperature for 20 h. Only the terminal chlorine atoms were replaced to give **1ac** (Eq. (2)). The structure of this compound is apparent from IR spectrum. Appearance of ν(N≡C) at 2065 cm^{-1} indicates the presence of a terminal NCS group since this group at the bridging position should give the N≡C stretching band at around 1960 cm^{-1} [11]. The bridging chlorine never underwent substitution even by exposing **1aa** to a large excess amount of NaSCN, a quite different outcome from conventional tetraalkyldistannoxanes which usually give 1,3-diisothiocyanato derivatives upon treatment with two equivalents of NaSCN [10]. In 1,3-dichlorotetraalkyldistannoxanes, the bonds between tins and bridging chlorine are rather weak as is evident from ionic bonding mode on the basis of X-ray analysis [12]. On the hand, it is assumed that the dimeric association in **1aa** is tight because the surface fluoroalkyl groups induce contraction of the dimerized structure due to incompatibility of these groups with organic surroundings (vide infra).



(2)

All fluoroalkyldistannoxanes thus prepared were isolated as crystals, yet they were not obtained in a suitable form for X-ray analysis. However, ^{119}Sn-NMR spectra gave rise to two distinct singlets diagnostic of characteristic dimeric distannoxane formulation [13]. Moreover, broadening of one of the ^{119}Sn signals observed for **1ac** (Section 3) confirms the bonding of the NCS group to tin [13].

As expected, these compounds are sparingly soluble in common organic solvents except acetone and ethyl acetate. The solubility of **1aa** (g l^{-1}) at room temperature is as follows: toluene, benzene, ≪1; hexane, <1; CH_2Cl_2, ca. 1; methanol, 2; acetonitrile, 9; acetone, 40; ethyl acetate, 48. On the other hand, this compound is well soluble in fluorocarbon solvents such as FC-72, FC-40, and octafluorocyclopentene: for example, solubility in FC-72 is 41 g l^{-1} at room temperature. Next, we determined the partition coefficients of this compound between FC-72/organic solvent as given in Table 1 [14].

The perfect bias into the FC-72 phase against toluene and benzene was revealed consistent with the previous

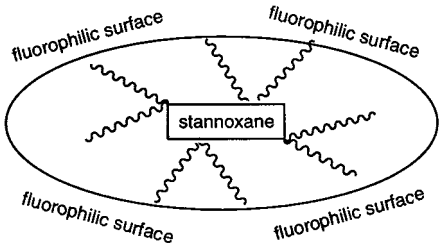


Fig. 2. Double layered structure of fluoroalkyldistannoxane.

results where quantitative recovery of the catalyst was attained in the fluorous biphasic transesterification using the FC-72/toluene binary system [8]. The high partition coefficients were also found with CH_2Cl_2, CH_3OH, and THF. The value for acetone (32) is rather surprising because the solubility of **1aa** in pure FC-72 and acetone is comparable. Apparently, the fluorophilic character of **1aa** is responsible for the highly biased distribution. Further, unique solubility is highlighted by comparison with $(C_6F_{13}C_2H_4)_2SnO$ (**4a**). According to Curran et al., partition coefficients of this compound are as follows: toluene, 1.9; CH_2Cl_2, 1.7; CH_3CN, 0.28 [5]. On account of this relatively low partition coefficients, repeated washings were necessary for recovery of the oxide from the reaction mixture in fluorous biphasic bezoylation of diols. By contrast, **1aa** was recovered in 100% without any sign of decomposition from the 1:1 FC-72/toluene binary system in our transesterification [8]. It follows therefore, that the double layered structure composed of the surface fluoroalkyl groups and the stannoxane core renders **1aa** completely fluorophilic (Fig. 2) while the wrapping of the inorganic moiety by the fluoroalkyl groups may be insufficient in **4a**. It should be noted that **1ab** exhibited the similar solubility to that of **1aa**.

The partition coefficients of **1ba** and **1bb** are given in Table 2. These compounds are also virtually fluorophilic, yet the degree is somewhat lower than that of **1aa**. This is quite reasonable in terms of the shorter fluoroalkyl chain length and clearly demonstrates the crucial role of the fluoroalkyl groups for the fluorophilicity.

In summary, a variety of 1,3-disubstituted tetrakis(fluoroalkyl)distannoxanes were synthesized. These compounds are more tightly associated leading to dimerization than normal distannoxanes and possess unique solubility in fluorocarbon solvents. The applications of these compounds as Lewis acid catalysts in fluorous biphase system are in progress.

