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Synthesis and Structural Features of *N*-Mono- and *N,N*-Bis(trimethylstannyl)acetamide Derivatives

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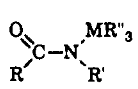
The synthesis of $CF_3C(O)NH(SnMe_3)$ (**1**), $CH_3C(O)NR(SnMe_3)$ (**2**, R = H; **3**, R = Me; **4**, R = Ph) and $CH_3C(O)N(SnMe_3)_2$ (**5**) are reported. The IR and NMR (^1H, ^{13}C, ^{119}Sn) spectra are consistent with strong dominance of the planar amidate (rather than an imidate) tautomer. The ^{119}Sn NMR spectra of **1**−**5** are temperature invariant. The structures of **3** and **5**, determined by X-ray means, revealed the presence of an intramolecular Sn- - -O interaction in which the $SnMe_3$ group is *cis* to the carbonyl, and an intermolecular O- - -Sn interaction which is stronger. Comparison of the solution and solid state ^{119}Sn NMR chemical shifts of **3** and **5** indicates that both types of Sn- - -O interactions are more robust in the solid state. Crystallographic data for **3**: space group $P2_1/n$, a = 9.866 (3) Å, b = 9.574 (4) Å, c = 9.881 (3) Å, α = 90°, β = 98.90 (1)°, γ = 90.0°, V = 922.1 (6) Å^3, R = 0.0284. Crystallographic data for **5**: space group $P2_1/n$, a = 6.898(1) Å, b = 16.884(1) Å, c = 11.222(3) Å, α = 90.0°, β = 94.54(1)°, γ = 90.0°, V = 1302.9(4) Å^3, R = 0.025.

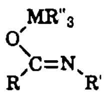
Introduction

Trialkylstannyl amides ($RC(O)NR'SnR''_3$) have been prepared either by azeotropic dehydration of a mixture of $(R''_3Sn)_2O$ and an appropriate amide[1] or by treating R''_3SnOR with an amide.[2−4] These compounds are generally moisture sensitive and the Sn−N bond is readily cleaved by protic reagents such as alcohol.[5]

Sharma[3] reported the preparation of tributylstannyl amides from tributylstannyl isopropoxide and primary amides. On the basis of the strong absorption band near 1650 cm^{-1} which was assigned to the C=O absorption in all of the products, it was suggested that the tributylstannyl group was bonded to nitrogen in the amide form **A** rather than to oxygen in the imidate form **B**. However Noltes[2] and Yoder *et al.*[6,7] suggested that the assignment of a structure on the basis of C=O or C=N absorption was unreliable because of severe overlap of these bands.



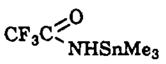
A



B

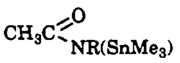
Yoder et al.[4] have described the preparation of a series of (trimethylstannyl)- and (triethylstannyl)formamides by the reaction of R''_3SnOMe and formamide at 110−120 °C. They observed two doublets of unequal intensities and couplings in the *N*-methyl region of the ^1H NMR spectrum of the acetamide derivative $MeC(O)NHSnMe_3$ which can be attributed to methyl groups in magnetically nonequivalent positions in accord with the *syn* and *anti* forms that can be adopted by the amide form **A**. Similar assignments for a series of analogues could not be made because their ^1H NMR spectra displayed evidence for only one conformation. In the same paper,[4] it was suggested that all trimethylstannyl amides favored a conformation in which the trimethylstannyl group is *cis* to the carbonyl. Such a conformation would be consistent with the relatively low steric requirement of the Me_3Sn group and/or donation of electron density from the carbonyl oxygen to the tin in a dative bond. This type of interaction was also mentioned for the (trimethylgermyl)formamide analog, but no direct evidence was put forth. It has also been proposed on the basis of ^{119}Sn Moessbauer[8] and infrared[9] spectral experiments on $HC(O)NRSnBu_3$ (R = Ph, Np) that intermolecular associations are present in these solids.

In an effort to further elucidate the nature of the possible intra and intermolecular interactions occurring in this class of compounds, we report the preparation of the new (trimethylstannyl)acetamide derivatives **1**−**5**, an NMR investigation of these compounds, and the structural determination of **3** and **5** by X-ray means.



