not explained by Chauveau is the broadening of the peaks of the twelve-tungsten signal ($\Delta\nu_{1/2}$ = 5.2 Hz for each). (See Figure 2.) We attribute this otherwise unexplained broadening to the proximity of these W's to the quadrupolar ^{23}Na atom within the complex. The same effect of broadening of belt W signals was observed in the diamagnetic $[(H_2O)ZnO_5H_2F_6NaW_{17}O_{50}]^{9-}$ complex, which undoubtedly contains a central Na^+ ion as explained below. No such broadening of signals from belt W's is observed for conventional Wells-Dawson complexes.[22-25]

^{19}F and ^{1}H NMR Spectroscopy. Our ^{19}F and ^{1}H NMR spectra and their interpretations confirmed those given by Chauveau et al.[4] The six structurally equivalent F atoms are at the vertices of the interior trigonal prism. The two F_3O tetrahedra, each formed by the three coplanar F atoms of one end of the F_6 prism and the one remaining interior O atom at the same end of the complex, contain one H atom apiece. See Figure 1. In each F_3O tetrahedron we conclude that the single H is covalently bonded to the O and H-bonded to F. At a given instant the H is probably preferentially H-bonded to a given F, but the exchange of the H's position relative to the three F atoms is rapid, and the resulting ^{19}F NMR signal coalesces to a single resonance (split by H-F coupling to a doublet). The ^{1}H NMR signal is a quartet owing to the presence of the three neighboring F atoms adjacent to each H. The quartet collapses to a singlet when F is decoupled.

Since each F atom is a nearest neighbor of the quadrupolar Na atom, the ^{19}F NMR signal is markedly broadened. The H-decoupled ^{19}F NMR spectra reported by Chauveau et al. show $\Delta\nu_{1/2} \cong 20$ Hz[4] for the 18-tungstosodate, but $\Delta\nu_{1/2}$ is only $\sim$2 Hz[3] for the F's in $[HF_3OW_{12}O_{36}]^{4-}$, which contains no Na but has the F's in the same sort of HF_3O tetrahedron. This additional previously unexplained difference in line widths also substantiates the presence and location of the Na atoms. The H-decoupled ^{19}F spectrum of the 12-tungsto complex shows clearly resolved W-F coupling.[3] The W-F coupling is undetectable in the H-decoupled ^{19}F NMR spectrum of the 18-tungstosodate[4] owing to the broadening of the signal.

^{23}Na NMR Spectroscopy. ^{23}Na NMR spectroscopy in general exhibits only a very small relative chemical shift range (about 30 ppm). ^{23}Na, being quadrupolar, produces a broad NMR line when the Na atom is in an unsymmetrical environment and a sharp line when it is in a centrosymmetric site (as is the case for hydrated simple Na^+ in water).

Since a trigonal prism is not centrosymmetric, the ^{23}Na NMR signal from the $[H_2F_6NaW_{18}O_{56}]^{7-}$ complex consists of a single symmetrical broad peak ($\Delta\nu_{1/2} \cong 2500$ Hz) centered at 4.2 ppm. This was not detectably different from the ^{23}Na signal for the Zn-substituted isomorph, α_1-$[(H_2O)ZnO_5F_6NaW_{17}O_{50}]^{9-}$, at the same concentration. Addition of simple $^{23}Na^+$ to the solution produces a relatively sharp spike ($\nu_{1/2}$ = 25 Hz) superimposed on the broad signal and centered at 0.19 ppm. The area of the sharp spike is proportional to the concentration of simple $^{23}Na^+$ present.

Other Evidence. The X-ray crystal structure determination of α_1-$(NH_4)_9[(H_2O)ZnO_5H_2F_6NaW_{17}O_{50}]\cdot 9H_2O$ revealed electron density at the center of the complex corresponding to one Na^+. Since that was a special crystallographic position, which might conceivably have accumulated errors to produce the apparent electron density as an artifact, a refinement based on omitting the Na^+ was run. This resulted in significant increase of R, substantiating the reality of the electron density.