3. Experimental

THF and Et_2O were distilled from Na–benzophenone. CH_3CN, $CHCl_3$, CH_2Cl_2 and CH_3COCH_3 were distilled from CaH_2. FC-72 (perfluorohexane, 3 M) was used without purification. Silica gel (Daiso gel IR-60) was used for column chromatography. NMR spectra were recorded at 25 °C on Brucker ARX-400, JEOL Lambda 300 and JEOL Lambda 500 instruments and calibrated with Me_4Si, trifluoromethylbenzene or Me_4Sn as an internal standard. Mass spectra were recorded on JEOL MStation JMS-700, Shimadzu/Kratos MALDI 4 and Platform II single quadrupole mass spectrometers (Micromass, Altrinchan, UK). Elemental analyses were performed by the Perkin–Elmer PE 2400.

3.1. Preparation of $(PhCH_2)_2SnBr_2$ [15]

In a 300 ml two neck-flask, a mixture of tin powder (17.8 g, 0.15 mol), water (1 ml) and $C_6H_5CH_3$ (150 ml) was heated to reflux with stirring, and BnBr (26.6 g, 0.15 mol) was added slowly with syringe. After the reaction mixture had been heated under reflux for 3 h, the reaction mixture was cooled and filtered. The obtained solid was dissolved in CH_3COCH_3 and filtered to remove tin powder. The filtrate was evaporated, and the residue was recrystallized from EtOAc to afford $(PhCH_2)_2SnBr_2$ (60.7 g, 88%,). M.p. 135–136 °C.

3.2. Preparation of *2a* and *2b*

Under Ar, $C_6F_{13}C_2H_4I$ (14.22 g, 30 mmol) in dry Et_2O (20 ml) was added dropwise to a stirring suspension of Mg turnings (0.826 g, 34 mmol) with stirring in dry Et_2O (40 ml) at 0 °C. The reaction mixture was stirred for 3 h at room temperature (r.t.) and, then, was diluted with Et_2O (30 ml). Dibenzyltin dibromide (4.6 g, 10 mmol) in THF (15 ml) was added at 0 °C. After being stirred for 24 h at r.t., the reaction mixture was

Table 2
Partition coefficients (PC) of **1ba** and **1bb** in the binary FC-72/organic solvent system at room temperature

Solvent	**1ba** (distribution)			**1bb** (distribution)		
	FC-72	Organic solvent	PC	FC-72	Organic solvent	PC
$C_6H_5CH_3$	97	3	32	94	4	24
C_6H_6	99	1	99	99	1	99
CH_2Cl_2	98	2	49	98	2	49

diluted with C_6H_{14} (60 ml) and filtered through a celite pad. The filtrate was evaporated and the residue was subjected to column chromatography (C_6H_{14}) on silica gel to afford pure **2a** as a colorless oil (8.06 g, 81%). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 0.82–1.05 (m, 4H), 1.80–1.99 (m, 4H), 2.46 (s, $^2J(^1H–^{119}Sn) = 60.4$ Hz, 4H), 6.90–7.24 (m, 10H); ^{119}Sn-NMR (112 MHz, $CDCl_3$): δ −19.1.

An analogous procedure using $C_4F_9C_2H_4Br$ afforded **2b** in 99% yield. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 0.80–1.06 (m, 4H), 1.80–2.00 (m, 4H), 2.45 (s, $^2J(^1H–^{119}Sn) = 60.2$ Hz, 4H), 6.90–7.25 (m, 10H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ −1.4 ($^1J(^{13}C–^{117/119}Sn) =$ 308 Hz, 2C), 18.5 ($^1J(^{13}C–^{117/119}Sn) = 274/287$ Hz, 2C), 27.2 ($^2J(^{13}C–^{19}F) = 46$ Hz, 2C), 106.0–121.5 (complex pattern, 8C), 124.2 (2C), 127.0 (4C), 128.9 (4C), 140.9 (2C); ^{119}Sn-NMR (112 MHz, $CDCl_3$): δ −19.2.

3.3. Preparation of *3a* and *3b*

Under Ar, Br_2 (1.74 g, 10.8 mmol) was added to a solution of **2a** (5.20 g, 5.40 mmol) in CCl_4 (70 ml) at r.t. After 3 h, the reaction mixture was evaporated, and the residue was subjected to column chromatography (C_6H_{14} followed by EtOAc) to provide **3a** in a pure form. A white solid was obtained by recrystallization from C_6H_{14} (5.03 g, 96%). M.p. 56–58 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 2.04 (t, $J = 7.7$ Hz, $^2J(^1H–^{117/119}Sn) = 60.0$ Hz, 4H), 2.30–2.85 (m, 4H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 14.9 ($^1J(^{13}C–^{117/119}Sn)$ = 457 Hz, 2C), 27.1 ($^2J(^{13}C–^{19}F) = 23$ Hz, 2C), 106.6–123.1 (complex pattern, 12C); ^{119}Sn-NMR (112 MHz, $CDCl_3$): δ 54.8.

