Organometallics **1990,** *9,* 3043–3053 3043

Synthesis, Molecular Structures, and Solution-Phase Behavior of New Anionic Pentacoordinate Triorganotin(IV) Compounds: Tris(dimethylamino)sulfonium Dichlorotriorganostannates, Bis(2,6-dimethylphenoxy)triorganostannates, and Chloro(2,6-dimethylphenoxy)triorganostannates[†]

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Received June 5, 1990

Chloro- and (2,6-dimethylphenoxy)triorganostannanes react with tris(dimethylamino)sulfonium (TAS) chloride or 2,6-dimethylphenoxide in acetonitrile to form the corresponding pentacoordinate stannate complexes. The solution-phase behavior and solid-state structures of the TAS stannates have been examined by use of NMR and far-infrared spectroscopy, Mössbauer measurements, and X-ray crystallography, revealing the hypervalent nature of the anionic Sn(IV) species with trigonal-bipyramidal structures. Reaction of the stannanes and anions is reversible, and the stability of the TAS stannates is highly affected by the nature of the equatorial organic groups and apical heteroatom substituents. The aryloxy chloro mixed-ligand stannate is more stable than a 1:1 mixture of the bis(aryloxy)- and dichlorostannates. The X-ray structure indicates that the three-center, four-electron apical bond is highly polarizable. In the mixed-ligand stannate, the Sn–O bond is considerably shorter than those in the dioxy compound, while the Sn–Cl distance is longer than those of the dichloro compound, which is consistent with the solution behavior of the mixed-ligand anionic complex, where chloride ion is preferentially liberated.

Introduction

Increasing investigation of hypervalent species containing Sn(IV) has been focused mainly on (1) acquiring well-defined solid-state structures to learn more about the nature of the unusual bonding scheme,[1] (2) gaining insight into the dynamic behavior in solution, particularly in connection with the anion transport model in membranes[2] and triggers for biocidal applications,[3] and (3) utilizing them in selective organic syntheses[4,5] via, for instance, reactivity control of enolate intermediates[4] or phase-transfer catalysis.[5a] However, our understanding of such fundamental chemistry still remains insufficient.[3a,6] Anionic pentacoordinate triorganotin(IV) compounds (10-Sn-5 system)[7] are predicted to possess a trigonal-bipyramidal (TBP) arrangement with the organic and electronegative groups occupying the equatorial and apical positions, respectively, and the hypervalency is characterized by the three-center, four-electron configuration for the apical bonds.[1] Although the existence of such Sn compounds has frequently been suggested to explain various chemical phenomena, a detailed study was made only with the dihalogen complexes[8] and some special limited compounds.[9-11] Tetrahedral (T_d) Sn(IV) compounds that have an electronegative group(s) react with certain anions to form pentacoordinate stannate complexes through the expansion of the coordination sphere. However, this process is reversible in nature,[2] and therefore, NMR spectra, for example, of an isolated pentacoordinate Sn(IV) compound or a 1:1 mixture of a tetracoordinate Sn compound and an anion do not always indicate the correct properties of the formulated stannate compounds.[12] In addition, as outlined in eqs 1–4, a mixture of stannate complexes may undergo disproportionation to establish an equilibration between homo- and mixed-ligand complexes.

$$R_3SnX + X^- \rightleftarrows [R_3SnX_2]^- \qquad (1)$$

$$R_3SnX + Y^- \rightleftarrows [R_3SnXY]^- \qquad (2)$$

$$R_3SnY + X^- \rightleftarrows [R_3SnXY]^- \qquad (3)$$

$$R_3SnY + Y^- \rightleftarrows [R_3SnY_2]^- \qquad (4)$$

[†] Dedicated to the memory of the late Professor John K. Stille.

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Chart I

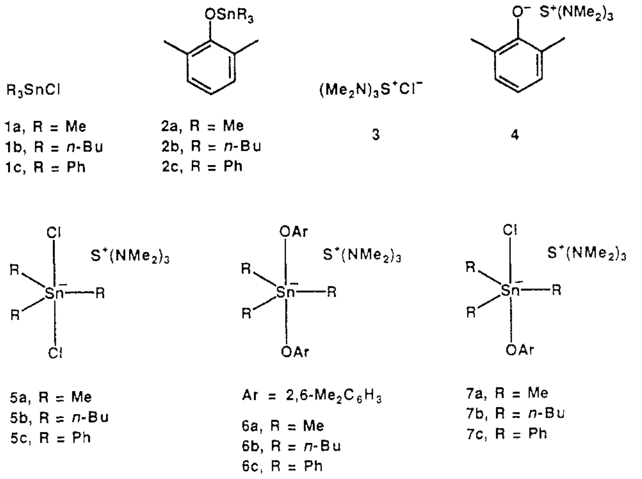

Table I. Aggregation States of Triorganostannane Derivatives[a]

compd	solvent	concn, M	aggregation no.[b]	$^1J(^{119}Sn-^{13}C)$, Hz
1a	CH_3CN	0.3	1.0	430
1a	benzene[c]	0.6	1.0	378
1b	CH_3CN	0.3	1.0	375
1c	CH_3CN	0.1	1.0	680
2a	benzene[c]	0.2	1.0	389
2a	CH_3CN	0.8	1.0	421
2b	benzene[c]	0.3–0.7	1.1–1.2	354
2b	THF	0.1–1.4	1.0–1.1	368
2b	CH_3CN	0.3	1.0	364
2c	benzene[c]	0.4	1.1	640
2c	CH_3CN	0.2	1.0	651

[a] Measured at 22 °C by the vapor-pressure osmometry method. [b] Calculated by the ratio of observed molecular weight to theoretical value. [c] Measured by the cryoscopic method.

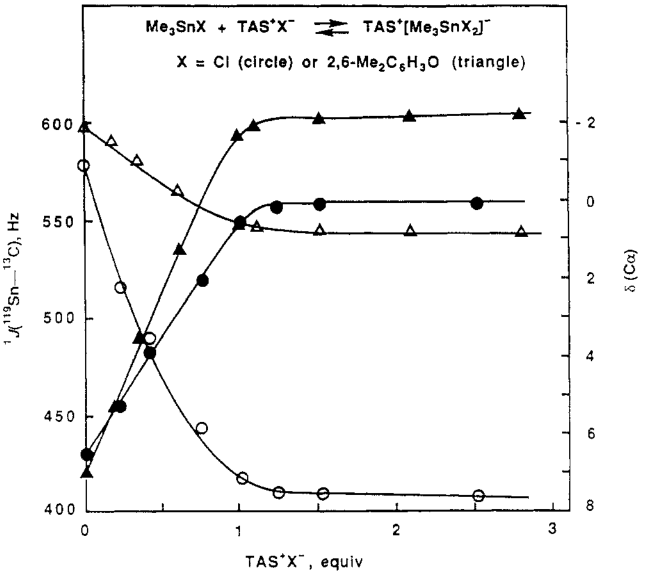

Figure 1. Changes of $^1J(^{119}Sn-^{13}C)$ (solid symbols) and $\delta(C_\alpha)$ values (open symbols) against the amounts of added TAS salts in going from the chloro- and (aryloxy)stannanes to the dichloro- and bis(aryloxy)stannates, respectively.

This fundamental problem has not attracted as much attention as it deserves. In this study, we selected as anionic ligands an oxy anion and chloride ion because of their ubiquitousness and versatility. Our purpose was *not* to synthesize structurally unique compounds but to obtain general information about organotin chemistry, particularly the bonding nature of the stannate compounds, which requires the use of simple nonchelating ligands lacking steric constraints. Described herein are the solution-phase properties and solid-state structures of certain anionic homo- and mixed-ligand Sn(IV) complexes and the factors controlling the stability of the hypervalent compounds.

Results and Discussion

Behavior of Triorganotin(IV) Compounds in Solution. Our starting tetracoordinate Sn(IV) compounds were chlorotriorganostannanes (1) and (2,6-dimethylphenoxy)triorganostannanes (2) (Chart I). Use of the latter bulky phenoxy compounds avoided the unnecessary complications caused by dimerization.[13] Table I lists the aggregation numbers of these compounds measured in acetonitrile or THF (vapor-pressure osmometry method)[14] and in benzene (freezing-point-depression method). These compounds exist mainly as monomers in acetonitrile and THF at room temperature in the molarity range of 0.1–1.4 M. Such solvents may reversibly form some coordination complexes with the Sn(IV) compounds,[15] but this does not disturb the interpretation of the chemistry in solution. Tris(dimethylamino)sulfonium (TAS) chloride (3) and tris(dimethylamino)sulfonium 2,6-dimethylphenoxide (4) were used as donor compounds, since the cation is uniquely stable and bulky and has negligible interaction with the counteranions.[17]

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(15) Addition of acetonitrile increases the $^1J(^{119}Sn-^{13}C)$ value (380 Hz) of 1a in C_6H_6, which reaches 421 Hz after addition of 15 equiv of the donor. The degree of the increase (ΔJ = 41 Hz) is slightly smaller than the effect of acetone (ΔJ = 53 Hz)[16] and much smaller than that of HMPA (ΔJ = 166 Hz). Such tendencies are correlated with the donor number (DN; donicity), which increases in the order benzene (0.1) < acetonitrile (11.9) < acetone (17.0) < THF (20.0) < HMPA (38.8).[16] For some implications on the weak interaction between donor solvents and tetracoordinate stannanes, see: (a) Ochiai, M.; Iwaki, S.; Ukita, T.; Matsuura, Y.; Shiro, M.; Nagao, Y. *J. Am. Chem. Soc.* **1988**, *110*, 4606. The continuous sp^3 to sp^2 structural change by the ligand coordination has been discussed by: (b) Lockhart, T. P.; Manders, W. F. *J. Am. Chem. Soc.* **1987**, *109*, 7015. (c) Wharf, I.; Piehler, L.; Sailofsky, B. M.; Onyszchuk, M.; Simard, M. G. *Can. J. Chem.* **1987**, *65*, 639. See also: (d) Holmes, R. R.; Dieters, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 3318.

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Table II. ^{13}C NMR Data of Triorganostannates 5–7 and Related Compounds in CD_3CN

compd[d]	chem shift, δ^{a-c}					$^1J(^{119}Sn-^{13}C)$, Hz
	C_{ip}	C_m and C_o		C_p	Sn–C	
Me_3SnOAr (**2a**)	160.2	128.9	128.9	118.6	−1.9	421
n-Bu_3SnOAr (**2b**)	160.3	129.0	129.0	119.1	17.5	364
Ph_3SnOAr (**2c**)	160.1	129.5	129.1	120.0	139.8	651
$TAS^+[Me_3SnCl_2]^-$ (**5a**)					7.6	559
$TAS^+[n\text{-}Bu_3SnCl_2]^-$ (**5b**)					26.1	511
$TAS^+[Ph_3SnCl_2]^-$ (**5c**)					149.5	853
$TAS^+[Me_3Sn(OAr)_2]^-$ (**6a**)	166.1	128.3	127.1	111.7	0.8	606
$TAS^+[n\text{-}Bu_3Sn(OAr)_2]^-$ (**6b**)	166.1	128.4	127.1	111.9	20.8	568
$TAS^+[Ph_3Sn(OAr)_2]^-$ (**6c**)	165.4	128.3	127.8	113.0	149.8	916
$TAS^+[Me_3Sn(OAr)Cl]^-$ (**7a**)	163.2	128.5	128.2	115.3	3.4	572
$TAS^+[n\text{-}Bu_3Sn(OAr)Cl]^-$ (**7b**)	163.2	128.5	128.1	115.2	22.2	526
$TAS^+[Ph_3Sn(OAr)Cl]^-$ (**7c**)	163.5	128.1	127.7	114.3	148.6	*e*
5a + HMPA					7.7	557
6a + HMPA	165.8	128.4	127.2	112.2	1.0	603
TAS^+ArO^- (4)	168.2	127.9	127.9	107.6		

[a] Measured at 25 °C. [b] The range of concentration is 0.3–0.5 M. [c] External standard TMS, 0 ppm. [d] Abbreviations: ArO, 2,6-dimethylphenoxy; ip, ipso; o, ortho; m, meta; p, para. [e] Not measureable.

