

Synthesis, stability, and reactions of 10-Sn-5 tin ate complexes bearing four tin–carbon bonds [☆]

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Abstract

The monocyclic organostannates (*o*-C₆H₄C(CF₃)₂O)SnR₂(*p*-CH₃C₆H₄)[−]Li⁺ (**2a**-Li⁺ (R = Me), **2b**-Li⁺ (R = ^tBu)) bearing four Sn–C bonds, which can be prepared from the reaction of tetracoordinate tin **3a** (R = Me) and **3b** (R = ^tBu) with *p*-CH₃C₆H₄Li, were found to be thermally stable but were unstable to moisture giving **3** quantitatively upon aqueous workup. These ate complexes were inert toward some typical electrophiles such as *p*-methoxybenzaldehyde, but were reactive enough toward 1,3-bis(methoxycarbonyl)pyridinium chloride (**8**) to give corresponding alkylated(arylated) dihydropyridines (**9**). These are quite unique examples in the respect that organostannanes bearing four Sn–C bonds, which have been known to be reluctant to form compounds of higher coordination numbers, formed stable pentacoordinate ate complexes and showed unique reactivity which differed from that of lithium reagents such as *p*-CH₃C₆H₄Li which could have formed upon dissociation from the ate complexes. The reaction of **3a** with ⁿBuLi gave complex mixtures after treatment with water indicating that the expected ate complexes (*o*-C₆H₄C(CF₃)₂O)SnMe₂(ⁿBu)[−]Ki⁺ (**2c**-Li⁺) was thermally unstable and existed in an equilibrium with a ring-opened structure **5c**.

Keywords: Tin ate complex; Pentacoordinate; Anion; Hypervalent; Tin; Bidentate ligand

1. Introduction

Organotin(IV) compounds containing electronegative atoms such as halogen and oxygen show Lewis acidic character and the Lewis acidity increases with the number of the electronegative atoms [1]. In fact, tetraorganostannanes bearing four Sn–C bonds have been known to be reluctant to form pentacoordinate or hexacoordinate ate complexes, although a weak donor–acceptor complex Me₃SnCF₃ · P(NMe₂)₃ [2] and some intramolecular N → Sn coordinated compounds [3] have been reported along with a report of the formation of pentacoordinate (η¹-C₅H₅)₂SnC₄(C₆H₅)₄X[−]Li⁺ which did not include a description of ¹¹⁹Sn NMR data [4]. Quite recently an X-ray structure of 1,2-oxastannetanide has been reported [5]. Pentaorganotin ate complexes bearing five Sn–C bonds have been considered to be intermediates in the lithium–tin exchange reaction [6] and have been observed by NMR to be in equilibrium

with tetraorganotin and lithium reagents in THF/HMPA solution [7].

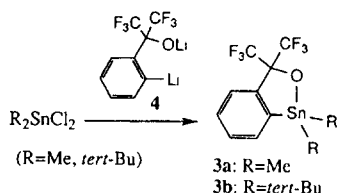
Recently, we have reported the formation and some reactions of stable bicyclic 10-Sn-5 [8] triorganoate complexes ((*o*-C₆H₄C(CF₃)₂O)₂SnR[−]R'₄N⁺ (1-R'₄N⁺)) which incorporate two molecules of five-membered ring ligands [9], the so-called Martin ligand [10]. Here we report upon the stability of monocyclic tetraorganoate complexes **2** bearing one Martin ligand and the reactivity of the thermally stable ate complexes **2a** and **2b**. The presence of one Martin ligand and one electronegative aryl group was found to be sufficient for **2** to be thermally stable and the reaction of the ate complexes with strong electrophiles such as 1,3-bis(methoxycarbonyl)pyridinium chloride (**8**) could be carried out to give corresponding alkylated(arylated) dihydropyridines (**9**).

2. Results and discussion

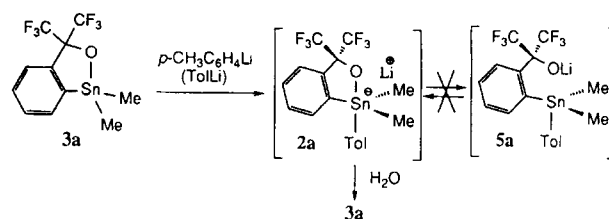
1,1-Dialkyl-3,3-bis(trifluoromethyl)-3*H*-2,1-benzoxastannole (**3a,b**) were prepared from the dilithio reagent

[☆] Dedicated to Prof. Hideki Sakurai on the occasion of his retirement from Tohoku University.

