Synthesis, Structure, and Reactions of 10-Sn-5 Organotin Ate Complexes[†]

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Stable anionic 10-Sn-5[1] species, tetraalkylammonium bis[α,α-bis(trifluoro-methyl)benzenemethanolato(2-)-C^2,O]alkylstannates(1-) [**2a** (R=Ph), **2b** (R=p-CH$_3$-C$_6$H$_4$), **2c** (R=n-Bu), and **2d** (R=Me)], were prepared. Reaction of **2a** and **2b** with sulfuryl chloride gave chlorostannate (**3a**), which could be converted to fluorostannate (**3b**). **3a** and **3b** reacted with organolithium reagents to give **2**. The X-ray crystallographic analysis of **3b**-n-Bu$_4$N$^+$ revealed a distorted trigonal bipyramidal structure.

Active attention to hypervalent organotin compounds has been focused and limited mainly on structures of pentacoordinated tin compounds, which include a number of intramolecularly weakly coordinated compounds.[2] Reactions of hypervalent organotin compounds have not been investigated so much as they deserve[3] due to the difficulty to prepare them as distinctive species since pentacoordinated species is generally in equilibrium with tetracoordinated species, consequently characteristic reactions of pentacoordinated species are difficult to be sorted out.[4]

In this paper, we report successful syntheses of novel covalently pentacoordinated alkylstannates **2a-d** and halostannates **3a-b** by use of dilithiohexafluorocumyl alcohol ligand (**1**)[5] and X-ray crystallographic analysis of **3b**. In addition, electrophilic reactions of hypervalent alkylstannates **2**, and *nucleophilic* reactions of organolithiums with *anionic* halostannates **3** are also described.

A typical compound **2a**-Me$_4$N$^+$ was synthesized by the following procedure. A 15 ml THF solution of p-CH$_3$C$_6$H$_4$SnCl$_3$ (1.52 g, 5.02 mmol) was added to a precooled (-78 °C) THF solution of dilithiated reagent **1**, prepared from bis(trifluoromethyl)benzyl alcohol (1.85 ml, 11.1 mmol), n-BuLi (23.3 mmol in 15.0 ml of hexane), and N,N,N',N'-tetramethylethylenediamine (TMEDA: 0.37 ml, 2.45 mmol) and a small amount (ca. 1.5 ml) of THF. The mixture was allowed to warm to room temperature and was stirred overnight. Aqueous workup followed by treatment with tetramethylammonium bromide (2.68 g, 17 mmol) in dichloromethane (100 ml) gave **2a**-Me$_4$N$^+$ (3.02 g, 80%; recrystallized from acetone-dichloromethane) as colorless crystals. By use of similar procedures compounds **2b-2d**[6] were obtained. These compounds were found to be remarkably stable towards atmospheric moisture and gave correct elemental analyses.

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Notable is an upfield shift of **2a-d** (δ -77 - -146 ppm) relative to 8-Sn-4 stannane (**4**, +62 ppm),[7] indicative of an increase in the coordination number of tin.[8] Each pair of CF_3 (a=a', b=b') should be magnetically identical since only one pair of quartets in ^{19}F NMR is observed. Coalescence of the CF_3 signals in ^{19}F NMR could not be observed even at 150 °C in DMSO-d$_6$. The free energy of activation of the CF_3 exchange should be higher than 20-21 kcal/mol at 150 °C.
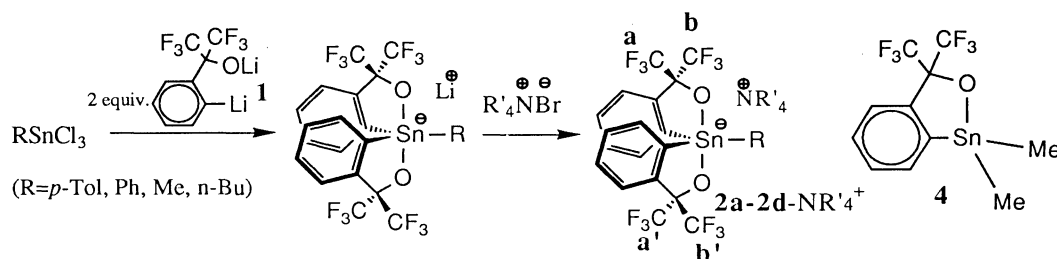