Structures of the neutral and anionic Sn(IV) compounds in solution were investigated by NMR spectroscopy (Table II).[3a,12,18] When chlorostannane **1a** and chloride **3** were mixed in acetonitrile-d_3 at room temperature, the corresponding TAS stannate **5a** was formed in a reversible manner. As described by Simon earlier,[2] the $^1J(^{119}Sn-^{13}C)$ values increased monotonously from 430 Hz for **1a** and became 559 Hz after addition of 2.5 equiv of **3**, while $\delta(C_\alpha)$ moved down from δ 0.9, approaching a constant value, δ 7.6 (Figure 1). An equimolar mixture of **1a** and **3** gave the stannate in only 93% yield. In a like manner, the reaction of the aryloxystannane **2a** and the TAS aryloxide **4** afforded the anionic bis(aryloxy)triorganostannate **6a** in a reversible fashion.[19] As expected, the $^1J(^{119}Sn-^{13}C)$ value increased from 421 Hz for tetracoordinate **2a** to 606 Hz for pentacoordinate **6a** (ΔJ = 185 Hz). In addition, a distinct downfield shift of the signal of α-carbons (Sn–C) is seen on going from the tetracoordinate to pentacoordinate arrangements (Figure 1).

The polarity of the Sn–O bond in the aryloxy compounds affects the charge distribution of the aromatic ring; the increase of the bond polarity induces the downfield shift of the ipso carbon and the upfield shift of the para carbon.[17a,c] The chemical shifts suggest that the charge density at the oxygen in the stannates is higher than that of the stannanes but is close to that of the ion-pair TAS aryloxide 4 (Table II).[17a,c]

The pentacoordinate Sn complexes appear to undergo metathesis via a dissociative mechanism by way of tetracoordinate species (eqs 1–4). Significantly, when chloride and aryloxide ions are present in amounts equal to that of the Sn(IV) species, convergency into the aryloxy chloro mixed stannates of type **7** has been observed. Thus, identical NMR spectra are obtained by mixing (1) equal amounts of the dichlorostannate **5a** and bis(aryloxy)stannate **6a** (equilibrating with the stannanes and anions) in acetonitrile-d_3, (2) chlorostannane **1a** and TAS aryloxide **4** in a 1:1 mole ratio, and (3) (aryloxy)stannane **2a** and chloride **3** in equal amounts. These mixtures, giving $^1J(^{119}Sn-^{13}C)$ = 544 ± 2 Hz and $\delta(C_\alpha)$ 3.2 ± 0.1, appeared to contain **7a** as the sole stannate complex equilibrating with ca. 15% of **2a**. As illustrated in Figure 2, the coupling constant and the chemical shift of the α-carbon of (aryloxy)stannane **2a** change by addition of chloride ion. After addition of ca. 1.2 equiv of the chloride **3**, the *J* value was saturated and thereafter remained almost constant despite the presence of an excess (up to 3 equiv) of **3**. This value of 572 Hz, however, is not identical with the 559 Hz for dichlorostannate **5a** obtained earlier but can be assigned to the mixed-ligand complex **7a**. A similar tendency was observed for the α-carbon chemical shift of this mixture, δ 3.4, which was different from δ 7.6 for **5a**. Since chlorostannane **1a** reacts readily with chloride ion to form **5a**, this observation suggests that, under such conditions, the mixed stannate **7a** does not dissociate into **1a** and aryloxide **4** to any appreciable extent. The profile of the spectrum change of chlorostannane **1a** caused by TAS aryloxide **4** is different. As shown in Figure 3, the NMR parameters

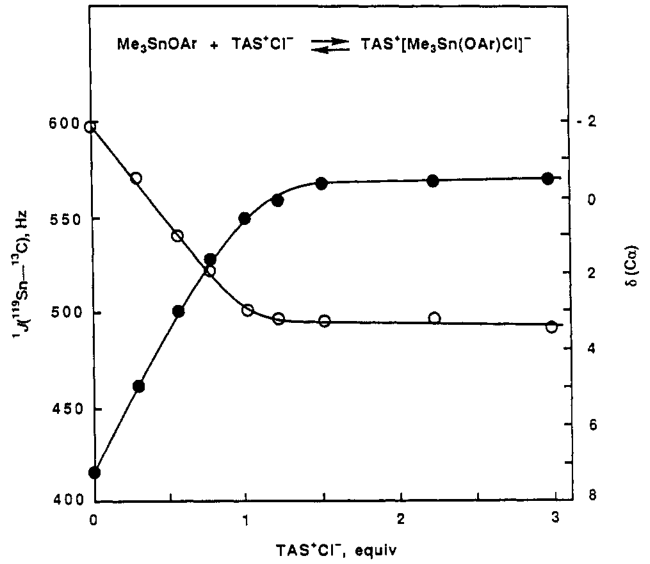

Figure 2. Changes of $^1J(^{119}Sn-^{13}C)$ (solid symbols) and $\delta(C_\alpha)$ values (open symbols) against the amount of added TAS chloride (**3**) in going from (aryloxy)trimethylstannane (**2a**) to TAS chloro(aryloxy)trimethylstannate (**7a**). ArO = 2,6-$Me_2C_6H_3O$.

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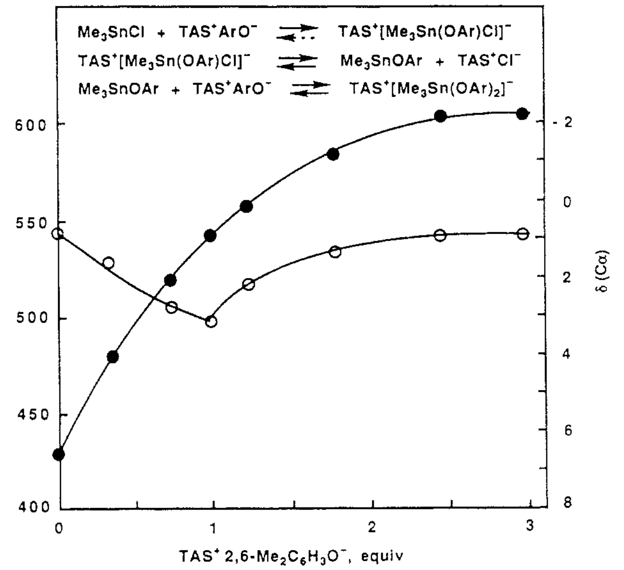

Figure 3. Changes of $^1J(^{119}Sn-^{13}C)$ (solid symbols) and $\delta(C_\alpha)$ values (open symbols) against the amount of added TAS aryloxide **4** in going from chlorotrimethylstannane (**1a**) to TAS bis(aryloxy)trimethylstannate (**6a**). ArO = $2,6-Me_2C_6H_3O$.

continue to vary until addition of ca. 2.5 equiv of **4**. The $^{119}Sn-^{13}C$ coupling constant increased consistently with an increase of the anion up to the addition of ca. 2.5 equiv of **4**, while the α-carbon signal moved downfield with an increase of **4** until the addition of an equimolar amount and then turned upfield to reach a constant value. The final constant values, $^1J(^{119}Sn-^{13}C)$ = 606 Hz and $\delta(C_\alpha)$ 0.8, agree well with those of the bis(aryloxy)stannate **6a**. This spectral change may be interpreted in terms of the initial formation of the mixed stannate **7a**, which liberates chloride ion. The resulting (aryloxy)stannane **2a**, as noted earlier, is captured by excess aryloxy anion to form **6a**.

With regard to the stannane structure, chlorine in **1a** can be displaced by the aryloxy group to form **2a**, but the oxygen ligand in **2a** is not displaced by chlorine under these conditions. The position of the equilibrium TAS stannate ⇌ stannane + TAS salt is apparently influenced by the nature of the stannane substituents and anions. The system described above establishes dynamic equilibria in acetonitrile consisting basically of four kinds of reversible processes (eqs 1–4; X = Cl, Y = 2,6-dimethylphenoxy), where chloro- and (aryloxy)stannanes are acting as Lewis acids and chloride and aryloxide ions as bases. The chlorotriorganostannanes are evidently stronger acids than the aryloxy analogues, whereas the aryloxy anion is a much stronger base in comparison to chloride ion. The dichloro- and dioxystannates **5** and **6** are adducts formed by the stronger acceptor/weaker donor and weaker acceptor/stronger donor combinations, respectively. On the other hand, the mixed-ligand stannate **7** is viewed as either a strong acceptor/strong donor complex or a weaker acceptor/weaker donor adduct. In fact, the reaction of the chlorostannane **1** and aryloxy anion **4** or interaction of the (aryloxy)stannane **2** and chloride ion **3** leads readily to the expected mixed-ligand stannate **7**. A mixture of the two homo-ligand stannates **5** and **6** is also converted to the more stable mixed-ligand stannate **7**. The mixed-ligand complex can kinetically liberate either anion but, actually, dissociates into weakly basic chloride ion and the (aryloxy)stannane, which has a weaker Lewis acidity, under thermodynamic control.

The equilibrium constants (*K*) of the reaction of triorganotin chlorides or aryloxides and TAS salts are summarized in Table III.

Table III. Equilibrium Constants

$$R_3SnX + TAS^+Y^- \overset{K}{\rightleftharpoons} TAS^+[R_3SnXY]^-$$

X	Y	R	*K*, L mol^{-1}	degree of association
Cl	Cl	Me	950	0.93
		n-Bu	287	0.82
		Ph	3593	0.97
ArO[a]	ArO	Me	1306	0.94
		n-Bu	253	0.82
		Ph	144	0.83
ArO	Cl	Me	126	0.85
		n-Bu	49	0.77
		Ph	*b*	*b*

[a] ArO = 2,6-dimethylphenoxy. [b] Not measurable.