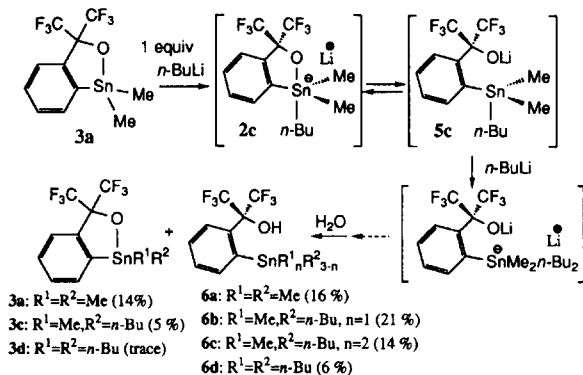
^{*} Corresponding author.



Scheme 1.



Scheme 3.



Scheme 2.

4 with R_2SnCl_2 in 63% ($\text{R} = \text{Me}$) and 51% ($\text{R} = \text{t-Bu}$) yield, respectively (Scheme 1). These compounds were isolated as hydrates after the usual workup.

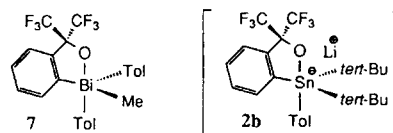
A THF solution of anhydrous **3** may be obtained by treating a THF solution of the hydrate with CaH_2 followed by filtration of Ca(OH)_2 . Reactions of anhydrous **3a** with 1 equiv. of $n\text{-BuLi}$ at 0°C gave complex mixtures of butylated compounds **6a–d** and **3c–d** after the reaction was quenched with water. This result indicates that the initially formed ate complex **2c** was unstable at the temperature employed and was in equilibrium with a ring-opened structure **5c**, and that **5c** reacted with unreacted $n\text{-BuLi}$ leading to **6** and **3** after treatment with water (Scheme 2).

In contrast, **3a** was recovered quantitatively after reaction of **3a** with $p\text{-methylphenyllithium}$ at 0°C followed by treatment with water. This result indicates that the thermally stable ate complex **2a** was not in equilibrium with **5a** and that **2a** reacted directly with water to give **3** (Scheme 3).

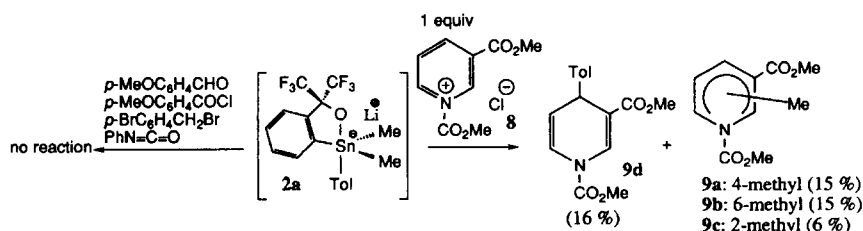
^{119}Sn NMR spectra of the solution of **3a** with $p\text{-methylphenyllithium}$ showed a remarkable upfield shift at $\delta -120$ ppm relative to $+62$ ppm for **3a**, indicative of an increase in the coordination number of tin [11]. In

order to check the possibility of equilibrium between **2a** and tetra-coordinate **3a** with $p\text{-methylphenyllithium}$, reactions of **2a** with several electrophiles such as $p\text{-methoxybenzaldehyde}$ were attempted (vide infra). However, addition products, which might have been formed if $p\text{-methylphenyllithium}$ existed in the reaction mixture even as a minor equilibrated component, were not detected. Thus, **2a** can be considered to be thermally stable without equilibrium with **3a**. It can be concluded that the electronegative $p\text{-methylphenyl}$ group was enough to stabilize the ate complex whereas the more electron-donating $n\text{-butyl}$ group was not. The structure of **2a** was considered to be trigonal bipyramidal and the $p\text{-methylphenyl}$ group should occupy the apical position because the $p\text{-methylphenyl}$ group was more apicophilic than the methyl group, as was reported in an X-ray structure for the bismuth compound (**7**) [12].

The ate complex **2a** was poorly reactive with electrophiles such as $p\text{-methoxybenzaldehyde}$, $p\text{-methoxybenzoyl chloride}$, $p\text{-bromobenzyl bromide}$ and phenyl isocyanate. However, a pyridinium salt (**8**) was reactive enough towards **2a** to give a mixture of dihydropyridine products (**9a–d**) [13]. Since organolithium reagents would have attacked the carbonyl group at the nitrogen atom to give pyridine [14], the actual reacting organometallic species can be considered to be the ate complex **2a** and not the organolithium species dissociated from **2a** (Scheme 4). Thus, this is the first example of a tetraorganotin ate complex for which characteristic reactions may be ascertained.