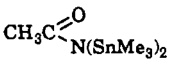
$CF_3C(=O)NHSnMe_3$

1



$CH_3C(=O)NR(SnMe_3)$

2 R = H
3 R = Me
4 R = Ph



$CH_3C(=O)N(SnMe_3)_2$

5

Experimental Section

All reactions and sample preparations for IR and NMR spectroscopy were carried out with exclusion of moisture. Solvents were dried by standard methods[10] and distilled under nitrogen prior to use. (Dimethylamino)trimethylstannane was either purchased from Aldrich Co.

® Abstract published in *Advance ACS Abstracts,* October 1, 1995.

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Table 1. Spectroscopic and Physical Data of Compounds **1–5**

cmpd	mp, °C	IR,[a] cm^{-1}	δ(^{1}H), ppm	δ(^{119}Sn), ppm	elem anal.[b]	
					% C	% H
$CF_3C(O)NH(SnMe_3)$ (**1**)	58–60	1668, C=O 3398, N–H 797, Sn–CH_3	0.54 (s, 9 H, $SnCH_3$) 5.70 (br, 1 H, N-H)	77.00[c]	21.56 (21.75)	3.70 (3.63)
$MeC(O)NH(SnMe_3)$ (**2**)	100.5–101.5	1576, C=O 775, Sn–CH_3	0.39 (s, 9 H, $SnCH_3$) 2.01 (s, 3 H, CCH_3)	39.81[c]		
$MeC(O)NMe(SnMe_3)$ (**3**)	100–101	1562, C=O 773, Sn–CH_3	0.36 (s, 9 H, $SnCH_3$) 2.02 (s, 3 H, CH_3C) 2.82 (s, 3 H, CH_3N)	41.11[c] –61[d]	30.48 (30.53)	6.20 (6.36)
$MeC(O)NPh(SnMe_3)$ (**4**)	134–136	1549, C=O 771, Sn–CH_3	0.28 (s, 9 H, $SnCH_3$) 1.82 (s, 3 H, CH_3C) 6.88–7.31 (m, 5 H, C_6H_5)	49.66[c]	44.57 (44.34)	5.91 (5.71)
$MeC(O)N(SnMe_3)_2$ (**5**)	113–115	1516,.1495, C=O 758, Sn–CH_3	0.35 (s, 18 H, $SnCH_3$) 2.05 (s, 3 H, CH_3C)	40.66,[c] 126.6[c] 0.28, –19.35[d]	24.59 (24.95)	5.67 (5.46)

[a] In KBr. [b] Calculated values are in parentheses. [c] In $CDCl_3$. [d] CP/MAS value for the neat compound.

Table 2. ^{13}C NMR Data for $C^1X_3C^2(O)NR[SnC^3H_3)_3]$, **1–5**[a]

compound	δ(C^1),[b] ppm	δ(C^2),[b] ppm	δ(C^3),[b] ppm		δ(C(R)),[b] ppm
$CF_3C(O)NH(SnMe_3)$ (**1**)	115.59 (289.14)[c]	162.86 (35.76)[c]	–5.00 (417.00)[d] (400.41)[e]		
$MeC(O)NH(SnMe_3)$ (**2**)	23.82 (10.64)[f]	177.20 (10.04)[f]	–5.85 (406.44)[d] (388.34)[e]		
$MeC(O)NMe(SnMe_3)$ (**3**)	19.28 (9.06)	176.94 (3.54)[f]	–5.22 (406.44)[d] (388.34)[e]		32.74 (9.06)[f]
$MeC(O)NPh(SnMe_3)$ (**4**)	20.69 (5.06)	175.72	–4.47 (401.38)[d] (383.28)[e]	143.22 127.09 (6.04)[f]	128.93 (3.54)[f] 125.57 (4.00)[f]
$MeC(O)N(SnMe_3)_2$[g] (**5**)	24.87 (12.52)[f]	180.60	–3.15 (389.56)[d] (374.76)[e]		–6.92 (379.74)[d] (362.68)[e]

[a] In $CDCl_3$. [b] Sn–C couplings (Hz) in parentheses. [c] *J*(CF). [d] *J*($^{119}Sn^{13}C$). [e] *J*($^{117}Sn^{13}C$). [f] *J*(SnC). [g] Measured at 253 K.

or prepared according to a literature report.[11] Trimethylstannyl hydroxide also was prepared by a literature method.[12]

^{1}H NMR spectra were obtained on a Nicolet NT 300 instrument in $CDCl_3$ with TMS as internal standard. ^{13}C NMR spectra were recorded on either a VXR 300 or on a Nicolet NT 300 instrument. The chemical shift was referred to the middle peak of $CDCl_3$ at 76.9 ppm. Solution ^{119}Sn NMR spectra were obtained in $CDCl_3$ on a Bruker WM 200 instrument with tetramethylstannane as external standard. Solid state ^{119}Sn NMR spectra were recorded on a Bruker MSL 300 spectrometer under proton decoupling using the CP-MAS technique. Tetracyclohexylstannane was used as the external reference at –47.35 ppm. IR spectra on solid samples were recorded on an IBM FT-IR machine. Melting points and elemental analyses for compounds prepared herein are collected in Table 1 and spectroscopic data are listed in Tables 1 and 2.