Table 1. Synthesis of 10-Sn-5 Alkylstannates (**2 a** - **2 d**)

	R	R'	Yield %	^{119}Sn NMR (δ from Me_4Sn)	^{19}F NMR (δ from $CFCl_3$)
2 a	Ph	Me	80	-145.7	-73.4 (q, 6F), -74.7 (q, 6F)
2 b	p-$CH_3C_6H_4$	Et	58	-143.2	-73.4 (q, 6F), -74.7 (q, 6F)
2 c	n-Bu	Et	65	- 89.4	-73.0 (q, 6F), -73.7 (q, 6F)
2 d	Me	Et	46	- 77.7	-74.5 (q, 6F), -75.0 (q, 6F)

These compounds did not react with benzaldehyde at all even under refluxing THF for 4 days in spite of their anionic character. However, strong electrophiles such as sulfuryl chloride did react with **2a** or **2b** in CH_2Cl_2 and gave a chlorostannate **3a**[9] almost quantitatively at room temperature. This compound, however, was moisture-sensitive, and could not be purified enough to give correct elemental analysis. Therefore, **3a** was converted to a fluorostannate **3b**[10] by treatment with tetrabutylammonium fluoride (TBAF). The fluorostannate was remarkably stable toward air and water and gave a crystal for X-ray structural analysis (*vide infra*). The ^{19}F NMR of the compound showed a singlet for the two CF_3 groups at room temperature, and showed a pair of quartets at low temperatures, the coalescence temperature was -40 °C. Thus, the free energy of activation of the CF_3 exchange was calculated to be 10.7 kcal/mol at -40 °C. It should be noted that the ^{19}F NMR of **3b** also showed a singlet for Sn-F with satelite coupling constants of 2463 Hz ([117]Sn-^{19}F) and 2577 Hz ([119]Sn-^{19}F). The ^{13}C NMR of **3b** showed a peak for Sn-C with a coupling constant of 11 Hz ($^2J_{CSnF}$), which set a lower limit for the barrier for dissociation of the fluoride ion as ca. 13 kcal/mol at 25 °C.[11] This indicates that the fluorine atom is bound to the tin atom during the CF_3 exchange, and Berry type pseudorotaion is responsible for the isomerization. Therefore, its configurational instability, which was in contrast to the alkylstannates (**2a-2d**), is due to stabilization of the transition state in pseudorotation by the electonegative fluorine atom.[12]
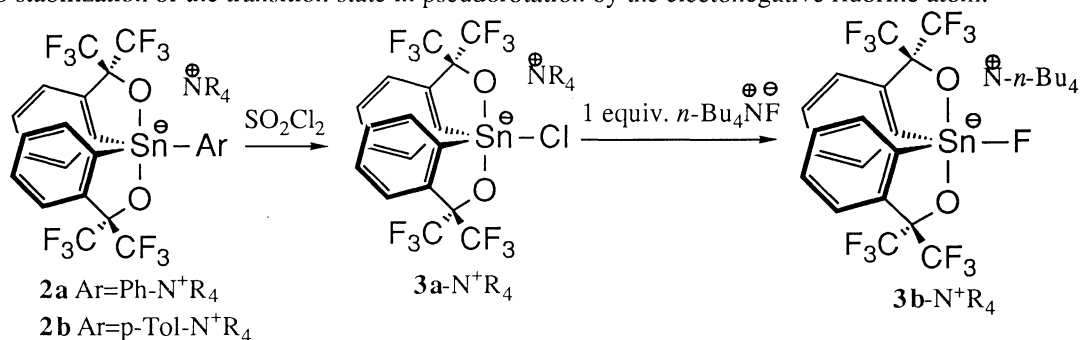
The X-ray crystallographic analysis of **3b**(X=F)-*n*-Bu4N[+13)] supports the observations in solution. The ORTEP drawing of **3b**-*n*-Bu4N^{+} and selected structural values of this compound are shown below. In the crystals, no special interactions between cations and anions are observed except van der Waals interaction, and also there are no significant intermolecular interactions. The configuration about the tin atom is distorted trigonal bipyramid, where the two oxygen atoms occupy the apical positions with Sn-O bond lengths of 2.110, 2.101 Å and the O-Sn-O angle is 178.7°, respectively. It should be noted here that the Sn-F bond length (1.993 Å) in **3b**-*n*-Bu4N^{+} strongly shows the covalent nature.