Formation of another stable ate complex **2b** by the reaction of **3b** with $p\text{-methylphenyllithium}$ was also



Scheme 4.

confirmed by a notable upfield shift (δ –124 ppm relative to +88 ppm for **3b**) in the ^{119}Sn NMR spectrum. The reaction of **2b** with **8** was found to be very slow probably because of the steric hindrance and only 7% of **9d** was isolated after 1 d at room temperature.

Therefore, it can be concluded that the presence of one Martin ligand and one electronegative aryl group is enough to give thermodynamically stable 10-Sn-5 ate complexes **2a** and **2b** whereas the ate complex **2c** without an aryl group was found to be thermally unstable.

3. Experimental

Melting points were taken on a Yanagimoto micro melting point apparatus and are uncorrected. ^1H NMR (400 MHz), ^{19}F NMR (376 MHz), ^{13}C NMR (100 MHz) and ^{119}Sn NMR (149 MHz) spectra were recorded on a JEOL EX-400 spectrometer. ^1H NMR (90 MHz) and ^{19}F NMR (85 MHz) spectra were recorded on a Hitachi R-90H spectrometer. Chemical shifts are reported (δ scale) from internal tetramethylsilane for ^1H and ^{13}C , from fluorotrichloromethane for ^{19}F or from tetramethyltin for ^{119}Sn spectroscopies. Elemental analyses were performed on a Perkin Elmer 2400CHN elemental analyzer. Flash column chromatography was carried out on Merck silica gel 9385. Thin-layer chromatography was performed with Merck silica gel GF-254 plates. All reactions were carried out under N_2 or Ar. The preparation of the dilithio derivative of bis(trifluoromethyl)benzyl alcohol followed published procedures [10]. THF and diethyl ether were distilled from sodium/benzophenone.

3.1. 1,1-Dimethyl-3,3-bis(trifluoromethyl)-3H-2,1-benzoxastannole (**3a**)

The dilithio reagent **4**, which was prepared from bis(trifluoromethyl)benzyl alcohol (3.34 ml, 20.0 mmol), $^n\text{BuLi}$ (40 mmol in 25.8 ml of hexane) and N,N,N',N' -tetramethylethylenediamine (TMEDA, 0.60 ml, 4.0 mmol) and a small amount (ca. 3 ml) of THF, was dissolved in 30 ml of THF and added dropwise to a cold (-78°C) stirred solution of Me_2SnCl_2 (4.39 g, 20 mmol) in 100 ml of THF. The mixture was allowed to warm to room temperature and was stirred for a further 12 h. After the reaction mixture was treated with water, the crude product was subjected to column chromatography (n-hexane/ethyl acetate = 1/1) to give colorless crystals (5.20 g, yield 63%). **3a** · H_2O : m.p. 130–133 $^\circ\text{C}$. ^1H NMR (CD_3CN) 0.61 (s, d, J 117 $_{\text{Sn}-\text{CH}_3}$ = 68.1 Hz; d, J 119 $_{\text{Sn}-\text{CH}_3}$ = 71.2 Hz; 6H), 2.38 (s, 2H), 7.31–7.97 (m, 4H). ^{19}F NMR (CD_3CN) –76.7 (s). ^{13}C NMR ($\text{DMSO}-d_6$) –4.97 (s, d, J 117 $_{\text{Sn}-\text{CH}_3}$ = 526.5 Hz; d, J 119 $_{\text{Sn}-\text{CH}_3}$ = 551.4 Hz), 83.1 (sep, J = 27.4

Hz), 126.5 (q, J = 291.9 Hz), 126.9 (s, d, J = 66.3 Hz), 129.3 (s), 129.6 (s), 137.7 (s, d, J = 45.6 Hz), 142.0 (s, d, J = 57.7 Hz). Anal. Calc. for $\text{C}_{11}\text{H}_{10}\text{F}_6\text{OSn} + \text{H}_2\text{O}$: C, 32.31; H, 2.96%. Found: C, 32.32; H, 2.85%.