***N*-(Trimethylstannyl)-2,2,2-trifluoroacetamide, 1. Method A.** To a stirred solution of 5.10 g (45.0 mmol) of trifloroacetamide in 190 mL of anhydrous triethylamine was added dropwise 18.9 g (94.7 mmol) of melted trimethylstannyl chloride (mp. 38 °C), followed by stirring and refluxing under nitrogen for 10 h. The precipitate was filtered and washed twice with triethylamine. The filtrates were combined and evaporated under vacuum, and the residue was distilled under reduced pressure. The fraction between 80–88 °C at 0.5 Torr was collected, which crystallized at room temperature giving 8.23 g (66.2% yield) of product.

Method B. A mixture of trifluoroacetamide (221 mg, 1.96 mmol) and Me_3SnOH (354 mg, 1.96 mmol) in 20 mL of anhydrous benzene was refluxed for 3 h in a flask equipped with a Dean Stark trap. After the benzene was removed under vacuum, 530 mg (100%) of product was obtained as a white powder. Its ^{1}H and ^{119}Sn spectra and its melting point were the same as the product obtained by method A.

***N*-(Trimethylstannyl)acetamide, 2.** The preparation procedure was the same as that described in method B for **1**. Thus, acetamide 0.986 g (16.7 mmol) and trimethylstannyl hydroxide (3.02 g, 16.7 mmol) gave **2** (3.10 g, 83.8%) after purification by sublimation at 120 °C/0.5 Torr.

***N*-Methyl-*N*-(trimethylstannyl)acetamide, 3. Method A.** To a solution of *n*-butyllithium (12.0 mL, 26.4 mmol) in 20 mL of a 3:1 mixture of benzene and THF was added dropwise at 0 °C *N*-methylacetamide (1.91 g, 26.2 mmol) in 15 mL of the same mixed solvent. After the addition, the reaction mixture was allowed to reach room temperature, and then it was stirred for 1 h. Trimethylstannyl chloride (5.22 g, 26.2 mmol) in 15 mL of the same mixed solvent was then added dropwise after cooling the mixture was cooled to 0 °C. After being stirred at room temperature for 3 h, the mixture was filtered and the filtrate evaporated to a white solid, which was recrystallized from THF to give 4.15 g (67.2% yield) of crystalline product.

Method B. To a stirred solution of *N*-methylacetamide, 1.065 g (14.57 mmol) in 25 mL of anhydrous toluene was added dropwise Me_3SnNMe_2 (3.018 g, 14.52 mmol). The mixture was stirred for 3 h at room temperature, and then it was stored in a refrigerator overnight to give a crystalline product which was filtered and recrystallized from toluene in 88% yield (3.0 g).

***N*-Phenyl-*N*-(trimethylstannyl)acetamide, 4.** To a stirred solution of *n*-butyllithium (8.0 mL, 18 mmol) in 20 mL of ether was added dropwise 2.373 g (17.56 mmol) of *N*-phenylacetamide in 15 mL of ether at 0 °C. After the addition, the mixture was allowed to reach room temperature, and then it was stirred for 1 h before Me_3SnCl (3.498 g, 17.56 mmol) was added. After overnight stirring at room temperature, the mixture was filtered. After the filtrate was stored at 0 °C for 1 d, a white solid product had formed (2.50 g), which was filtered off. The filtrate was then evaporated under vacuum to dryness and the remaining solid was sublimed at 120 °C/0.05 Torr giving an additional 2.00 g of **4** for a total yield of 86.0%.

***N,N*-Bis(trimethylstannyl)acetamide, 5.** To a stirred solution of acetamide (0.6794 g, 11.50 mmol) in 40 mL of anhydrous THF was added dropwise Me_2NSnMe_3 (4.782 g, 23.08 mmol) at room temperature. After being stirred for 24 h at 45 °C, the mixture was evaporated to dryness, giving a white solid that was recrystallized from THF giving 3.90 g (88.6% yield) of **5**.