Fig. 1.   ORTEP Drawing of **3b**-*n*-Bu4N^{+}.

Table 2.   Selected Data of **3b**-*n*-Bu4N^{+}

Bond lengths (Å)	
Sn-O1(ap)	2.110(6)
Sn-O2(ap)	2.101(6)
Sn-C1(eq)	2.10(1)
Sn-C10(eq)	2.07(1)
Sn-F	1.993(6)
Bond angles (deg)	
O1(ap)-Sn-O2(ap)	178.7(3)
O1(ap)-Sn-C1(eq)	81.5(3)
O2(ap)-Sn-C10(eq)	81.4(3)
C1(eq)-Sn-C10(eq)	135.4(4)
C1(eq)-Sn-F	111.8(3)
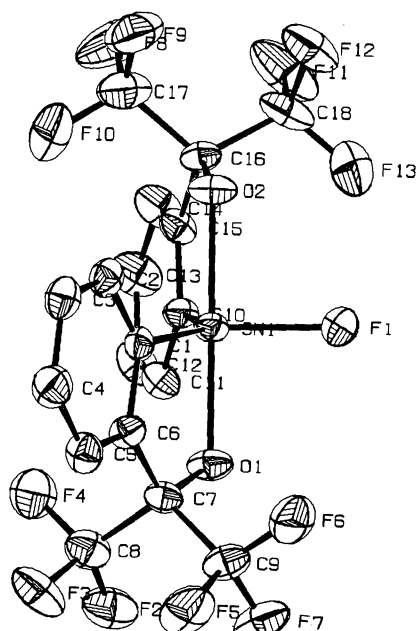
It is quite interesting and important to note that the halostannates **3a** and **3b** react with organolithiums to give alkyl(or aryl)stannates **2a-2d** in spite of being anionic molecules. The results of reactions of **3a** and **3b** with several organolithiums are listed in Table 3. Based on the stability of the Sn-F bond in **3b** against dissociation, the transition state (or intermediate) for the nucleophilic reaction should be hexacoordinated dianion **A**. Well-characterized covalently coordinated tin(IV) dianions are rare, but several reports have appeared recently for nucleophilic reactions toward pentacoordinate silicon.[14)] The detailed mechanism of the nucleophilic reactions in addition to reactions of **2** and **3** with other nucleophiles are currently under investigation.

3a(X=Cl), **3b**(X=F)   **A**   **2a-2d**
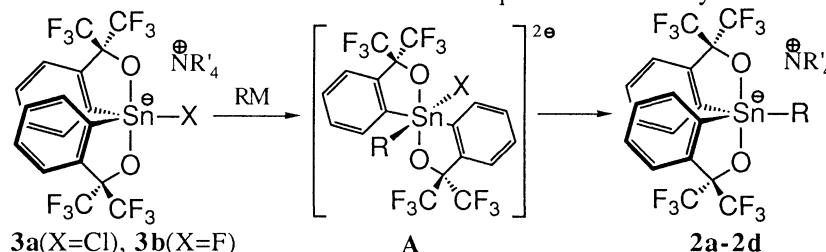
Table 3.   Reaction of **3 a** and **3 b** with Organolithiums

Stannate	R'	Organometallic reagent	Condition	Product (R)	Isolated yield/%
3a	Et	MeLi (3.7 equiv.)	r.t. overnight	**2d** (Me)	49
3b	*n*-Bu	MeLi (2.9 equiv.)	r.t. 21.5 h	**2d** (Me)	51
3a	*n*-Bu	*p*-CH3C6H4Li (5.2 equiv.)	r.t. overnight	**2a** (*p*-CH3C6H4)	42