Thus, the solution-phase investigations have revealed that (1) the stannane/stannate chemistry is a subject of equilibrium and the stannates dissociate into the stannanes and anions to a considerable extent in acetonitrile, (2) the stability of the pentacoordinate structure depends on the organic moiety and higher stability is obtained by use of methyl and phenyl groups rather than butyl groups (Table III), (3) the halogen/oxygen mixed-ligand stannates are much more stable than the dihalo or dioxy homo-ligand stannates, (4) the Sn–O bond of a homo- or mixed-ligand (aryloxy)stannate is more polar than that of the corresponding (aryloxy)stannane, (5) the chloro/aryloxy mixed stannate liberates chloride preferentially, and (6) hexacoordinate Sn complexes are not formed by the addition of excess chloride, aryloxide, HMPA, or a combination of them, as judged by NMR analysis (Table II).[8g,20,22]

Solid-State Structures of the Anionic Pentacoordinate Stannate Compounds. Trimethyl- and triphenylstannyl aryloxides readily accept oxide or halide ions to form novel pentacoordinate stannate complexes. Thus, the reaction of **2a** and **4** in a 1:1 mole ratio in acetonitrile at room temperature gave, after recrystallization from an acetonitrile/benzene mixture, the homo-ligand anionic complex **6a** (mp 135 °C) in 94% yield. In a similar manner, the crystalline mixed-ligand stannate **7c** (mp 163 °C) was obtained in 92% yield from **2c** and **3**. These TAS stannates were extremely sensitive to air and moisture.

A. Tris(dimethylamino)sulfonium Bis(2,6-dimethylphenoxy)trimethylstannate (6a). X-ray crystallographic analysis was conducted at −50 °C. The crystallographic data and selected bond lengths and angles are summarized in Tables IV and V. The molecular structure of **6a** is depicted in Figure 4 with the atomic numbering scheme. The unit cell contains two (aryloxy)stannate anions and two TAS cations, which have a pyramidal structure. The sulfur atom of the TAS cation of **6a** is placed on the extension of the equatorial plane made by three Sn-methyl groups. The central pentacoordinated Sn(IV) ion has a TBP geometry, where the three methyl groups lie on the equatorial plane and the two aryloxy groups occupy the apical positions. Here, the Sn, O(1), C(3), O(2), C(7), C(2), N(1), and S atoms lie on the crystallographic mirror plane and the two aryloxy

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(20) The HMPA ligand in the **1a**/HMPA complex[21] was facilely replaced by chloride ion to form **5a** by addition of chloride **3** (see Experimental Section).

(21) Spencer, J. N.; Coley, S. M.; Otta, J. C.; Grushow, A.; Enders, B. G.; Nachlis, W. L.; Yoder, C. H. *J. Organomet. Chem.* **1988**, *346*, 161.

(22) The formation of the hexacoordinate tin complex $[Me_4N]_2^+[Me_3SnCl_3]^{2-}$ in the solid state has been confirmed by its Mössbauer spectrum: Barbieri, R.; Stocco, G. C. *Gazz. Chim. Ital.* **1974**, 149; *Chem. Abstr.* **1974**, *81*, 62664.

Table IV. Crystallographic Data and Details of Measurements for Tris(dimethylamino)sulfonium Bis(2,6-dimethylphenoxy)trimethylstannate (6a) and Tris(dimethylamino)sulfonium Chloro(2,6-dimethylphenoxy)triphenylstannate (7c)

complex	**6a**	**7c**
mol formula	$C_{25}H_{25}N_3O_2SSn$	$C_{32}H_{42}ClN_3OSSn$
mol wt	570.38	670.88
cryst size, mm^3	0.30 × 0.31 × 0.10	0.50 × 0.32 × 0.18
space group	*Pnma*	$P2_1/a$
cell dimens		
a, Å	21.596 (5)	19.984 (7)
b, Å	13.664 (3)	11.417 (2)
c, Å	9.799 (2)	14.867 (1)
β, deg		98.16 (1)
V, Å^3	2891.6 (1)	3357.5 (1)
Z	4	4
ρ_{measd}, g/cm^3	1.282	1.325
ρ_{calcd}, g/cm^3	1.281	1.328
color	colorless	colorless
diffractometer[a]	Enraf-Nonius CAD4 (60 kV, 26 mA)	Rigaku AFC-5R (50 kV, 50 mA)
radiation	Mo Kα (0.710 69 Å)	Cu Kα (1.541 84 Å)
scan type	$\omega-2\theta$	$\omega-2\theta$
scan speed, deg/min	4-12	4
2θ scan limit, deg	60	126
scan interval	$0.8 + 0.35 \tan\theta$	$1.3 + 0.5 \tan\theta$
std indices	(535), (1,1,13),(277)	(−5,−5,−5), (−1,−3,−8), (−7,−3,7)
total no. of rflns scanned	4813	5265
no. of unique rflns	2343 ($I > 3\sigma(I)$)	4472 ($F_o > 3\sigma(F_o)$)
cell dimens determn	25 rflns, $11° < 2\theta < 14°$, t = 223 K	20 rflns, $53° < 2\theta < 61°$, $t = 293 \pm 2$ K
μ, cm^{-1}	9.78	76.99
hkl range	$0 \le h \le 13$, $0 \le k \le 19$, $0 \le l \le 30$	$-20 \le h \le 19$, $0 \le k \le 13$, $0 \le l \le 14$
R	0.057	0.070
R_w	0.063	0.081

[a] Graphite-monochromated radiation.

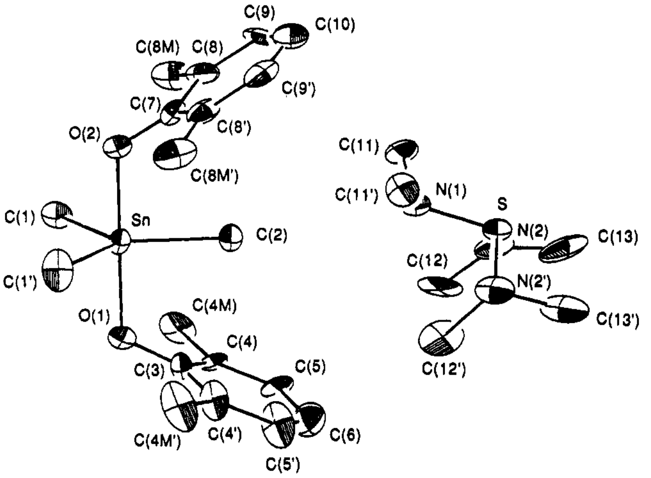

Figure 4. Molecular structure of tris(dimethylamino)sulfonium bis(2,6-dimethylphenoxy)trimethylstannate (**6a**) in an ORTEP drawing with the atomic numbering scheme. The hydrogen atoms are omitted for better clarity. Shown are the 40% thermal ellipsoids.

Table V. Selected Bond Distances and Angles with Esd's of Tris(dimethylamino)sulfonium Bis(2,6-dimethylphenoxy)trimethylstannate (6a) and Tris(dimethylamino)sulfonium Chloro(2,6-dimethylphenoxy)triphenylstannate (7c)

		6a[a]			
		Bond Distances (Å)			
Sn–O(1)	2.212 (7)	Sn–O(2)	2.225 (7)	Sn–C(1)	2.135 (9)
Sn–C(2)	2.12 (1)	Sn–C(1′)	2.135 (9)	O(1)–C(3)	1.32 (1)
O(2)–C(7)	1.32 (1)	S–N(1)	1.683 (9)	S–N(2)	1.627 (7)
		Bond Angles (deg)			
O(1)–Sn–O(2)	180.0 (1)	O(1)–Sn–C(1)	89.7 (3)		
O(1)–Sn–C(2)	89.7 (3)	O(1)–Sn–C(1′)	89.7 (3)		
O(2)–Sn–C(1)	90.5 (3)	O(2)–Sn–C(2)	90.1 (3)		
O(2)–Sn–C(1′)	90.5 (3)	C(1)–Sn–C(1′)	112.1 (3)		
C(1)–Sn–C(2)	124.0 (2)	C(1′)–Sn–C(2)	124.0 (2)		
Sn–O(1)–C(3)	125.4 (6)	Sn–O(2)–C(7)	122.1 (6)		
O(1)–C(3)–C(4)	120.7 (5)	O(2)–C(7)–C(8)	120.4 (5)		
S–N(1)–C(11)	110.7 (6)	N(1)–S–N(2)	99.9 (3)		
		7c			
		Bond Distances (Å)			
Sn–O(1)	2.102 (6)	Sn–Cl	2.693 (2)	Sn–C(9)	2.143 (8)
Sn–C(18)	2.166 (9)	Sn–C(21)	2.113 (8)	O(1)–C(1)	1.344 (12)
		Bond Angles (deg)			
Cl–Sn–O(1)	177.1 (2)	Cl–Sn–C(9)	87.4 (11)		
Cl–Sn–C(15)	88.7 (12)	Cl–Sn–C(21)	86.0 (13)		
C(9)–Sn–C(15)	120.7 (3)	C(9)–Sn–C(21)	115.7 (3)		
C(15)–Sn–C(21)	123.0 (3)	Sn–O(1)–C(1)	131.4 (5)		
O(1)–Sn–C(15)	90.4 (3)	O(1)–Sn–C(21)	92.3 (3)		

[a] Primed atoms are related to their unprimed equivalents by mirror image.

groups are oriented on the same side as the C(2) atom. The equatorial plane is nearly flat with 360.1° for the sum of the three C–Sn–C angles (112.1 (3), 124.0 (2), and 124.0 (2)°), and the lengths of the Sn–C bonds are nearly equal. The two axial Sn–O bonds are approximately the same, 2.212 (7) and 2.225 (7) Å, which are longer than the ordinary covalent bond of 2.06 Å[23] but much shorter than the van der Waals distance of ca. 3.3 Å.[24] The O(1)–Sn–O(2) angle is 180.0°. The linear geometry is consistent with the hypervalent nature of the apical bonds. In addition, the two aryloxy moieties are oriented so as to minimize the nonbonded repulsion between the ortho methyl groups and Sn-methyl groups.

B. Tris(dimethylamino)sulfonium Chloro(2,6-dimethylphenoxy)triphenylstannate (7c). The solid-state structure of this new mixed-ligand complex has been determined in various ways. Far-infrared spectra below 500 cm^{-1} offer useful information on the stretching and bending modes of Sn–C and Sn–heteroatom bonds.[25] In the solid state, the tetracoordinate chloro and aryloxy compounds **1c** and **2c** exhibit Sn–C stretching bands at 448 and 447 cm^{-1}, respectively, while the corresponding band of the mixed stannate **7c** occurs at slightly higher frequency, 458 cm^{-1}. The tetracoordinate compounds **1c** and **2c** afford Sn–Cl and Sn–O stretching bands at 331 and 380 cm^{-1},[25a,b] respectively, which move to lower frequencies, 306 and 364 cm^{-1},[25b-k] in the pentacoordinate Sn compound **7c**. Such blue and red shifts are consistent with the geometrical change;[25g-k] as one goes from the T_d to TBP structure, the equatorial Sn–C bonds become shorter, owing to the increase of s character, and the axial Sn–het-

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[23] Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 224.