Structure Solution of 3. The space group $P2_1/n$ was chosen based on systematic absences and intensity statistics. This assumption proved

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Table 3. Crystal Data for **3** and **5**

	3	**5**
formula	$C_6H_{15}NOSn$	$C_8H_{21}NOSn_2$
fw	235.88	384.64
space group	$P2_1/n$	$P2_1/n$
a, Å	9.866(3)	6.898(1)
b, Å	9.574(4)	16.884(1)
c, Å	9.881(3)	11.222(3)
β, deg	98.90(1)	94.54(1)
V, Å^3	922.1(6)	1302.9(4)
Z	4	4
d_{calc}, g/cm^3	1.699	1.961
μ(Mo Kα), cm^{-1}	38.18	38.18
data colln instrum	Enraf-Nonius CAD4	Enraf-Nonius CAD4
temp, °C	223(1)	−75(1)
scan method	$\omega-2\theta$	$\theta-2\theta$
data colln range (2θ) deg	2.71−24.96	4.0−50.0
no. of unique data, total	3269	2287
no. of obsd data	1510[a]	2118[b]
R^c	0.0284	0.025
R (weighted)	0.0714[d]	0.039[e]

[a] With $I \geq 2\sigma(I)$. [b] With $F_o^2 > 3\sigma(F_o^2)$. [c] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [d] $wR2 = [\sum[w(F_o^2 - F_c^2)]^2]/\sum[w(F_o^2)^2]]^{1/2}$. [e] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

to be correct by a successful direct-methods solution[13] and subsequent refinement. All non-hydrogen atoms were placed directly from the *E*-map. All non-hydrogen atoms were refined with anisotropic displacement parameters and all hydrogens were treated as rigid groups with individual isotropic thermal parameters and C−H distances equal to 0.96 Å. Final refinements were carried out with SHELXL-93.[14,15] The primitive monoclinic lattice can be transformed to a pseudo-*C*-centered orthorhombic lattice, but axial photographs indicated that the former is correct. A hemisphere of data was collected in the pseudo-*C*-centered orthorhombic lattice, and these data were later transformed back to the primitive monoclinic lattice.

Data collection and structure solution were conducted at the Iowa State Molecular Structure Laboratory. Refinement calculations were performed on a Digital Equipment Corp. MicroVAX 3100 computer using SHELXL-Plus[13] and SHELXL-93.[14]

Structure Solution of 5. Systematic absences unambiguously indicated that the space group was $P2_1/n$ (No. 14). All 12 non-hydrogen atoms were found in a direct-methods *E*-map.[16] Following full-matrix refinement of the positions and isotropic thermal parameters, all of the hydrogen atom positions appeared in a subsequent difference Fourier map. In the final stages of refinement, the non-hydrogen atoms were refined with anisotropic temperature factors. Hydrogen atoms were added in idealized positions, and the CH_3 groups were then refined as rigid entities. A single common isotropic temperature factor was refined for the hydrogen atoms. A secondary extinction coefficient was included and refined to a value of $2.8(1) \times 10^7$.[15]

Refinement calculations were performed on a Digital Equipment Corp. Micro VAX II computer using the SHELX-76 programs.[17] Data collection parameters, positional parameters and important structural metrics for **3** and **5** are collected in Tables 3−7.

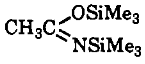
Discussion

Syntheses. Our original intent was to synthesize tin species which are analogous to the powerful silylating agent **6**.[18,19]

Table 4. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å^2 $\times$ 10^3) for **3**

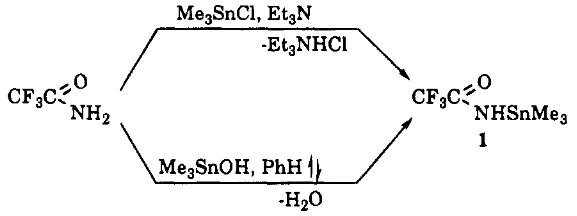
atom	*x*	*y*	*z*	*U*(eq)[a]
Sn	1540(1)	2210(1)	2575(1)	27(1)
C(1)	-257(5)	-1892(4)	3269(5)	40(1)
C(2)	598(4)	-650(4)	3027(3)	29(1)
O	1839(3)	-816(3)	2898(3)	40(1)
N	79(3)	616(3)	2961(3)	30(1)
C(3)	-1356(4)	846(4)	3077(5)	44(1)
C(4)	3072(4)	1933(5)	4306(4)	40(1)
C(5)	1733(4)	1611(5)	544(4)	40(1)
C(6)	247(5)	3955(5)	2775(5)	47(1)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.