References

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6) **2a**-Me$_4$N$^+$: Mp >300 °C; ^{1}H NMR (acetone-d_6) δ 3.40 (s, 12H), 7.1-8.0 (m, 13H). **2a**-Bu$_4$N$^+$: Mp 155.0-156.0 °C; ^{1}H NMR (CDCl$_3$) δ 0.90 (t, 12H, J = 7.1 Hz), 1.2-2.3 (m, 16H), 2.69 (t, 8H, J = 8.1 Hz), 7.2-8.1 (m, 13H). **2b**-Et$_4$N$^+$: Mp 249.0-251.5 °C; ^{1}H NMR (acetone-d_6) δ 1.40 (t of t, 12H, J = 7.3 Hz, 1.8Hz($^3J_{NH}$)), 2.23 (s, 3H), 3.45 (q, 8H, J = 7.3 Hz), 7.05 (d, 2H, J = 7.3 Hz), 7.93 (d, 2H, J = 7.3 Hz), 7.2-8.1 (m, 8H). **2c**-Et$_4$N$^+$: Mp 156.0-157.0 °C; ^{1}H NMR (CDCl$_3$) δ 0.81 (t of t, 12H, J = 7.3 Hz, 2.0Hz($^3J_{NH}$)), 2.49 (q, 8H, J = 7.3 Hz), 7.2-8.1 (m, 8H). **2d**-Et$_4$N$^+$: Mp 157.0-158.0 °C; ^{1}H NMR (acetone-d_6) δ 0.36 (s, (doublet, J^{117}Sn-CH$_3$ = 74.1 Hz; doublet, J^{119}Sn-CH$_3$ = 78.0 Hz, 3H), 1.40 (t of t, 12H, J = 7.3 Hz, 1.8Hz($^3J_{NH}$)), 3.50 (q, 8H, J = 7.3 Hz), 7.3-8.1 (m, 8H).

7) 1,1-Dimethyl-3,3-bis(trifluoromethyl)-3H-2,1-benzoxastannole (**4**) is prepared from **1** and dimethyltin dichloride in 56 % yield, followed by treatment with CaH$_2$.

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9) **3a**-Et$_4$N$^+$: ^{1}H NMR (acetone-d_6) δ 1.29 (t of t, 12H, J = 7.3 Hz, 1.8Hz($^3J_{NH}$)), 3.36 (q, 8H, J = 7.3 Hz), 7.4-8.1 (m, 8H); ^{19}F NMR (acetone-d_6) δ -76.7; ^{119}Sn NMR (acetone-d_6) δ -127.6.

10) **3b**-Bu$_4$N$^+$: Mp 191.0-191.5 °C; ^{1}H NMR (acetone-d_6) δ 1.00 (t, 12H, J = 7.3 Hz), 1.3-1.9 (m, 16H), 3.40 (t, 8H, J = 8.4 Hz), 7.4-8.1 (m, 8H); ^{19}F NMR (acetone-d_6) δ -74.7 (s, 12F), -181.6 (s, 1F, J^{117}Sn-F = 2463 Hz, J^{119}Sn-F = 2577 Hz); ^{119}Sn NMR (acetone-d_6) δ -184.6 (d, J^{119}Sn-F = 2577 Hz). ^{13}C NMR (acetone-d_6) δ 14.2, 20.7, 24.9, 59.8, 81.2 (sept, J_{C-C-F} = 28 Hz), 126.4 (q, J_{C-F} = 289 Hz), 127.8, 130.4, 130.8, 136.9, 140.1 (d, J_{C-Sn-F} = 11.0 Hz), 142.3.

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13) Crystallographic data for **3b**-n-Bu$_4$N$^+$: C$_{34}$H$_{44}$F$_{13}$NO$_2$Sn, FW=863.50, orthorhombic, space group Pbca, a=21.535(4) Å b=21.902(5) Å, c=16.412(9) Å, V=7741(4) Å^3, Z=8, Dc=1.48 g cm^{-3}, Mo $K\alpha$ radiation, 4452 reflections used, R=0.077, Rw=0.094.

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