The potassium salt of the Zn-substituted isomorph was prepared in the presence of radioactive $^{22}Na^+$ and purified. Precipitation of the radioactive complex with excess guanidinium ion resulted in all of the radioactivity, in the expected amount, being found in the precipitate. Exchange of $^{22}Na^+$ in the dissolved complex with excess $^{23}Na^+$ in solution for various time periods and at various temperatures was attempted. Even after the complex was allowed to stand for 1 week with excess ^{23}NaCl in solution at 60 °C, all of the radioactivity was still found in the complex after its precipitation.

Because the diamagnetic Zn-substituted complex is an isomorph of the subject $[H_2F_6NaW_{18}O_{56}]^{7-}$, these experiments taken with the identical broad ^{23}Na NMR spectra and the identical broadening of the signals from the belt W's substantiate the presence of one Na^+ at the center of each complex.

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Unusual Addition of the Indium-Butyl Bond to Organotin Oxides. Preparation and Characterization of Novel Dibutylindio- or Butyl(propionyloxy)indio-Substituted Stannoxanes

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Many organotin oxides are known to form μ-oxo-bridged aggregates[1] and are useful as reagents or catalysts in the field of synthetic chemistry.[2] Modification of these organometallic polymers or oligomers by replacing some of the tin atoms in the chains with other metallic species might lead to more sophisticated reagents, catalysts, and especially precursors for ceramics and electronics.[3] Several metallorganic polymers have been extensively studied for this purpose.[4] Here we describe the modification of organotin oxides by treating with tributylindium or dibutylindium propionate (**1**), aiming to prepare an effective precursor for highly conductive and transparent indium-tin oxide thin films.

Experimental Section

Analysis. IR and ^{1}H and ^{13}C NMR spectra were recorded on a Hitachi 260-30 spectrophotometer, and on a Hitachi R90H FT spectrometer, respectively. Fast-atom-bombardment (FAB) and electron-impact (EI) mass spectra were obtained with a JEOL JMS-DX303 instrument with a JEOL JMA-DA5000 data processing system (Faculty of Engineering, Osaka University). Molecularity was measured by using a Corona 117 type vapor pressure osmometer (VPO) calibrated by benzil. Contents of indium and tin in the indiostannoxanes were determined with a Rigaku ultratrace 0600 X-ray fluorescence analyzer. Thermal analysis was done by means of a SEIKO TG-DTA 20 type analyzer.

Materials. All organotin oxides were from commercial sources. Solvents and other reagents were used after distillation or recrystalliza-

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Table I. Yields, Boiling (Melting) Points, Analytical Data, and Molecular Weights of **2** and **3**[a]

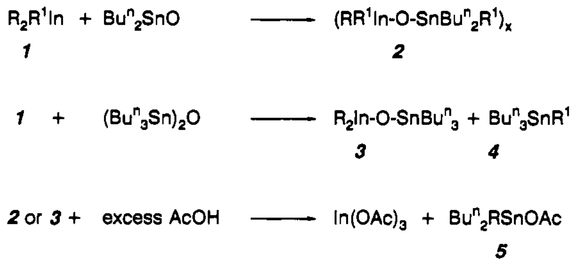
					anal./%					
					found		calcd			
R_2R^1In	Sn	products	yields/%	bp (*p*/Pa) [mp]/°C	C	H	C	H	formula	M_w[b]
a	Bu^n_2SnO	**2a**	79	25 (0.13)	43.94	8.79[c]	44.89	8.48	$C_{20}H_{45}InOSn$	1065[d]
1b		**2b**	75	140 (1.3)	44.88	7.74[e]	44.89	8.48	$C_{20}H_{45}InOSn$	1021[d]
1c		**2c**	87	[50][f]	42.40	7.54[g]	41.41	7.50	$C_{19}H_{41}InO_3Sn$	550[h]
1d		**2d**	75	[52][f]	42.24	7.60	41.41	7.50	$C_{19}H_{41}InO_3Sn$	535[h]
1a	$(Bu^n_3Sn)_2O$	**2a**[i]	79							
1b		**3b**[i]	75	150 (1.3)	44.48	8.11	44.89	8.48	$C_{20}H_{45}InOSn$	1130[d]