[24] Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

[25] (a) Beattie, I. R.; McQuillan, G. P. *J. Chem. Soc.* **1963**, 1519. (b) Srivastava, T. S. *J. Organomet. Chem.* **1967**, *10*, 373. (c) Srivastava, T. S. *J. Organomet. Chem.* **1967**, *10*, 375. (d) Clark, J. P.; Langford, V. M.; Wilkins, C. J. *J. Chem. Soc. A* **1967**, 792. (e) Kawasaki, Y.; Hori, M.; Uneka, K. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 2463. (f) Wharf, I.; Lobos, J. Z.; Onyszchuk, M. *Can. J. Chem.* **1970**, *48*, 2787. (g) Liengme, B. V.; Randall, R. S.; Sams, J. R. *Can. J. Chem.* **1972**, *50*, 3212. (h) Das, M. K.; Buckle, J.; Harrison, P. G. *Inorg. Chim. Acta* **1972**, *6*, 17. (i) Aitken, C. T.; Onyszchuk, M. *J. Organomet. Chem.* **1973**, *59*, 189; **1985**, *295*, 149. (j) Pelizzi, C.; Pelizzi, G.; Tarasconi, P. *J. Organomet. Chem.* **1977**, *124*, 151. (k) Wharf, I.; Piehler, L.; Sailofsky, B. M.; Onyszchuk, M.; Simard, M. G. *Can. J. Chem.* **1987**, *65*, 639 and references cited therein.

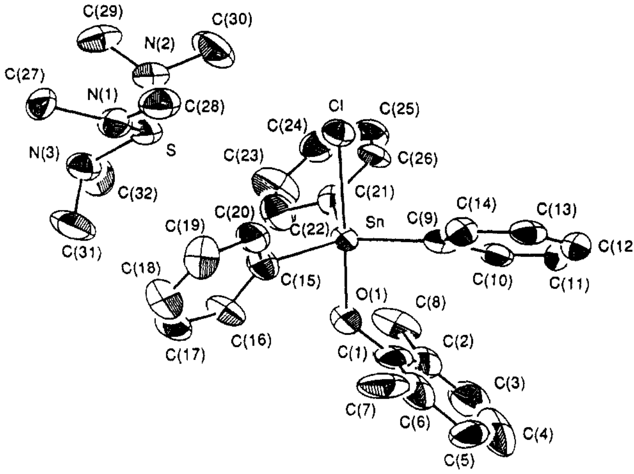

Figure 5. Molecular structure of tris(dimethylamino)sulfonium chloro(2,6-dimethylphenoxy)triphenylstannate (**7c**) in an ORTEP drawing with the atomic numbering scheme. The hydrogen atoms are omitted for better clarity. Shown are the 40% thermal ellipsoids.

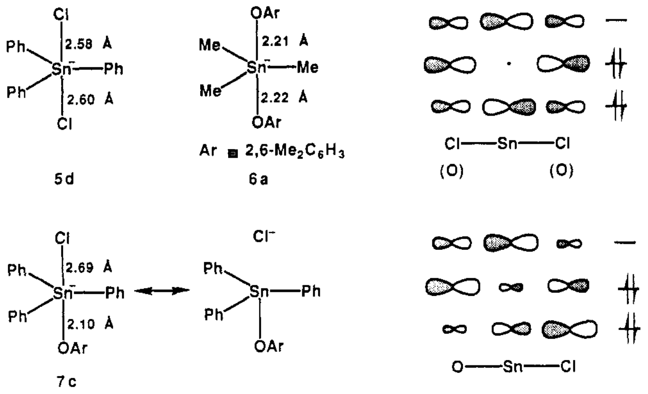

Figure 6. Lengths of apical bonds and molecular orbitals of homo- and mixed-ligand stannates.

eroatom bonds become longer with the increase on p character.[26]

The ^{119}Sn Mössbauer spectrum of **7c** taken at 77 K exhibited a typical quadrupole-split double-resonance spectrum.[8e,f] The isomer shift (δ) appeared at δ = 1.3 mm s^{-1}, and the value of the quadrupole splitting (Δ) was 2.7 mm s^{-1}. These Mössbauer parameters and the Δ/δ ratio of 2.07 are in good agreement with the previously reported values (δ = 1.31 mm s^{-1} and Δ = 2.86 mm s^{-1}) for a homo-ligand stannate, $(n\text{-}C_4H_9)_4N^+$ $[trans\text{-}(C_6H_5)_3SnCl_2]^-$,[8f] suggesting that the new type of the stannate also has a TBP geometry with electronegative ligands in the apical positions.[8e-g]

Figure 5 illustrates an ORTEP structure of **7c** obtained with its monoclinic crystal formed from a 2:1 acetonitrile/benzene mixture. The X-ray crystallographic data and selected bond lengths and angles are given in Tables IV and V. The complex **7c** consists of a mixed-ligand stannate anion and a pyramidal TAS cation. The sulfur atom of the TAS cation, unlike that of the stannate **6a** described above, is not in the equatorial plane and is closer to the chlorine atom than the oxygen. The stannate part is regarded as a mildly distorted TBP structure with the three phenyl groups lying in the equatorial plane and chlorine and aryloxy group occupying the apical positions with a trans relationship. The Cl–Sn–O(1) axis is approximately linear with an angle of 177.1 (2)°. Noteworthy are the bond distances between Sn and the heteroatoms. As observed with a homo-ligand complex, the Sn–Cl bond distance of 2.693 (2) Å is longer than that of the Sn–Cl covalent bond (2.4 Å)[23] but is much shorter than the van der Waals distance (ca. 3.4 Å).[24] The Sn–O bond length of 2.102 (6) Å shows a similar propensity, consistent with the hypervalent property. However, these bond lengths differ considerably from those of the corresponding homo-ligand stannate complexes (vide infra). Further, the three Sn–C bonds have slightly different distances (2.113 (8), 2.143 (8), and 2.166 (9) Å) and the C–Sn–C bond angles are considerably dissimilar (115.7 (3), 120.7 (3), and 123.0 (3)°) with a sum of 359.4°. The Sn atom is located 0.10 Å out of the plane formed by the three carbon atoms of the phenyl groups, C(9), C(15), and C(21), in the direction of the aryloxy oxygen. The three phenyl rings are twisted with twist angles of 50.5, 123.2, and 130.9°. The geometry of the aryloxy group with the C(9)–Sn–O(1)–C(1) torsional angle of −8.5° resembles that of the bis(aryloxy) complex **6a**, where the C–O bonds is eclipsed with one of the equatorial Sn–C bonds.

Correlation of the Solid-State and Solution-Phase Structures of the Stannate Compounds. The structures of the TAS stannates in acetonitrile solution and the crystalline state can be correlated by NMR analysis. The ^{119}Sn–^{13}C coupling constant in the cross-polarization, magic-angle spinning (CP/MAS) ^{13}C NMR spectrum of bis(aryloxy)stannate **6a**, 600 Hz, determined by the peak occurring at δ 1.7 with small satellites, and the chemical shift due to the ipso carbon, δ 164.9, are close to those obtained in acetonitrile solution, 606 Hz and δ 166.1, respectively, and far from the 421 Hz and δ 160.2 for tetracoordinate **2a** (Table II). Thus, the pentacoordinate structure of **6a** in solution is ascertained from this good correlation. The CP/MAS ^{13}C NMR spectrum of the mixed-ligand triphenylstannate **7c** is somewhat complicated, because the steric congestion, caused by the phenyl and aryloxy groups, reduced the molecular flexibility in the crystalline state. Such circumstances cause the differentiation of the ortho methyls in the aryloxy group at δ 19.1 and 19.6. The chemical shifts of the three Sn–C and the aryloxy ipso and para carbon signals, δ 149.4, 163.7, and 115.6, respectively, are in close accordance with the values obtained with the mobile, relaxed molecule in acetonitrile,[27] indicating that **7c**, like **6a**, dissociates little in acetonitrile and has TBP structures in both the solid state and solution phase.

Nature of the Apical Bonds and Hypervalency. The current MO theory predicts that pentacoordinate triorganostannates bearing two electronegative substituents have a hypervalent nature. The central Sn atom has three sp^2 orbitals forming the equatorial bonds and a p orbital. The latter is available for creating the apical bonds with three-center, four-electron configurations and, because the HOMO is derived from a nonbonding MO,[1] the electronegative groups are utilized to form such bonds (apicophilicity).[1] This consideration is fully supported by the structures of the known stannate **5d**[8e] and the new, sterically unrestricted simple stannates **6a** and **7c**. Figure 6 compares the lengths of the apical bonds of the homo- and mixed-ligand stannates with added MO pictures. As described above, the apical bonds are longer than the normal covalent Sn–Cl or Sn–O bonds but shorter than the van der Waals distances, in accord with the hypervalency.

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[26] Bent, H. A. *Chem. Rev.* **1961**, *61*, 275.

[27] The corresponding signals in the CP/MAS ^{13}C NMR spectrum for **2c** appear at δ 138.8, 158.0, and 119.8.

Notably, in the homo-ligand stannates **5d** and **6a**, the lengths of the Sn–heteroatom bonds are nearly equal,[8e,28] while, in the mixed-ligand stannate **7c**, the Sn–Cl bond is 4% longer than that of the dichloro complex **5d** and the Sn–O bond is 5% shorter than in the dioxy compound **6a**. Thus, the solid-state structure coupled with the higher stability of the mixed-ligand stannate in solution when compared to that of the corresponding homo-ligand complexes indicates that the hypervalent bond is highly polarizable, as depicted by resonance with a polar limiting structure and also by an MO scheme in Figure 6. This view is also valid in solution chemistry, as shown in Figures 3 and 4. Ligation of the aryloxy group, which has high donor ability, facilitates liberation of the less basic halide ligand in the trans position, in accordance with the dynamic behavior of the trimethyl analogue **7a** in acetonitrile, expelling chloride ion preferentially. The enhanced strength of the Sn–O bond is also seen by ^{13}C NMR chemical shifts of the aryloxy nuclei of **6a** and **7c**, 166.1 vs 163.5 ppm (Table II).

Experimental Section

General Considerations. Far-infrared spectra were obtained with a JASCO FT-IR 5M Fourier transform infrared spectrometer. The spectral measurements in the 100–500-cm^{-1} range were made at 1-cm^{-1} resolution with 256 scans for a solid sample mixed with a liquid paraffin.

Tin-119 Mössbauer spectra were measured at 77 K with an Eiscint Mössbauer spectrometer system (MFG-N-5, MDF-N-5, and MVT-4) operated with a constant-acceleration mode. Spectra were recorded on a Northern TN-1750 multichannel analyzer as 512 channel data. A Mössbauer source was Ca^{119m}SnO$_3$. Velocity calibration was done on the base of a natural iron foil, and the isomer shift is referenced relative to SnO$_2$ at room temperature.

^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM GX-270 spectrometer (acetonitrile-d_3, external standard). Chemical shifts are reported in ppm (δ) downfield from tetramethylsilane (δ 0). CP/MAS ^{13}C NMR spectra were obtained with a JEOL JNM GX-270 NM-GSH27MU/VTW instrument by using ca. 0.23 g of **6a** or **7c** (in a 120-μL rotor of the KL'F tube) at 67.8 MHz with a probe temperature of 300 K. The sample was put in the sample rotor and sealed tightly with solid paraffin. The high-resolution spectra were obtained with 270-MHz high-power proton decoupling, spin-locking cross-polarization with the ^{1}H and ^{13}C fields matched at 45 KHz for 2 ms and magic-angle spinning at 3500 Hz. Dwell times of 16 μs and repetition rates of 7 s were used. ^{13}C chemical shifts are relative to the methylene peak of adamantane (29.5 ppm from TMS) as an external standard.