$\mathrm{CH_3C}^{\mathrm{OSiMe_3}}_{\mathrm{NSiMe_3}}$

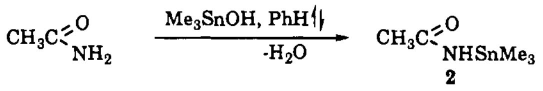
6

However, attempts to make such compounds parallel to the route used for **6** invariably gave the monosubstituted species **1** and **2**:



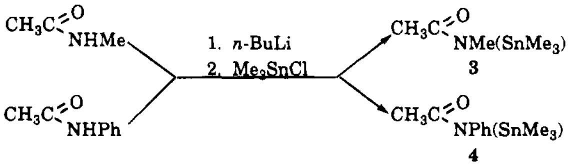
(1)

(2)



(3)

Prior formation of a delocalized anion by means of *n*-BuLi also resulted in N rather than O-stannylation:

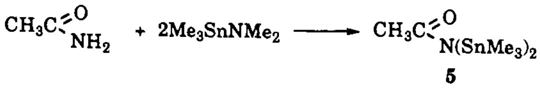


(4)

(5)

While we were not surprised to observe the formation of **3** in reaction 6, the facile formation of disubstituted **5** in reaction 7 was somewhat unexpected.

(6)



(7)

Structural Features. In solution, **1**−**5** display one set of peaks in their ^{1}H and ^{13}C NMR spectra. Some support for the amide form **A** for these compounds stems from the proximity (see later) of the ^{13}C=O NMR resonances to those in the amide starting materials.[20] In such compounds a vibrational peak in the 758−775 cm^{-1} region was assigned to the Sn-CH_3 stretching mode.[21] The IR and ^{1}H NMR spectroscopic data in Table 1

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Table 5. Selected Bond Lengths (Å) and Angles (deg) for **3**

	Bond Distances		
Sn−N	2.173(3)	N−C(3)	1.455(5)
C(2)−O	1.261(5)	Sn- - -O	1.925(4)[a]
C(2)−N	1.314(5)	Sn- - -O	2.564(4)[b]
	Bond Angles		
C(4)−Sn−C(5)	125.0(2)	O−C(2)−N	119.2(3)
C(4)−Sn−C(6)	112.7(2)	O−C(2)−C(1)	119.7(3)
C(5)−Sn−C(6)	116.2(2)	C(2)−N−C(3)	120.8(3)
C(4)−Sn−N	100.35(14)	C(2)−N−Sn	113.1(2)
C(5)−Sn−N	97.8(2)	C(3)−N−Sn	126.0(2)
C(6)−Sn−N	96.4(2)		

[a] Intramolecular distance. [b] Intermolecular distance.

Table 6. Positional Parameters and Their Estimated Standard Deviations for **5**[a]

atom	*x*	*y*	*z*	*B*, Å^2
Sn(1)	0.13083(3)	0.41731(1)	0.24561(2)	1.817(8)
Sn(2)	0.27249(3)	0.25710(1)	0.03435(2)	1.644(7)
O	−0.0462(4)	0.2913(2)	0.3456(2)	2.55(5)
N	0.1228(4)	0.3002(2)	0.1828(2)	1.91(5)
C(1)	0.0130(5)	0.2597(2)	0.2535(4)	2.15(7)
C(2)	−0.0461(7)	0.1757(3)	0.2262(4)	3.45(9)
C(3)	0.2490(6)	0.4856(3)	0.1058(4)	3.30(9)
C(4)	−0.1489(5)	0.4661(3)	0.2618(3)	2.84(8)
C(5)	0.3267(7)	0.4209(3)	0.4017(4)	3.18(9)
C(6)	0.5350(5)	0.3248(3)	0.0636(3)	2.81(8)
C(7)	0.0492(5)	0.2872(3)	-0.1011(3)	2.64(8)
C(8)	0.3369(6)	0.1368(2)	0.0785(3)	2.63(7)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter refined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Table 7. Selected Bond Distances (Å) and Angles (deg) for **5**