[a] Reaction conditions: R_2R^1In, 5 mmol; organotin oxides, 5 mmol; *p*-xylene, 20 mL; 140 °C; 3.5 h. [b] Measured by VPO in benzene at 35 °C. [c] In, 21.5; Sn, 22.1 (calcd: In, 21.46; Sn, 22.18). [d] Parent peaks were detected at m/z = 537 (M^+, $^{115}In-^{16}O-^{120}Sn$) (FAB). [e] In, 22.0; Sn, 22.1 (calcd: In, 21.46; Sn, 22.18). [f] Softening points. [g] In, 20.2, Sn, 21.1 (calcd: In, 20.84; Sn, 21.54). [h] Fragment peaks at m/z = 496 (M^+ − Bu, $^{115}In-^{16}O-^{120}Sn$) and 291 (M^+ − $^{16}O-^{115}InBu(OCOEt)$, ^{120}Sn) were detected (FAB). [i] In benzene, room temperature, 3.5 h.

Table II. Spectral Data for **2** and **3**

	IR/cm^{-1}			^{13}C NMR/δ				
				Bu				
compds	ν(In–O–Sn)	ν_{as}(COOOIn)	ν_s(COOIn)	α	β	γ	δ	others
2a	635			19.1	29.8	28.7	13.6 (In)	
				16.5	28.0	27.2	13.6 (Sn)	
2b	625			26.8	29.7	28.2 (Bu^i–In and –Sn)		
				17.2	27.6	26.5	13.6 (Bu^n–Sn)	
2c	658	1542	1410	16.3	27.1	27.9	13.7	10.1, 29.3, 184.0
2d	650	1541	1395	26.6	28.7	27.9		10.2, 29.5, 179.8
				28.2				
				17.0	27.1	26.4	13.7	
3b	625			27.3	30.1	28.3 (Bu^i)		
				16.5	28.3	27.4	13.6 (Bu^n)	

Scheme I



$$\underset{1}{R_2R^1In} + Bu^n_2SnO \longrightarrow \underset{2}{(RR^1In\text{-}O\text{-}SnBu^n_2R^1)_x}$$

$$1 + (Bu^n_3Sn)_2O \longrightarrow \underset{3}{R_2In\text{-}O\text{-}SnBu^n_3} + \underset{4}{Bu^n_3SnR^1}$$

$$2 \text{ or } 3 + \text{excess AcOH} \longrightarrow In(OAc)_3 + \underset{5}{Bu^n_2RSnOAc}$$

a, $R=R^1=Bu^n$; b, $R=R^1=Bu^i$; c, $R=Bu^n$, $R^1=OCOEt$; d, $R=Bu^i$, $R^1=OCOEt$.

tion. Tributylindium (**1a,b**)[5,6] and dibutylindium propionates (**1c,d**)[8,9] were prepared by the reported procedures. All the reactions were carried out under dry N_2, unless otherwise noted.

General Reaction of 1 with Organotin Oxides. Well-crushed Bu^n_2SnO (5 mmol) and *p*-xylene (20 mL) was placed in a 50-mL round-bottomed flask, and then 5 mmol of **1a** was added into the suspension with cooling and stirring. After the reaction under reflux for 3.5 h, the original precipitates of Bu^n_2SnO almost disappeared and the *p*-xylene layer increased viscosity. After filtration of unreacted Bu^n_2SnO and evaporation of *p*-xylene, slight yellow viscus oils were obtained. The oils were purified by distillation in vacuo (Kugelrohr distillator) to give indiostannoxanes (**2a**). Similarly, reactions of **1b–d** with Bu_2SnO gave analogous indiostannoxanes **2b–d**, respectively. Meanwhile, reactions of **1a,b** with $(Bu_3Sn)_2O$ were also examined and indiostannoxanes **2a** and **3b** together with mixed tetrabutyltin (**4**) were obtained, respectively.