X-ray Diffraction Analysis. Both of the single crystals selected for study were mounted in thin-walled glass capillaries and sealed under argon. Diffraction data for complexes **6a** and **7c** were obtained on an Enraf-Nonius CAD4 four-circle diffractometer at the Institute for Molecular Science and on a Rigaku AFC-5 four-circle diffractometer at the Chemical Instrument Center of Nagoya University, respectively. Crystal data and details of measurements for complexes **6a** and **7c** are summarized in Table IV. Three standard reflections were monitored every 2 h for **6a** and 100 measurements for **7c**, and their intensities showed no decay during the measurement. Reflection data were corrected for Lorentz and polarization effects. Empirical absorption corrections were applied. Both structures were solved by the heavy-atom method and refined anisotropically for non-hydrogen atoms by full-matrix least-squares calculations. Reliability factors are defined as $R = \sum|F_o| - |F_c|/|F_o|$ and $R_w = \sum w(|F_o| - |F_c|)^2$, where $w^{-1} = \sigma^2(F_o) + (0.02(F_o))^2$ for complex **7c** and $w^{-1} = \sigma^2(F_o) + (0.033(F_o))^2$ for complex **6a**. Atomic scattering factors and anomalous dispersion terms were taken from ref 30. Hydrogen atoms were included in the last cycle with fixed isotropic temperature factors of 8.0 Å^2 for both complexes; the positions of most hydrogen atoms were obtained by difference Fourier synthesis, and all other hydrogen atoms were calculated geometrically at their expected positions. The final R and R_w values were 0.057 and 0.063 for **6a** and 0.070 and 0.081 for **7c**. The final difference Fourier maps did not show significant features (the largest peaks, about 0.4 e/Å^3 for **7c** and 0.5 e/Å^3 for **6a**, were located around the Sn atoms). The calculations were carried out on the Micro VAX II computer by using the SDP program system[31] for **7c** and on the HITAC M-680H computer at the Computer Center of the Institute for Molecular Science by using the program system UNICS III[32] for **6a**.

Solvents and Materials. THF and diethyl ether were freshly distilled from a suspension with sodium/potassium alloy. Acetonitrile was used after distillation over CaH$_2$ and then dried on 3A molecular sieves. Dried 3A molecular sieves were prepared by baking with flame, evacuating in vacuo, and then filling with argon. All solvents for extraction were used after distillation by the guaranteed method. Alkyllithium reagents such as methyllithium and *n*-butyllithium were perchased from Aldrich and titrated with 1,3-diphenyl-2-propanone *p*-tosylhydrazone[33] as indicator. Chlorotrialkylstannanes (Aldrich) were purified under standard conditions: Me$_3$SnCl, sublimation (70 °C/0.01 mmHg); *n*-Bu$_3$SnCl, distillation (90–91 °C/0.01 mmHg); Ph$_3$SnCl, recrystallization from hexane. The purity of tris(dimethylamino)sulfonium difluorotrimethylsilicate (TAS-F; Aldrich) was raised as follows. The THF solution of TAS-F (1 g in 20 mL) was cooled (−20 °C) to give crystals. The supernatant was separated by a stainless steel cannula from crystals at this temperature. This supernatant contains the desired material in high purity, which was stored in sealed ampules as 1-mL portions under an argon atmosphere. The concentration of this solution was determined by ^{1}H NMR spectroscopy with benzene as an internal standard by comparing the signal intensity at δ 7.25 (C$_6$H$_6$) with that of δ −0.18 (Si–CH_3). Tris(dimethylamino)sulfonium chloride (mp 189–191 °C) was prepared according to the Middleton procedure.[34]

Unless otherwise stated, the apparatus used in the reactions were baked out with a heat gun under reduced pressure (0.001 mmHg) to remove any moisture and then filled with argon after the apparatus was cooled to room temperature. All experiments were performed under an argon atmosphere by using the standard Schlenk technique.

Methoxytriphenylstannane. In a 80-mL Schlenk tube were placed dry methanol (30 mL) and chlorotriphenylstannane (**1c**; 6.3 g, 16.3 mmol). To this was added a solution of *n*-BuLi in hexane (1.53 M, 11.8 mL, 17.9 mmol) dropwise at −30 °C. After the mixture was stirred for 30 min, methanol was evaporated under reduced pressure. To this residue was added benzene, and the precipitated LiCl was removed by centrifugation (4000 rpm, 20 min). The supernatant was evaporated under reduced pressure, giving a white solid, which was recrystallized with pentane to give 4.1 g (65.8%) of the title product: mp 69–71 °C in a sealed tube (lit.[35] mp 65–66 °C); ^{1}H NMR (90 MHz, C$_6$D$_6$) δ 3.62 (s, 3, OCH$_3$),

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(28) Certain dichloro- or trichlorostannates are known to have different apical bond lengths.[8c,e,29] The dissimilarity of the bond lengths may arise from intramolecular and/or intermolecular factors. X-ray analysis indicates that countercations of symmetrical stannates such as **5d** and **6a** are located in the equatorial plane and have the same distance to the apical ligands, while in most unsymmetrical compounds, the cations are closer to the more polarized heteroatom substituents. This is also valid with the TAS cation, which is thought to have negligible interaction with counteranions. Further detailed scrutiny is required to determine whether this is merely a coincidence or a necessary result of subtle attractive interactions between the apical ligands and countercations.

(29) Buttenshaw, A. J.; Duchene, M.; Webster, M. *J. Chem. Soc., Dalton Trans.* **1975**, 2230.

(30) Ibers, J. A.; Hamilton, W. C. In *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.2B and Table 2.31.

(31) SDP-PLUS, Structure Determination Package, B. A. Frenz and Associates, College Station, TX, and Enraf-Nonius, Delft, The Netherlands. 1982.

(32) Sakurai, T.; Kobayashi, K. *Rikagaku Kenkyusho Houkoku* **1979**, *55*, 69.

(33) Lipton, M. F.; Sorensen, C. M.; Sadler, A. C.; Shapiro, R. H. *J. Organomet. Chem.* **1980**, *186*, 155.

(34) Middleton, W. J. U.S. Patent 3,940,402, 1976.

6.76–6.91 (m, 9, meta and para), 7.24–7.39 (m, 6, ortho); ^{13}C NMR (22.5 MHz, C_6D_6) δ 53.7, 128.8, 135.6, 139.8. Anal. Calcd for $C_{19}H_{18}OSn$: C, 59.89; H, 4.76. Found: C, 59.88, H, 4.30.

(2,6-Dimethylphenoxy)trimethylstannane (2a). In a 50-mL round-bottomed flask were placed 3A molecular sieves and 2,6-dimethylphenol in THF (20 mL). After being submitted to ultrasonication, the solution was centrifugated (3500 rpm, 20 min). The supernatant was transferred to a 80-mL Schlenk tube through a stainless steel cannula and evaporated under reduced pressure. This residue was weighed (4.185 g, 34.3 mmol) and dissolved in dry THF (5 mL). After the solution was cooled to −78 °C, a hexane solution of *n*-BuLi (1.8 M, 19.2 mL, 34.3 mmol) was added at this temperature. The solution changed from a pale brown-yellow homogeneous solution to a white suspension. The suspension became a clear solution by raising the temperature to 10 °C. This solution containing lithium 2,6-dimethylphenoxide was used for the following reaction.

In a 20-mL test tube was placed Me_3SnCl (**1a**; 6.84 g, 34.3 mmol), and this was dissolved in dry THF (10 mL). This solution was added at 20 °C to a solution of lithium 2,6-dimethylphenoxide, prepared as above, by using a stainless steel cannula. The test tube was rinsed with additional THF (2 mL), which was transferred to the solution. The reaction mixture was a pale greenish yellow solution. After the mixture was stirred for 12 h, the solution was evaporated under reduced pressure. Benzene (50 mL) was added to the residual material to precipitate LiCl. After the mixture was subjected to centrifugation (5000 rpm, 30 min), the transparent supernatant was separated and evaporated under reduced pressure. The paste obtained was washed with dry petroleum ether (3 mL × 2). The resulting crystalline solid was dried in vacuo for 3 h, giving **2a** (6.36 g, 65% yield): mp 44 °C (sealed tube); ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.35 (s, 9, 3 CH_3), 1.94 (s, 6, 2 CH_3), 6.51 (t, 1, a para proton of the aryloxy group), 6.71 (d, 2, meta protons of the aryloxy group) (the purity of the product was >96% as judged by comparison of the integral of dimethyl groups (2.14 ppm) of the initial 2,6-dimethylphenol with those of the aryloxy group of the product **2a** (1.94 ppm)); ^{13}C NMR (67.5 MHz, acetonitrile-d_3) δ −1.9 (^1J = 421 Hz), 17.9, 118.6, 128.9, 160.2. Anal. Calcd for $C_{11}H_{18}OSn$: C, 46.36; H, 6.37. Found: C, 46.37; H, 6.21.

(2,6-Dimethylphenoxy)triphenylstannane (2c). This compound was prepared by a procedure similar to that described above with 2,6-dimethylphenol (632.2 mg, 5.18 mmol) in THF (10 mL), a hexane solution of *n*-BuLi (2.9 mL, 5.18 mmol), Ph_3SnCl (1.998 g, 5.18 mmol) in THF (10 mL), and benzene (50 mL) for the LiCl precipitation. (2,6-Dimethylphenoxy)triphenylstannane (**2c**) was obtained as a white solid (2.34 g, 96% yield): mp 69.5 °C (sealed tube); ^{1}H NMR (270 MHz, acetonitrile-d_3) δ 1.94 (s, 9, 3 CH_3), 6.51 (t, 1, a para proton of aryloxy, J = 7.3 Hz), 6.76 (d, 2, meta protons of aryloxy, J = 7.3 Hz), 7.36–7.47 (m, 9, meta and para protons of phenyls), 7.62–7.67 (m, 6, ortho protons of phenyls); ^{13}C NMR (67.5 MHz, acetonitrile-d_3) δ 18.4 (2 CH_3), 120.0 (para carbon of aryloxy), 129.1 (ortho carbons of aryloxy), 129.5 (meta carbons of aryloxy), 130.0 (meta carbons of phenyls), 131.3 (para carbons of phenyls), 137.4 (ortho carbons of phenyls), 139.8 (ipso carbons of phenyls, ^1J = 651 Hz), 160.1 (ipso carbon of aryloxy); far-IR (Nujol) 447, 380, 271, 237 cm^{-1}; CP/MAS ^{13}C NMR δ 17.6, 21.0, 119.2, 120.5, 122.7, 129.3, 138.8, 158.1. Anal. Calcd for $C_{26}H_{24}OSn$: C, 66.28; H, 5.18. Found: C, 66.27; H, 5.18.