An analogous procedure using **2b** afforded **3b** as a pale yellow solid (2.90 g, 94%). M.p. 30–31 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.80–2.00 (m, 4H), 2.45–2.75 (m, 4H); ^{119}Sn-NMR (112 MHz, $CDCl_3$): δ 53.3, (C_3H_6O-d_6) δ −57.0.

3.4. Preparation of *4a* and *4b*

To a solution of **3a** (5.03 g, 5.17 mmol) in THF (80 ml) was added dropwise 4 M NaOH aq. solution (3.9 ml, 15.5 mmol) at r.t. The mixture was stirred for 2 h and, then concentrated. The residual solids were washed with a 1:1 mixture of CH_2Cl_2 and water (2 × 10 ml). The remaining solids were dried by pumping to give **4a** as a white solid (4.07 g, 93%). ^{1}H-NMR (300 MHz, FC-72 with C_3H_6O-d_6 as external lock): δ 1.30–1.95 (br, 4H), 2.41–2.95 (br, 4H); ^{13}C-NMR (75 MHz, C_3H_6O-d_6): δ 10.0–14.0 (br, 2C), 25.0–27.0 (br, 2C); 104.0–123.0 (12C); ^{119}Sn-NMR (112 MHz, C_3H_6O-d_6): δ −168– −233 (complex pattern).

An analogous procedure using **3b** afforded **4b** as white solid in 92% yield. ^{1}H-NMR (300 MHz, C_3H_6O-d_6): δ 1.10–2.00 (m, 4H), 2.40–3.25 (m, 4H); ^{13}C-NMR (75 MHz, C_3H_6O-d_6): δ 10.0–13.0 (m, 2C), 25.0–27.0 (m, 2C), 106.0–122.0 (m, 8C); ^{119}Sn-NMR (112 MHz, C_3H_6O-d_6): δ −174– −210 (complex pattern).

3.5. Preparation of *1aa* and *1ba*

To **4a** (4.18 g, 4.95 mmol) in CH_3COCH_3 (50 ml) was added 4 M HCl (1.63 ml, 6.50 mmol) at r.t. After reaction mixture had been stirred at this temperature for 24 h, CH_2Cl_2 (150 ml) was added. The organic layer was washed with water (3 × 50 ml), dried (Na_2SO_4), and evaporated. To the residual solids was added FC-72 (30 ml), and the solution was washed with a 1:1 mixture of CH_2Cl_2 and water (2 × 10 ml). The FC-72 layer was evaporated, and the residue was recrystallized from hot CH_2Cl_2 to afford **1aa** in pure form (3.62 g, 85%). M.p. 71–72 °C; ^{1}H-NMR (300 MHz, FC-72 with $CDCl_3$ as external lock): δ 1.87–2.35 (m, 16H), 2.65–3.05 (m, 16H); ^{13}C-NMR (75 MHz, C_3H_6O-d_6): δ 13.7 (4C), 15.2 (4C), 25.8 ($^2J(^{13}C–^{19}F) = 23.2$ Hz, 4C), 26.0 ($^2J(^{13}C–^{19}F) = 23.2$ Hz, 4C), 106.3–122.3 (complex pattern, 48C); ^{119}Sn-NMR (112 MHz, C_3H_6O-d_6): δ −178.3, −202.5; Anal. Calc. for $C_{64}H_{32}Cl_4F_{104}O_2Sn_4$: C, 22.44; H, 0.94. Found: C, 22.58; H, 0.54.

An analogous procedure using **4b** afforded **1ba** in 84% yield. M.p. 82–84 °C; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 1.91–2.34 (m, 16H), 2.51–3.05 (m, 16H); ^{13}C-NMR (125 MHz, C_3H_6O-d_6): δ 13.7 (^1J-($^{13}C–^{117/119}Sn) = 699/725$ Hz, 4C), 15.2 ($^1J(^{13}C–^{117/119}Sn)$ = 717/750 Hz, 4C), 25.8 ($^2J(^{13}C–^{19}F) = 23.3$ Hz, 4C), 26.0 ($^2J(^{13}C–^{19}F) = 23.3$ Hz, 4C), 105.0–120.5 (32C); ^{119}Sn-NMR (112 MHz, C_3H_6O-d_6): δ −178.0, −201.9. Anal. Calc. for $C_{48}H_{32}Cl_4F_{72}O_2Sn_4$: C, 21.96; H, 1.23. Found: C, 22.13; H, 1.25%.