3.2. 1,1-Di-*n*-butyl-3,3-bis(trifluoromethyl)-3H-2,1-benzoxastannole (**3b**)

The dilithio reagent **4**, which was prepared from bis(trifluoromethyl)benzyl alcohol (1.21 ml, 7.24 mmol), $^n\text{BuLi}$ (15.9 mmol in 9.95 ml of hexane), TMEDA (0.24 ml, 1.59 mmol) and a small amount (ca. 1 ml) of THF, was dissolved in 10 ml of THF and was added dropwise to a cold (-78°C) stirred solution of $(^t\text{Bu})_2\text{SnCl}_2$ (2.2 g, 7.24 mmol) in 20 ml of THF. The mixture was allowed to warm to room temperature and was stirred for a further 12 h. After the reaction mixture had been treated with water, the crude product was recrystallized from n-pentane (1.83 g, yield 51%). **3b** · H_2O : m.p. 132–134 $^\circ\text{C}$. ^1H NMR (CDCl_3) 1.37 (s, d, J 117 $_{\text{Sn}-\text{CH}_3}$ = 82.4 Hz; d, J 119 $_{\text{Sn}-\text{CH}_3}$ = 86.4 Hz; 18H), 1.69 (s, 2H), 7.20–7.86 (m, 4H). ^{19}F NMR (CDCl_3) –73.6 (s, 6F). Anal. Calc. for $\text{C}_{17}\text{H}_{22}\text{F}_6\text{OSn} + \text{H}_2\text{O}$: C, 41.41; H, 4.91%. Found: C, 41.68; H, 4.86%.

Reaction of **3a** with $^n\text{BuLi}$ or $^n\text{BuMgBr}$. A mixture of **3a** · H_2O (234 mg, 0.57 mmol) and CaH_2 (190 mg, 4.5 mmol) was stirred in 10 ml of THF for 1 h. After filtration under N_2 , $^n\text{BuLi}$ (0.57 mmol in 0.356 ml of hexane) was added to the filtrate at 0°C and the mixture was stirred for 1.5 h at room temperature and was treated with 20 ml of aqueous sat. NaCl solution. The crude products were subjected to TLC (n-hexane/ethyl acetate = 1/1 and 27/1) to give 32 mg (14%) of **3a** · H_2O , 14 mg (5%) of 1-methyl-1-*n*-butyl-3,3-bis(trifluoromethyl)-3H-2,1-benzoxastannole (**3c** · H_2O), 38 mg (16%) of 1,1,1-trimethyl-1-[2-(2,2,2-trifluoro-1-hydroxy-1-(trifluoromethyl)ethyl)phenyl]stannane (**6a**), 54 mg (21%) of 1,1-dimethyl-1-*n*-butyl-1-[2-(2,2,2-trifluoro-1-hydroxy-1-(trifluoromethyl)ethyl)phenyl]stannane (**6b**), 40 mg (14%) of 1-methyl-1,1-di-*n*-butyl-1-[2-(2,2,2-trifluoro-1-hydroxy-1-(trifluoromethyl)ethyl)phenyl]stannane (**6c**), and 17 mg (6%) of 1,1,1-tri-*n*-butyl-1-[2-(2,2,2-trifluoro-1-hydroxy-1-(trifluoromethyl)ethyl)phenyl]stannane (**6d**).

A mixture of **3a** · H_2O (140 mg, 0.31 mmol) and CaH_2 (59 mg, 1.41 mmol) was stirred in 3 ml of THF for 1 h. After filtration under N_2 , $^n\text{BuMgBr}$ (0.31 mmol in 5 ml of THF) was added to the filtrate at 0°C and the mixture was stirred for 1.5 h at room temperature and treated with 20 ml of aqueous sat. NaCl solution. The crude products were subjected to TLC (n-hexane/ethyl acetate = 1/1 and 27/1) to give 56 mg (40%) of **3a** · H_2O , 12 mg (8%) of **3c** · H_2O , 22 mg (17%) of **6a**, 18 mg (13%) of **6b**, 11 mg (7%) of **6c**, and 6 mg (4%) of **6d**.

Reaction of **3a** with $p\text{-CH}_3\text{C}_6\text{H}_4\text{Li}$. A mixture of

3a · H₂O (339 mg, 0.83 mmol) and CaH₂ (166 mg, 3.94 mmol) was stirred in 5 ml of THF for 1.5 h. After filtration under N₂, *p*-CH₃C₆H₄Li (0.83 mmol in 0.72 ml of ether) was added to the filtrate at 0 °C and the mixture was stirred for 2.5 h at room temperature and was treated with 20 ml of aqueous sat. NaCl solution. The crude products were subjected to TLC (n-hexane/ethyl acetate = 6/5) to give 302 mg (89%) of **3a** · H₂O.