(2,6-Dimethylphenoxy)tributylstannane (2b). In a 20-mL Schlenk tube was placed a THF solution (5 mL) of 2,6-dimethylphenol (0.610 g, 5 mmol). To this was added methoxytributylstannane (1.604 g, 5 mmol) by using a glass syringe with cooling on an ice bath, and the mixture was stirred overnight at 15 °C. Methanol produced in the reaction was removed into a cold trap under high vacuum (0.001 mmHg), revealing the quantity of methanol to be 98% of theory. The residual oily product was distilled to give **2b** (137–138 °C/0.06 mmHg): ^{1}H NMR (270 MHz, acetonitriled-d_3) δ 0.91 (t, 9, 3 CH_3), 1.21 (m, 6, 3 CH_2), 1.34 (m, 6, 3 CH_2), 1.64 (m, 6, 3 CH_2), 1.75 (s, 6, 2 CH_3), 6.55 (t, 1, para proton of aryloxy, J = 7.3 Hz), 6.86 (d, 2, meta protons of aryloxy, J = 7.3 Hz); ^{13}C NMR (67.5 MHz, acetonitrile-d_3) δ 14.7, 17.5 (^1J = 364 Hz), 18.8, 28.5, 29.2, 119.1, 129.0, 129.3, 160.3. Anal. Calcd for $C_{20}H_{36}OSn$: C, 58.42; H, 8.83. Found: C, 58.40; H, 8.87.

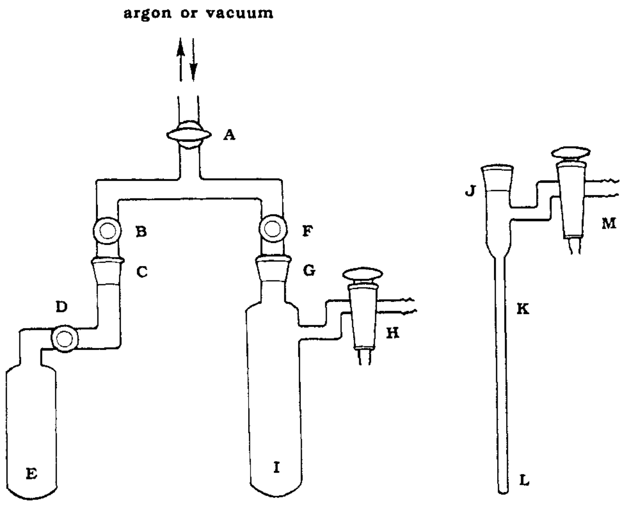

Figure 7. The apparatus used for the synthesis of air- and moisture-sensitive compounds: (A) two-way stopcock for argon inlet and vacuum; (B, D, and F) Young type cocks; (C and G) joints for connection of solvents or reaction vessels; (E) solvent reservoir; (H and M) three-way stopcocks; (I) reaction vessel; (J) adapter; (K) position for sealing NMR tube; (L) NMR tube.

Tris(dimethylamino)sulfonium 2,6-Dimethylphenoxide (4). In a 20-mL round-bottomed flask were placed a THF solution (5 mL) of 2,6-dimethylphenol (2.314 g, 18.94 mmol) and hexamethyldisilazane (4.2 mL, 3.257 g, 20.18 mmol, 1.07 equiv to phenol). The mixture was refluxed with 1 drop of concentrated H_2SO_4 for 12 h and then distilled under reduced pressure (100 °C/15 mmHg) to give (2,6-dimethylphenoxy)trimethylsilane (2.95 g, 80.1%) as a colorless oil: R_f 0.71 (5:1 hexane/ethyl acetate); ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.4 (s, 9, $SiCH_3$), 2.4 (s, 6, 2 CH_3), 6.8 (t, 1, para proton of aryloxy, J = 7.0 Hz), 7.0 (d, 2, meta protons of aryloxy, J = 7.0 Hz); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 0.9, 17.6, 121.2, 128.4, 152.5. Anal. Calcd for $C_{11}H_{18}OSi$: C, 67.98; H, 9.33. Found: C, 67.99; H, 9.30.

The apparatus used for the synthesis of tris(dimethylamino)sulfonium 2,6-dimethylphenoxide (**4**) are shown in Figure 7.

A solvent container *E*, where molecular sieves 3A or Na/K alloy is placed, connects with joint C. Outlet H is capped with rubber septa and sealed tighly by the thermoplastic Parafilm (Aldrich Parafilm M). Valves B, D, and F are cocks of Young's type. Evacuation of the inner atmosphere and introduction of argon gas are performed through A with use of a standard vacuum-line technique. Adapter J equipped with NMR tube L can be exchanged with another reaction vessel at joint C or G when necessary. Dry ether (10 mL) was placed in E and degassed by repeated freezing, pumping, and thawing operations. The THF solution (3 mL) of trimethyl(2,6-dimethylphenoxy)silane (635.5 mg, 3.27 mmol) was placed in I through H by using a stainless steel cannula and cooled to −78 °C. To this was added a THF solution (10 mL) of purified tris(dimethylamino)sulfonium difluorotrimethylsilicate (900 mg, 3.27 mmol) through H by a stainless steel cannula. The resulting solution was degassed by repeated freeze–pump–thaw cycles and then evaporated at 0 °C, to give a white solid, which was cooled again in a liquid-N_2 bath. Ether stored in E was then transferred to I by distillation under reduced pressure with release of cocks B, D, and F and cooling of the vessel I. The solid in I was vigorously dispersed in ether by using a portable ultrasonic cleaner (Omron HU-10). The resulting supernatant was removed by a syringe under argon pressure through H, and the remaining white solid was dried under reduced pressure at 0 °C, giving tris(dimethylamino)sulfonium 2,6-dimethylphenoxide (**4**) in 72% yield as a white solid, mp 55–56 °C (sealed tube). This compound is too unstable to be submitted for elemental analysis.

In an argon-filled glovebox, **4** (30 mg) was put into an NMR tube welded with an adapter J. After J was connected with joint G under an argon stream, dry acetonitrile-d_3 in another container

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(35) (a) Alleston, D. L.; Davies, A. G. *J. Chem. Soc.* **1962**, 2050. (b) Lorberth, J.; Kula, M.-R. *Chem. Ber.* **1964**, *97*, 3444. (c) Brilkina, T. G.; Safonova, M. K.; Sokolov, N. A. *Z. Obshch. Khim.* **1966**, *36*, 2202.

E was transferred by distillation under reduced pressure into a cooled NMR tube with the standard procedure described above. After freeze–pump–thaw cycles, tube L was sealed at the position of K during evacuation through the outlet with stopcock M and separated. The resulting sealed sample was subjected to NMR measurement: ^{1}H NMR (270 MHz, acetonitrile-d_3) δ 1.92 (s, 6, 2 CH_3), 2.78 (s, 18, TAS), 5.74 (t, 1, para proton of aryloxy, J = 7.0 Hz), 6.59 (d, 2, meta protons of aryloxy, J = 7.0 Hz); ^{13}C NMR (67.5 MHz, acetonitrile-d_3) δ 38.5 (TAS), 107.6 (para C), 127.9 (ortho and meta C), 168.2 (ipso C). These NMR parameters, including the chemical shifts of the carbons of the aromatic region, are close to the reported values corresponding to those of the TAS phenoxide.[17]

Aggregation States of the Stannanes Determined by Vapor-Pressure Osmometry.[14] Azobenzene recrystallized from a 1:1 mixture of water and THF was used as the standard. In separate 10-mL test tubes were placed the samples of standard azobenzene (16.5 mg) and (2,6-dimethylphenoxy)tributylstannane (**2b**; 18.7 mg), respectively, and these were dissolved in acetonitrile (1 mL). The solutions were transferred independently into each bulb of the osmometric apparatus by using stainless steel cannula, where two bulbs are connected by a glass tube. The test tubes were rinsed with more portions of acetonitrile (2 × 2 mL) and transferred into each bulb. The acetonitrile solvent was evaporated from each bulb until the volumes of the solutions became ca. 1.5 mL, respectively. While evaporation of the solvent was continued, the system was closed from the atmosphere. The volumes of the solutions in each bulb were measured by tilting the apparatus and draining the solutions into the graduated side arms. The volumes of each bulb became constant (0.9 mL for **2b** and 1.8 mL for azobenzene solution) after 10 days. The molecular weight of **2b** was calculated by using the Raoult equation $M_1 = G_1MV/GV_1$ where M, V, and G are the theoretical molecular weight, the volume of the solution, and the weight of the sample, respectively. The aggregation number is obtainable as the ratio of the observed molecular weight to the theoretical value. Thus, the observed molecular weight was 410.2 and, hence, the aggregation number was decided to be 1.0.

Aggregation numbers of other tin compounds in several solvents (Table I) were determined by a similar procedure.

Studies on the Dynamic Behavior of Tin(IV) Complexes in Acetonitrile Solution. Determination of Equilibrium Constants (*K*). Chlorotrimethylstannane (**1a**; 400 mg, 2 mmol) was placed into a Schlenk tube (10 mL) in an argon glovebox, and then the Schlenk tube was connected to joint G of the apparatus shown in Figure 7 under an argon atmosphere. The details for the operation of the apparatus are described in the synthesis of **4**. Dry acetonitrile-d_3 (7.2 mL) was distilled into this vessel. Separately, tris(dimethylamino)sulfonium chloride (**3**) was placed into nine test tubes (10 mL) in the portions 8 mg (0.04 mmol), 16 mg (0.08 mmol), 30 mg (0.15 mmol), 40 mg (0.20 mmol), 50 mg (0.25 mmol), 60 mg (0.30 mmol), and 100 mg (0.50 mmol) in an argon glovebox. The acetonitrile-d_3 solution (0.8 mL, 0.2 mmol) of **1** prepared above was independently added to these test tubes. The resulting nine mixtures were ultrasonicated for 5 min, and then each mixture was transferred into a separate NMR tube connected with an adapter by which the vacuum technique can be conducted (see the apparatus shown in Figure 7). The NMR tube was sealed under vacuum after freeze–pump–thaw cycles and subjected to NMR measurement. An NMR sample of **1** without concomitance of tris(dimethylamino)sulfonium chloride (**3**) was also prepared by a similar technique. The change of ^{13}C NMR parameters is indicated as

amt of **3**/**1a**, equiv	$\delta(C_\alpha)$	$^1J(^{119}Sn-^{13}C)$, Hz
0	0.9	430
0.2	2.2	457
0.4	3.5	482
0.75	5.5	519
1.0	7.2	550
1.25	7.5	556
1.5	7.5	558
2.5	7.6	559

The equilibrium constant (K) was determined on the basis of these ^1J values to be 950 L mol^{-1}. The equilibrium constants (K) for other cases were obtained by a similar procedure. The change of ^{13}C NMR parameters for mixing systems **3**/**2a** and **4**/**2a** are given in the supplementary material. Figures 1–3 and Table III were made on the basis of these NMR results. The *saturated values* of the ^{1}H and ^{13}C NMR parameters in acetonitrile-d_3 are shown as follows.

5a: ^{1}H NMR (270 MHz) δ 0.51 (s, 9, 3 CH_3, $^2J(Sn-CH_3)$ = 73.7 Hz), 2.80 (s, TAS); ^{13}C NMR (67.5 MHz) δ 7.6 (^1J = 559 Hz), 38.8.

5b: ^{1}H NMR (270 MHz) δ 0.82 (t, 9, 3 CH_3, J = 7.4 Hz), 1.10–1.30 (m, 12, $SnCH_2CH_2CH_2$), 1.59–1.65 (m, 6, $SnCH_2$), 2.82 (s, TAS); ^{13}C NMR (67.5 MHz) δ 14.3, 26.1 (^1J = 511 Hz), 27.8 (^3J = 80 Hz), 29.4 (^2J = 29 Hz), 38.9.