$Bu^n_3Bu^iSn$ (4b): colorless oil, bp 120 °C (0.4 kPa). ^{13}C NMR ($CDCl_3$): δ 9.4 t (α-CH_2 in Bu^n, $^1J_{^{13}C-^{119}Sn}$ = 315.1 Hz), 13.7 q (δ-CH_3), 27.5 t (γ-CH_2 in Bu^n, $^3J_{^{13}C-^{119}Sn}$ = 51.1 Hz), 29.7 t (β-CH_2 in Bu^n, $^2J_{^{13}C-^{119}Sn}$ = 19.3 Hz), 21.1 t (α-CH_2 in Bu^i), 26.8 q (γ-CH_3 in Bu^i, $^3J_{^{13}C-^{119}Sn}$ = 49.8 Hz), 27.2 d (β-CH in Bu^i). Anal. Calcd for $C_{16}H_{36}Sn$: C, 55.35; H, 10.45. Found: C, 55.21; H, 10.37. MS (EI): m/z 291 (M^+, ^{120}Sn).

Table III. Acetolysis of **2a,b**[a]

		yield/%	
indiostannoxanes	AcOH/mmol	$In(OAc)_3$	**5**
2a	8	80	97
2b	2	61[b]	60
	8	98	82

[a] Acetolysis was carried out using a solution of the mixed stannoxanes (2 mmol) in benzene (5 mL) at room temperature for 3.5 h. [b] Corresponding dibutylindium acetates were obtained.

Table IV. Selected Thermal Analysis Data for **2**[a]

2	DTA peaks exo (product)[b]/°C	TGA end of weight loss/°C
2a	262 ($C_{3.5}H_{11.0}In_{2.2}O_{9.2}Sn_{1.9}$)[c]	352
2b	247	305
2c	265 ($C_{6.6}H_{10.0}In_{0.9}O_{4.8}Sn_{1.0}$)[d]	348
2d	262	342

[a] Thermal analysis conditions: room temperature to 600 °C, at 10 °C/min, under N_2 flow. [b] Esimated with respect to the elemental analysis data. [c] This formula indicates that one butyl group remained per two In–O–Sn units. [d] This formula indicates that one propionate and one butyl group remained per one In–O–Sn unit.

Acetolysis of 2. Into a benzene solution (5 mL) of **2b** (2 mmol) was added acetic acid (8 mmol), and the solution was stirred for 3.5 h at room temperature. After the reaction, precipitates of $In(OAc)_3$ were filtered off and washed with benzene three times. After evaporation of benzene, crystalline mixed tributyltin acetate (**5b**) was obtained. When the reaction of **2b** and 2 equiv of acetic acid were carried out, dibutylindium acetate in place of $In(OAc)_3$ was obtained but the yield was low.

$In(OCOCH_3)_3$: white powders, mp 285 °C dec (lit. 280 °C[9]).

$Bu^i_2In(OAc)$: colorless needles, mp 95–96.5 °C. IR (KBr): 1530 (s, ν_{as}(COOIn)). ^{13}C NMR ($CDCl_3$): δ 23.2 q (CH_3CO), 27.0 (α-CH_2), 27.7 q (γ-CH_3), 33.2 d (β-CH), 180.1 s (CO). Anal. Calcd for $C_{10}H_{21}InO_2$: C, 41.69; H, 7.35. Found: C, 41.33; H, 7.35. MS (EI): m/z 288 (M^+, ^{115}In).