3.6. Preparation of *1ab* and *1bb*

To **4a** (2.00 g, 2.37 mmol) in CH_3COCH_3 (50 ml) was added 4 M HBr (0.76 ml, 3.08 mmol) at r.t. After the reaction mixture had been stirred for 24 h, CH_2Cl_2 (150 ml) was added. The organic layer was washed with water (3 × 50 ml), dried (Na_2SO_4), and evaporated. To the residual solids was added FC-72 (30 ml) and the solution was washed with a 1:1 mixture of CH_2Cl_2 and water (2 × 10 ml). The FC-72 layer was evaporated, and the residue was recrystallized from hot $C_6H_5CH_3$ to afford **1ab** in a pure form as a white solid (1.65 g, 78%). M.p. 68–70 °C; ^{1}H-NMR (500 MHz, FC-72 with $CDCl_3$ as external lock): δ 1.75–2.35 (m, 16H), 2.45–3.25 (m, 16H); ^{13}C-NMR (75 MHz, C_3H_6O-d_6): δ 14.9 (4C), 16.9 (4C), 25.9 ($^2J(^{13}C–^{19}F) = 23.0$ Hz, 4C), 26.5 ($^2J(^{13}C–^{19}F) = 23.0$ Hz, 4C), 105.8–122.3 (complex pattern, 48C); ^{119}Sn-NMR (112 MHz, C_3H_6O-d_6): δ −182.9, −205.0. Anal. Calc. for $C_{64}H_{32}Br_4F_{104}O_2Sn_4$: C, 21.33; H, 0.90. Found: C, 22.13; H, 1.25%.

An analogous procedure using **4b** afforded **1bb** in 84% yield. M.p. 120–122 °C; ^{1}H-NMR (500 MHz, C_3H_6O-d_6): δ 1.93–2.38 (m, 16H), 2.60–3.14 (m, 16H); ^{13}C-NMR (125 MHz, C_3H_6O-d_6): δ 14.9 (4C), 16.9 (4C), 25.6 ($^2J(^{13}C–^{19}F) = 23.2$ Hz, 4C), 26.2 ($^2J(^{13}C–^{19}F) = 23.2$ Hz, 4C), 104.0–122.0 (32C); ^{119}Sn-NMR (112 MHz, C_3H_6O-d_6): δ −205.2, −183.8. Anal. Calc. for $C_{48}H_{32}Br_4F_{72}O_2Sn_4$: C, 20.57; H, 1.15. Found: C, 20.96; H, 1.14%.

3.7. Preparation of *1ac*

To **1aa** (172 mg, 0.1 mmol, calculated as a monomer) in FC-72 (10 ml) was added NaSCN (5.5 g, 67.8 mmol) in water (5 ml) at r.t. The reaction mixture was stirred at r.t. for 20 h. After separation, the FC-72 layer was washed with water (2 × 5 ml) and evaporated. The residue was recrystallized from MeOH–THF to afford **1ac** in pure form (165 mg, 95%). M.p. 143–145 °C; ^{1}H-NMR (500 MHz, FC-72 with $CDCl_3$ as external lock): δ 1.65–2.30 (m, 16H), 2.35–3.00 (m, 16H); ^{13}C-NMR (75 MHz, C_3H_6O-d_6): δ 13.0 (4C), 13.9 (4C), 25.8 ($^2J(^{13}C–^{19}F) = 23.0$ Hz, 8C), 106.0–123.0 (complex pattern, 48C), 140.4 (2C); ^{119}Sn-NMR (112 MHz, C_3H_6O-d_6): δ −244.0, −191.4. IR (Nujol mull): 2900 (s), 2065, 1140, 1060, 890, 730, 540 cm^{-1}; Anal. Calc. for $C_{66}H_{32}Cl_2F_{104}N_2O_2S_2Sn_4$: C, 22.84; H, 0.93; N, 0.81. Found: C, 22.97; H, 0.93; N, 0.75%.

3.8. Determination of partition coefficient

A sample of **1aa** (86 mg, 0.05 mmol, calculated as a monomer) was dissolved in FC-72 (5 ml) to afford a clear solution, and an organic solvent (5 ml) was added. This mixture was stirred or shaken at r.t. for 30 min and kept still until both organic and FC-72 layers become clear. After separation, the organic and FC-72 layers were evaporated, respectively, and **1aa** recovered was weighed.

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