5c: ^{1}H NMR (270 MHz) δ 2.72 (s, 18, TAS), 7.19–7.36 (m, 9, meta and para protons of phenyls), 8.02–8.18 (m, 6, ortho protons of phenyls); ^{13}C NMR (67.5 MHz) δ 38.8, 128.6 (^3J = 71 Hz), 129.0, 137.7 (^2J = 50 Hz), 149.5 (^1J = 853 Hz).

6a: ^{1}H NMR (270 MHz) δ 0.28 (s, 9, 3 CH_3, $^2J(Sn-CH_3)$ = 72.2 Hz), 2.01 (s, 12, 4 CH_3), 2.73 (s, TAS), 6.06 (t, 2, para protons of aryloxys, J = 7.4 Hz), 6.68 (d, 4, meta protons of aryloxys, J = 7.4 Hz); ^{13}C NMR (67.5 MHz) δ 0.8 (^1J = 606 Hz), 19.0, 39.1, 111.7, 127.1, 128.3, 166.1.

6b: ^{1}H NMR (270 MHz) δ 0.75 (t, 9, 3 CH_3, J = 7.4 Hz), 1.00–1.20 (m, 12, $SnCH_2CH_2CH_2$), 1.58–1.65 (m, 6, $SnCH_2$), 2.04 (s, 12, 4 CH_3), 2.73 (s, TAS), 6.08 (t, 2, para protons of aryloxys, J = 7.0 Hz), 6.68 (d, 4, meta protons of aryloxys, J = 7.0 Hz); ^{13}C NMR (67.5 MHz) δ 14.3, 19.0, 20.8 (^1J = 568 Hz), 28.5 (^3J = 92 Hz), 29.7 (^2J = 27 Hz), 38.9, 111.9, 127.1, 128.4, 166.1.

6c: ^{1}H NMR (270 MHz) δ 1.65 (s, 12, 4 CH_3), 2.73 (s, TAS), 6.12 (t, 2, para protons of aryloxys, J = 7.0 Hz), 6.55 (d, 4, meta protons of aryloxys, J = 7.0 Hz), 7.14–7.20 (m, 9, meta and para protons of phenyls), 7.86–7.91 (m, 6, ortho protons of phenyls); ^{13}C NMR (67.5 MHz) δ 19.5, 38.7, 113.0, 127.8, 128.1 (^3J = 79 Hz), 128.3, 137.7 (^2J = 42 Hz), 149.8 (^1J = 916 Hz), 165.4.

7a: ^{1}H NMR (270 MHz) δ 0.35 (s, 9, 3 CH_3, $^2J(^{119}Sn-^1H)$ = 73 Hz), 1.97 (s, 6, 2 CH_3), 2.76 (s, 18, TAS), 6.18 (t, 1, a para proton of aryloxy, J = 7.3 Hz), 6.70 (d, 2, meta protons of aryloxy, J = 7.3 Hz); ^{13}C NMR (67.5 MHz) δ 3.4 (^1J = 572 Hz), 18.1, 38.9, 115.3, 128.2, 128.5, 163.2.

7b: ^{1}H NMR (270 MHz) δ 0.82 (t, 9, 3 CH_3, J = 7.0 Hz), 0.92–1.05 (m, 6, $SnCH_2CH_2CH_2$), 1.17–1.35 (m, 6, $SnCH_2CH_2$), 1.52–1.69 (m, 6, $SnCH_2$), 2.12 (s, 6, 2 CH_3), 2.81 (s, TAS), 6.35 (t, 1, a para proton of aryloxy, J = 7.3 Hz), 6.75 (d, 2, meta protons of aryloxy, J = 7.3 Hz); ^{13}C NMR (67.5 MHz) δ 14.3, 18.0, 22.2 (^1J = 526 Hz), 28.1 (^3J = 79 Hz), 29.3 (^2J = 27 Hz), 38.9, 115.2, 128.1, 128.5, 163.2.

7c: ^{1}H NMR (270 MHz) δ 2.12 (s, 6, 2 CH_3), 2.81 (s, TAS), 6.35 (t, 1, para proton of aryloxy, J = 7.3 Hz), 6.75 (d, 2, meta protons of aryloxy, J = 7.3 Hz), 7.14–7.20 (m, 9, meta and para protons of phenyls), 7.86–7.91 (m, 6, ortho protons of phenyls); ^{13}C NMR (67.5 MHz) δ 18.6, 38.5, 114.3, 127.3, 127.5, 127.7, 128.1, 136.8 (^2J = 43 Hz), 148.6, 163.5.

Convergency into the Mixed-Ligand Stannates 7. Identical NMR spectra were obtained by the following three methods (A–C).

Method A. (Aryloxy)trimethylstannane (**2a**; 57.0 mg, 0.2 mmol) and tris(dimethylamino)sulfonium chloride (**3**; 40.0 mg, 0.2 mmol) was placed in a test tube and dissolved in acetonitrile-d_3 (0.7 mL) in an argon-filled glovebox. This solution was ultrasonicated for 5 min. The sample was subjected to NMR measurement: ^{1}H NMR (270 MHz) δ 0.45 (s, 9, 3 CH_3, $^2J(^{119}Sn-^1H)$ = 71 Hz), 2.05 (s, 6, 2 CH_3), 2.77 (s, 18, TAS), 6.23 (t, 1, para proton of aryloxy, J = 7.0 Hz), 6.65 (d, 2, meta protons of aryloxy, J = 7.0 Hz); ^{13}C NMR (67.5 MHz) δ 3.2 (^1J = 546 Hz), 18.7, 38.8, 115.6, 128.4, 128.4, 162.3.

Method B. The sealed tube containing tris(dimethylamino)sulfonium 2,6-dimethylphenoxide (**4**; 42.9 mg, 0.17 mmol) prepared above was opened in an argon-filled glovebox. To this was added an equimolar amount of chlorotrimethylstannane (**1a**; 33.2 mg, 0.17 mmol), and the mixture was dissolved in acetonitrile-d_3 for subjection to ^{1}H and ^{13}C NMR measurements: ^{1}H NMR (270 MHz) δ 0.45 (s, 9, 3 CH_3, $^2J(^{119}Sn-^1H)$ = 71 Hz), 2.05 (s, 6, 2 CH_3), 2.77 (s, 18, TAS), 6.23 (t, 1, para proton of aryloxy, J = 7.0 Hz), 6.65 (d, 2, meta protons of aryloxy, J = 7.0 Hz); ^{13}C NMR (67.5 MHz) δ 3.3 (^1J = 545 Hz), 18.6, 38.8, 116.1, 128.4, 128.5, 162.3.

Method C. The crystals of tris(dimethylamino)sulfonium dichlorotrimethylstannate (**5a**; 40 mg, 0.1 mmol) and tris(dimethylamino)sulfonium bis(2,6-dimethylphenoxy)trimethylstannate (**6a**; 57 mg, 0.1 mmol) were placed in a test tube and dissolved in acetonitrile-d_3 (0.7 mL) in an argon-filled glovebox.

Table VI. Positional Parameters (×10^4) and Equivalent Isotropic Temperature Factors for Tris(dimethylamino)sulfonium Bis(2,6-dimethylphenoxy)trimethylstannate (6a)$^{a-c}$

atom	x	y	z	B_{eq}, Å^2
Sn	3672.3 (3)	2500	858.4 (7)	3.09 (1)
S(1)	5595 (1)	2500	−5159 (3)	3.97 (6)
O(1)	2826 (3)	2500	−445 (7)	3.7 (1)
O(2)	4516 (3)	2500	2162 (7)	3.6 (1)
N(1)	4938 (4)	2500	−4230 (1)	3.9 (2)
N(2)	5917 (3)	1508 (5)	−4576 (8)	5.6 (2)
C(1)	3349 (4)	3796 (7)	1845 (9)	6.0 (2)
C(2)	4236 (5)	2500	−920 (10)	4.9 (2)
C(3)	2835 (4)	2500	−1790 (10)	3.7 (2)
C(4)	2824 (3)	3399 (6)	−2532 (9)	4.7 (2)
C(4M)	2863 (4)	4336 (6)	−1770 (10)	6.5 (2)
C(5)	2811 (3)	3365 (8)	−3951 (9)	6.2 (2)
C(6)	2806 (6)	2500	−4680 (10)	7.1 (4)
C(7)	5081 (5)	2500	1640 (10)	4.5 (3)
C(8)	5386 (4)	1603 (8)	1340 (9)	6.4 (2)
C(8M)	5073 (6)	668 (8)	1700 (1)	8.4 (3)
C(9)	5943 (5)	1610 (10)	700 (10)	9.6 (3)
C(10)	6228 (7)	2500	410 (20)	12.0 (7)
C(11)	4572 (4)	3390 (7)	−4508 (9)	5.6 (2)
C(12)	6377 (5)	1105 (9)	−5510 (10)	9.0 (3)
C(13)	6007 (5)	1313 (8)	−3140 (10)	7.3 (3)

[a] Atomic numbering is shown in Figure 4. [b] Esd's are given in parentheses. [c] $B_{eq} = {}^4/_3(B_{11}a^2 + B_{22}b^2 + B_{33}c^2 + 2B_{12}ab(\cos\gamma) + 2B_{13}ac(\cos\beta) + 2B_{23}bc(\cos\alpha))$.

This solution was ultrasonicated for 5 min for subjection to NMR measurement: ^{1}H NMR (270 MHz) δ 0.45 (s, 9, 3 CH_3, ^2J-(^{119}Sn–^{1}H) = 71 Hz), 2.05 (s, 6, 2 CH_3), 2.77 (s, 18, TAS), 6.23 (t, 1, para proton of aryloxy, J = 7.0 Hz), 6.65 (d, 2, meta protons of aryloxy, J = 7.0 Hz); ^{13}C NMR (67.5 MHz) δ 3.1 (^1J = 542 Hz), 18.6, 38.7, 115.9, 128.4, 128.4, 162.4.

Conversion of the 1a/HMPA Complex to 5a. The **1a**/HMPA complex was formed by addition of 2.5 equiv of HMPA to **1a** in acetonitrile-d_3, as judged by the saturated ^1J value (546 Hz). To a solution consisting of **1a** (50 mg, 0.25 mmol) and HMPA (131.6 mg, 0.73 mmol, 2.5 equiv to **1a**) was added tris(dimethylamino)sulfonium chloride (**3**; 50 mg, 0.25 mmol, 1.0 equiv to **1a**). The ^1J value increased and become close to that obtained by an equimolar mixture of **1a** and tris(dimethylamino)sulfonium chloride (**3**) in acetonitrile-d_3: ^{13}C NMR (67.5 MHz) δ 7.3 (Sn–CH_3, ^1J = 557 Hz), 37.1 (HMPA), 38.9 (TAS).