$Bu^n_2Bu^iSn(OAc)$ (5b): colorless crystals, mp 55–56 °C. IR (KBr): 1580 and 1560 (ν_{as}(COOSn)). ^{13}C NMR ($CDCl_3$): δ 21.4 q (CH_3CO), 13.6 q (δ-CH_3 in Bu^n), 16.4 t (α-CH_2 in Bu^n, $^1J_{^{13}C-^{119}Sn}$ = 360.7 Hz), 27.0 t (γ-CH_2 in Bu^n, $^3J_{^{13}C-^{119}Sn}$ = 66.3 Hz), 27.9 t (β-CH_2 in Bu^n, $^2J_{^{13}C-^{119}Sn}$ = 20.7 Hz), 26.3 t (α-CH_2 in Bu^i, $^1J_{^{13}C-^{119}Sn}$ = 354.7 Hz), 26.5 q (γ-CH_3 in Bu^i, $^3J_{^{13}C-^{119}Sn}$ = 60.0 Hz), 28.2 d (β-CH), 176.6 s (CO). Anal. Calcd

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for $C_{14}H_{30}O_2Sn$: C, 48.17; H, 8.66. Found: C, 48.47; H, 8.72. MS (EI): *m/z* 350 (M^+, ^{120}Sn).

Results

The preparation and reactivity studies of new indiostannoxanes (**2a–d** and **3b**) treated in this paper are summarized in Scheme I. A characterization was undertaken for **2a–d** and **3b**, whose results are presented in Tables I and II. Finally, chemical and thermal reactivity studies were undertaken, and the results obtained are presented in Tables III and IV. These will be introduced at appropriate places in the section that follows.

Discussion

Addition of **1c** or **1d** to dibutyltin oxide proceeded in an abnormal fashion. Thus new indiostannoxanes **2c,d** were obtained via a cleavage of the In–C bonds as illustrated in Scheme I, respectively. Vibrational absorption bands appeared at 1540 and 1400 cm^{-1}, and higher values of $\delta(^{13}CO)$ than 180 ppm indicated an existence of indium carboxylate linkages.[9] In addition fragment ion peaks observed at around 291 were assignable to $(Bu_3{}^{120}Sn)^{\bullet+}$. These spectral data reasonably suggested the presence of In–OCOEt bonds in **2c,d**. The reactions of **1a,b** with Bu_2SnO also gave indiostannoxanes **2a,b**. Similarly, reactions of **1a,b** with $(Bu_3Sn)_2O$ were carried out, and indiostannoxanes **2a** and **3b** together with mixed tetrabutyltin were obtained. Consequently, it is assumed that the formation of **2** took place through a migration of a butyl group and not of a propionato group.

It is well-known that the reactions of organotin compounds with several organometallics including boron or thallium derivatives proceed via a migration of electronegative substituents such as halides or carboxylates to tin centers.[10] It should be remembered, however, that dibutyltin oxide sometimes behaves as an alkyl acceptor to give trialkyltin derivatives under specific conditions.[11] Further, certain dialkylindium derivatives donate their alkyls onto a neutral or less basic substrate such as triethylstibine oxide or thiobenzaldehyde, etc.[12] Thus, the butyl migration discussed in this article can be justified by a consideration that dibutyltin oxide and bis(tributyltin) oxide behave as an alkyl acceptor like triethylstibine sulfide.