3.3 Reaction of ate complex **2a** with 1,3-bis(methoxycarbonyl)pyridinium chloride

A mixture of **3a** · H₂O (429 mg, 1.05 mmol) and CaH₂ (200 mg, 4.8 mmol) was stirred in 4 ml of THF for 1 h. After filtration under N₂, *p*-CH₃C₆H₄Li (1.05 mmol in 0.91 ml of ether) was added to the filtrate at 0 °C and the mixture was stirred for 1 h at room temperature. To this solution was added 1,3-bis(methoxycarbonyl)pyridinium chloride (**8**), which was prepared from methyl nicotinate (144 mg, 1.05 mmol) and methyl chloroformate (0.081 ml, 1.05 mmol), and the mixture was stirred for 21 h at room temperature and was treated with 30 ml of aqueous 5% sodium bicarbonate solution. The crude products were subjected to flash column chromatography (n-hexane/ethyl acetate = 6/1, 4/1, 2/1, 1/1, 0/1) to give 214 mg (50%) of **3a** · H₂O, 166 mg (34%) of **3b** · H₂O, 32 mg (15%) of 1,3-dimethoxycarbonyl-4-methyl-1,4-dihydropyridine (**9a**), and a mixture (96 mg) of 1,3-dimethoxycarbonyl-6-methyl-1,6-dihydropyridine (**9b**) (15%), 1,3-dimethoxycarbonyl-2-methyl-1,2-dihydropyridine (**9c**) (6%) and 1,3-dimethoxycarbonyl-4-(*p*-methylphenyl)-1,4-dihydropyridine (**9d**) (16%) (The yields of products were calculated by the integral ratio of protons of products in the mixture.) Separation and characterization of **9a–d** has been described previously [13].

3.4. Reaction of ate complex **2a** with *p*-methoxybenzaldehyde, *p*-methoxybenzoyl chloride, *p*-bromobenzyl bromide and phenyl isocyanate

A mixture of **3a** · H₂O (329 mg, 0.80 mmol) and CaH₂ (160 mg, 3.8 mmol) was stirred in 5 ml of THF for 1 h. After filtration under N₂, *p*-CH₃C₆H₄Li (0.80 mmol in 0.69 ml of ether) was added to the filtrate at 0 °C and the mixture was stirred for 1 h at room temperature. To this solution was added *p*-methoxybenzoyl chloride (0.074 ml, 0.53 mmol), and the mixture was stirred for 28 h at room temperature and treated with 30 ml of water. The crude products were subjected to TLC (n-hexane/ethyl acetate = 3/1) to give 299 mg (91%) of **3a** · H₂O without detection of products from the expected reaction of *p*-methoxybenzoyl chloride with **2a**. Reactions of **2a** with *p*-methoxybenzaldehyde, *p*-bromobenzyl bromide and phenyl isocyanate were carried out under similar conditions, but no products from

the expected reaction of **2a** with the electrophiles were isolated (only **3a** · H₂O was isolated in > 90% yield in every case).

3.5. Reaction of **3b** with *p*-CH₃C₆H₄Li

A mixture of **3b** · H₂O (355 mg, 0.72 mmol) and CaH₂ (146 mg, 3.5 mmol) was stirred in 5 ml of THF for 1.5 h. After filtration under N₂, *p*-CH₃C₆H₄Li (0.72 mmol in 0.56 ml of ether) was added to the filtrate at 0 °C and the mixture was stirred for 2 h at room temperature and was treated with 20 ml of aqueous sat. NaCl solution. After usual workup 322 mg (91%) of **3b** · H₂O was recovered.

3.6. Reaction of ate complex **2b** with 1,3-bis(methoxycarbonyl)pyridinium chloride

A mixture of **3b** · H₂O (350 mg, 0.71 mmol) and CaH₂ (280 mg, 6.7 mmol) was stirred in 5 ml of THF for 1 h. After filtration under N₂, *p*-CH₃C₆H₄Li (0.56 ml, 0.71 mmol in ether) was added to the filtrate at 0 °C and the mixture was stirred for 1 h at room temperature. To this solution was added 1,3-bis(methoxycarbonyl)pyridinium chloride (**8**), which was prepared from methyl nicotinate (97 mg, 0.71 mmol) and methyl chloroformate (0.055 ml, 0.71 mmol), and the mixture was stirred for 21 h at room temperature and was then treated with 30 ml of aqueous 5% sodium bicarbonate solution. The crude products were subjected to TLC (n-hexane/ethyl acetate = 5/2) to give 162 mg (46%) of **3b** · H₂O, and 15 mg (7%) of **9d**.

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