Preparation of a Single Crystal for X-ray Crystallographic Analysis. Tris(dimethylamino)sulfonium Bis(2,6-dimethylphenoxy)trimethylstannate (6a). The mixing of (2,6-dimethylphenoxy)trimethylstannane (**2a**; 142.5 mg, 0.5 mmol) and TAS aryloxide **4** (142.7 mg, 0.5 mmol) in THF (2 mL) was conducted at 0 °C by a procedure similar to that described in the determination of the equilibrium constant (K). The reaction mixture was evaporated at 0 °C to give a white solid, which was dissolved in a benzene/acetonitrile (1:1) solvent mixture (2.5 mL) and the solution placed in a test tube (10 mm i.d) under an argon atmosphere. This test tube was placed inside a larger diameter Schlenk type tube, and diethyl ether was filled up to a slightly higher level than that of the solvent in the inner tube. The Schlenk tube was stoppered and stood in a cold room (4 °C). Diethyl ether slowly diffused into the benzene/acetonitrile solution to induce the formation of crystals. The transparent crystals of **6a** appeared after 10 days: mp (sealed tube) 136–137 °C; CP/MAS ^{13}C NMR δ 1.7 (Sn–C, ^1J = ca. 600 Hz), 20.2 (four methyls of aryloxys), 38.9 (TAS), 115.7 (para carbons of aryloxys), 128.3 (ortho and meta carbons of aryloxys), 164.9 (ipso carbons of aryloxys). Anal. Calcd for $C_{25}H_{45}N_3O_2SSn$: N, 7.36; C, 52.64; H, 7.95. Found: N, 7.30; C, 52.57; H, 8.03. The crystals thus obtained were suitable for X-ray crystallographic analysis. A single crystal was mounted in a glass capillary in an argon-filled glovebox and sealed under an argon atmosphere for subjection to X-ray analysis. The sample decomposed gradually at room temperature during the irradiation of the X-ray beam, so the intensities were collected at −50 °C. Atomic positional parameters are given in Table VI.

Tris(dimethylamino)sulfonium Chloro(2,6-dimethylphenoxy)triphenylstannate (7c). In a 10-mL Schlenk tube was placed (2,6-dimethylphenoxy)triphenylstannane (**2c**; 106.1 mg, 0.225 mmol), and this was dissolved in dry benzene (1 mL). In another dry test tube was placed tris(dimethylamino)sulfonium chloride (**3**; 44.9 mg, 0.225 mmol), and this was dissolved in dry acetonitrile (0.5 mL); then, the mixture was transferred to the solution prepared above through a stainless steel cannula under a slight argon pressure. The mixture was then cooled at 0 °C overnight, giving colorless crystals. This crude product was recrystallized from acetonitrile, giving the stannate **7c** (139 mg, 92%), mp 163 °C (sealed tube). Crystals suitable for X-ray crystallography were obtained by further recrystallization from a 2:1 mixture of acetonitrile and benzene at −20 °C under an argon atmosphere: far-IR (Nujol) 458, 364, 306, 272, 235, 212, 200, 163, 147 cm^{-1}; CP/MAS ^{13}C NMR δ 19.4, 37.8, 113.8, 116.0, 116.9, 117.8, 129.3, 136.2, 148.3, 164.9. Anal. Calcd for $C_{32}H_{42}OSN_3ClSn$: C, 57.29; H, 6.31; N, 6.26. Found: C, 57.26; H, 6.39; N, 6.23. A single crystal sealed in a glass capillary under an argon atmosphere was submitted to X-ray crystallographic analysis. Atomic positional parameters are given in Table VII.

Table VII. Positional Parameters (×10^4) and Equivalent Isotropic Temperature Factors for Tris(dimethylamino)sulfonium Chloro(2,6-dimethylphenoxy)triphenylstannate (7c)$^{a-c}$

atom	x	y	z	B_{eq}, Å^2
Sn	6597 (2)	5112 (1)	2307 (1)	4.8
Cl	6691 (1)	4252 (2)	643 (1)	6.3
S	7947 (1)	1744 (2)	1985 (2)	6.3
O(1)	6566 (3)	5727 (6)	3633 (4)	6.0
N(1)	8582 (4)	1966 (7)	1472 (5)	6.6
N(2)	7473 (5)	621 (8)	1611 (6)	7.6
N(3)	8314 (5)	1177 (8)	2975 (6)	8.3
C(1)	6297 (5)	6702 (9)	3939 (5)	6.0
C(2)	6703 (7)	7668 (9)	4228 (6)	7.9
C(3)	6431 (9)	8663 (12)	4548 (8)	10.5
C(4)	5748 (9)	8714 (13)	4575 (8)	11.5
C(5)	5326 (7)	7751 (14)	4329 (8)	10.3
C(6)	5602 (7)	6731 (12)	3981 (7)	8.3
C(7)	5138 (7)	5688 (16)	3693 (9)	10.0
C(8)	7464 (7)	7611 (12)	4179 (8)	8.7
C(9)	5927 (4)	6416 (7)	1651 (5)	4.6
C(10)	5366 (5)	6143 (8)	1040 (6)	5.8
C(11)	4943 (5)	7016 (11)	632 (7)	7.3
C(12)	5089 (6)	8160 (11)	805 (8)	7.9
C(13)	5654 (6)	8465 (9)	1411 (8)	7.8
C(14)	6070 (5)	7616 (8)	1835 (6)	5.9
C(15)	6215 (4)	3426 (8)	2668 (6)	5.4
C(16)	5844 (5)	2710 (8)	2023 (7)	6.1
C(17)	5565 (6)	1689 (6)	2282 (9)	8.1
C(18)	5630 (6)	1351 (10)	3170 (9)	8.4
C(19)	5996 (7)	2061 (12)	3818 (9)	9.6
C(20)	6282 (6)	3109 (10)	3571 (7)	7.7
C(21)	7640 (5)	5486 (8)	2388 (6)	5.5
C(22)	7879 (5)	6215 (9)	1741 (6)	6.2
C(23)	8553 (5)	6519 (10)	1808 (8)	7.2
C(24)	9014 (5)	6074 (12)	2504 (9)	8.3
C(25)	8799 (6)	5396 (14)	3139 (9)	9.3
C(26)	8128 (6)	5064 (10)	3086 (8)	7.7
C(27)	7760 (7)	−594 (10)	1662 (8)	8.8
C(28)	6971 (7)	892 (13)	811 (9)	9.5
C(29)	9081 (6)	1088 (12)	1338 (8)	8.5
C(30)	8543 (8)	2926 (14)	847 (10)	10.7
C(31)	8886 (8)	1928 (12)	3421 (8)	10.6
C(32)	7814 (9)	948 (15)	3604 (9)	12.2

[a] Atomic numberic is shown in Figure 5. [b] Esd's are given in parentheses. [c] $B_{eq} = {}^4/_3(B_{11}a^2 + B_{22}b^2 + B_{33}c^2 + 2B_{12}ab(\cos\gamma) + 2B_{13}ac(\cos\beta) + 2B_{23}bc(\cos\alpha))$.

Acknowledgment. We thank Professor T. Shinjo and Dr. N. Hosoito of Kyoto University for the measurement of Mössbauer spectra. We also thank Drs. T. Ishizuka and A. Tsuge of Nagoya Government industrial Research Institute for the measurement of far-infrared spectra. We indebted to Mr. A. Kawamoto of our department for his kind guidance in X-ray crystallographic analysis. We are also indebted to JEOL Ltd. for the measurement of the

CP/MAS NMR spectrum. This work was partly supported by a Grant-In-Aid for Specially Promoted Research (No. 62065005) from the ministry of Education, Science, and Culture of Japan.

Registry No. **1a**, 1066-45-1; **1a**-HMPA, 65941-34-6; **1b**, 1461-22-9; **1c**, 639-58-7; **2a**, 130063-57-9; **2b**, 98217-98-2; **2c**, 130063-58-0; **3**, 59094-54-1; **4**, 130063-59-1; **5a**, 130063-60-4; **5b**, 130063-61-5; **5c**, 130063-62-6; **6a**, 130063-64-8; **6b**, 130063-66-0; **6c**, 130063-68-2; **7a**, 130063-70-6; **7b**, 130063-72-8; **7c**, 130063-74-0; TAS-F, 59218-87-0; methoxytriphenylstannane, 1091-26-5; 2,6-dimethylphenol, 576-26-1; methoxytributylstannane, 1067-52-3; (2,6-dimethylphenoxy)trimethylsilane, 16286-54-7.

Supplementary Material Available: Tables of atomic parameters, anisotropic temperature factors, and complete bond angles and distances for **6a** and **7c** in X-ray crystallographic analyses, actual far-IR spectra of **1c**, **2c**, and **7c**, a Mössbauer spectrum of **7c**, CP/MAS ^{13}C NMR spectra of **2c**, **6a**, and **7c**, and lists of NMR parameters ($^1J(^{119}\text{Sn}-^{13}\text{C})$ and $\delta(\text{Sn}-C_\alpha)$ values) in acetonitrile-d_3 for the various ratios of **3**/**2a** and **4**/**2a** (17 pages); listings of observed and calculated structure factors for **6a** and **7c** (24 pages). Ordering information is given on any current masthead page.

Preparation and Reactions of Functionalized Benzylic Organometallics of Zinc and Copper[†]

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Received February 7, 1990

The reaction of zinc dust with primary or secondary benzylic halides **1** bearing various functional groups such as an ester, halide, cyano, or even a ketone group, in THF or, in the case of benzylic chlorides, in THF:DMSO (4:1), furnishes the corresponding zinc organometallics **2** in high yields. The reaction is accompanied by less than 10% of Wurtz coupling products. The benzylic copper organometallics **3**, obtained after a transmetalation of **2** with the THF-soluble copper salt CuCN·2LiCl at −20 °C, react in excellent yields (70–95%) with various electrophiles such as acid chlorides, enones, aldehydes, allylic bromides, ethyl propiolate, and tributyltin chloride, leading to the polyfunctional molecules of type **4**.

Introduction

Unlike allylic organometallics,[1] benzylic organometallic compounds have found relatively few synthetic applications. This is certainly due in part to the difficulties encountered in their preparation. Special experimental reaction conditions are often required to minimize the formation of Wurtz coupling products.[2] The formation of benzylic magnesium derivatives is best achieved by reacting magnesium anthracene[3] with benzylic chlorides or, less efficiently, with benzylic bromides. The direct metalation is achieved in high yields only in special cases[4] and often requires the use of strong bases, which can lead to the formation of ring-metalated products.[5] Benzyltin derivatives,[6] benzylic ethers[7] and thioethers,[8] and benzylic selenides[9] have also been used to prepare in most cases nonfunctionalized benzylic lithium compounds. Previously,[10] we reported a general preparation of functionalized primary benzylic zinc bromides by the reaction of benzylic bromides with zinc in THF.[11] The corresponding benzylic copper derivatives obtained after a transmetalation with CuCN·2LiCl were found to be versatile reagents that react with a variety of organic electrophiles (see Scheme I). Further work showed that this preparation of benzylic copper and zinc organometallics had a very broad scope and could be extended to the preparation of secondary benzylic zinc derivatives. We wish to report herein a full account of our results.

Results and Discussion

The slow addition (1 drop/5–10 s) of a 1.0–2.0 M THF solution of a primary benzylic bromide **1** (R = H; X = Br) at 0–5 °C to a stirred mixture of 1.2–1.5 equiv of cut zinc foil (Alfa, 99.9% pure) that was previously activated with 1,2-dibromoethane[12] leads to the complete formation of the corresponding benzylic zinc organometallic **2** after 2–3 h of stirring at 5 °C. Capillary GLC analysis of a hydrolyzed aliquot containing an internal standard indicates a yield

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[†] Dedicated to the memory of Professor John K. Stille.

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