Although $M^+ + 1$ peaks were detected in the FAB MS spectra for the indiostannoxanes **2a,b** and **3b**, their molecularity measurements showed that they formed a dimmeric aggregate in a solution. Perhaps, **2a,b** and **3b** exist in a ladder type dimer[9,13] but we could not clarify their structures in detail. In contrast the indiostannoxanes **2c,d** were monomeric in solution, because chelation by the carboxylato ligand prevented an intermolecular coordination. A formation of the chelation was confirmed by their values of $\nu_{as}(COOIn)$.[14] Meanwhile, the reaction of **1** with butanestannoic acid proceeded very fast even at room temperature but gave polymeric products that readily underwent a change into solid gels. Overall, the reactivities of the organotin oxides employed here were estimated as being $BuSnO_2H > (Bu_3Sn)_2O > Bu_2SnO$ with respect to the reaction temperatures. In contrast, it is curious that no reaction occurred in cases of **1** with diphenyltin oxide, dimethyltin oxide, bis(triphenyltin) oxide, benzenestannoic acid, and methanestannoic acid. We, however, could not explain the low reactivities of other organotin oxides than the butyl derivatives in view of their acidity and basicity.[15]

Next, we attempted a cleavage of In–O–Sn linkage by acetolysis. As shown in Table III, the reactions of **2a,b** with an equivalent amount of acetic acid gave the corresponding monoacetato derivatives, Bu_2InOAc and Bu_3SnOAc, in somewhat low yields. In the reactions of **2a,b** with excess acetic acid, In–O–Sn linkages were cleaved quantitatively and the mixed tributyltin acetates **5** and $In(OAc)_3$ were obtained in quantitative yields. The formation of **5** also supported the proposed structures of **2** and **3** because of the absence of Sn–propionato linkage in **5**.

The indiostannoxanes **2** and **3** formed wet gels[16] via hydrolysis–polycondensation in benzene on standing for a week by an addition of the catalytic amounts of water (10 mol %). Thermal properties of **2a–d** were also investigated. These indiostannoxanes were found to release butyl groups at 260–280 °C with exotherms, and the thermal weight loss ended at 300–350 °C to give indium–tin oxide powders quantitatively. Consequently these results indicated that the indiostannoxanes are excellent precursors for indium–tin oxide (ITO) thin layers via the solution pyrolysis method.[5,17]

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(Pentafluoro-λ^6-sulfanyl)difluoromethanesulfonyl Fluoride and Derivatives

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Introduction

Fluorinated-carbon-containing sulfonyl fluorides (R_FSO_2F) are of considerable interest.[2] The simplest member, trifluoromethanesulfonyl fluoride, CF_3SO_2F, has found multiple uses and is employed in the preparation of trifluoromethanesulfonic acid or triflic acid (CF_3SO_3H).[3]

We have prepared a number of fluorinated (pentafluoro-λ^6-sulfanyl)methanesulfonyl fluorides and their respective acids. In particular, we have previously prepared $SF_5CH_2SO_2F$ ($SF_5CH_2SO_3H\cdot H_2O$) and SF_5CHFSO_2F (SF_5CHFSO_3H).[4,5] In addition, for the ethane series, the following SF_5 alkanesulfonic acids, $F_5SCH_2CH_2SO_3H$, $F_5SCH_2CF_2SO_3H\cdot H_2O$, and $F_5SCHFCF_2SO_3H\cdot H_2O$, are known.[6] We now report the successful preparation of the completely fluorinated member of the methane series, $SF_5CF_2SO_2F$, and its corresponding acid, ester, and salts.

Results and Discussion

We have found that static fluorination of SF_5CFHSO_2F under mild conditions and in the presence of NaF gave $SF_5CF_2SO_2F$ in good yield (57%):

$$SF_5CFHSO_2F + F_2 + NaF \rightarrow SF_5CF_2SO_2F + NaHF_2 \qquad (1)$$

Compound **1** is a clear water-like liquid with a boiling point of 51 ± 1 °C. Basic hydrolysis of **1** gave the corresponding stable sulfonate salts (**2**):

$$2SF_5CF_2SO_2F + 2M(OH)_2 \rightarrow \underset{\mathbf{2}}{M(SF_5CF_2SO_3)_2} + MF_2 + 2H_2O \qquad (2)$$

$$M = Ca\ (\mathbf{2a}),\ Ba\ (\mathbf{2b})$$

The corresponding acid was distilled from concentrated sulfuric

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