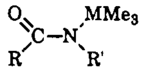
	Bond Distances		
Sn(1)−N	2.098(3)	C(1)−C(2)	1.502(5)
Sn(2)−N	2.155(3)	Sn(1)- - -O	2.732(3)[a]
O−C(1)	1.260(5)	Sn(2)- - -O	2.672(3)[b]
N−C(1)	1.329(5)		
	Bond Angles		
N−Sn(1)−C(3)	105.1(1)	C(6)−Sn(2)−C(7)	122.3(2)
N−Sn(1)−C(4)	113.3(1)	C(6)−Sn(2)−C(8)	108.4(2)
N−Sn(1)−C(5)	107.6(1)	C(7)−Sn(2)−C(8)	121.2(2)
C(3)−Sn(1)−C(4)	104.7(2)	Sn(1)−N−Sn(2)	125.2(1)
C(3)−Sn(1)−C(5)	109.4(2)	Sn(1)−N−C(1)	106.6(2)
C(4)−Sn(1)−C(5)	116.2(2)	Sn(2)−N−C(1)	128.2(2)
N−Sn(2)−C(6)	98.8(1)	O−C(1)−N	120.6(3)
N−Sn(2)−C(7)	96.1(1)	O−C(1)−C(2)	117.9(4)
N−Sn(2)−C(8)	104.3(1)		

[a] Intramolecular distance. [b] Intermolecular distance.

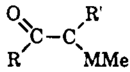
and the ^{13}C NMR data in Table 2 are consistent with the amidate form (**A**) for the new compounds **1−5**. Solution ^{119}Sn NMR chemical shifts of tin bound to nitrogen and oxygen are easily distinguishable[22] and the range of these shifts for **2-5** (18−77 ppm, Table 1) is typical of tin bound to nitrogen,[22] thus lending further support to the amidate form **A** of these systems.

Schraml reported that the ^{29}Si−N chemical shift in **6** (2.48 ppm) is upfield of those for typical (trimethylsilyl)amines, and that $\delta(^{29}\text{Si}-\text{O})$ in **6** (24.48 ppm) is downfield of those of typical trimethylsilyl alkoxides but comparable to those in trimethylsilyl carboxylates.[23] If the imidate form **B** were to make a significant contribution to **5** in solution, two ^{119}Sn chemical shifts should be observed, as indeed there are. If tautomer **B** were the only one in solution, ^{119}Sn chemical shifts about 100 ppm apart could be expected based on the shifts observed for typical (trimethylstannyl)amines and trimethylstannyl alkoxides, and approximately 130 ppm apart based on (trimethylstannyl)amines and trimethylstannyl carboxylates. The observed separation in the ^{119}Sn peaks is 86 ppm, which is not inconsistent with at least some imidate form **B** for **5** in solution in equilibrium with the amidate form **A** which could be expected to undergo facile C−N bond rotation leading to isochronous ^{119}Sn chemical shifts. Militating against this hypothesis, however, is the temperature insensitivity of the ^{119}Sn NMR solution spectrum. Moreover, this spectrum is sensitive to the concentration of **5**, an unexpected phenomenon if there were a simple equilibrium between forms **A** and **B** for this compound. Thus dilution causes the peak at 41 ppm to move downfield to 123.0 ppm while the peak at 126.6 ppm shifts only slightly to 127.2 ppm. These results lead us to suggest that the concentration-sensitive peak at *ca.* 41 ppm is associated with an intermolecular Sn- - -O interaction which is disrupted upon dilution. The downfield movement of the ^{119}Sn chemical shift is thus associated with a decrease in coordination number of the tin from five to four in species that are rapidly exchanging on the NMR time scale. The concentration-insensitive peak at 126.6 ppm in **5** is suggested to be associated with a considerably weaker intramolecular Sn- - -O interaction. In the solid state, the intermolecular Sn- - -O interaction in **5** appears at −19.35 ppm (Table 1). The peak at 0.28 ppm in solid **5** is assigned to the weaker intramolecular interaction.

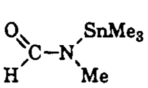
Compounds **1−4** also display only one ^{119}Sn chemical shift in CHCl$_3$ down to −60 °C. This behavior could be ascribed to facile C(O)−N bond rotation or stable conformers of type **C** or **D** in this temperature range. On the basis of VT ^{1}H NMR studies of **7** and **8−10**, it has been concluded that in solutions of these compounds conformer **C** dominates rather than **D**.[24] The same conclusion was also reached for **11** although its ^{1}H NMR spectrum (like those of **1-5**) is also temperature invariant.[24] We propose that for **1-4** and **11**, the dominant conformer is also **C** but with a strong concentration dependence of their ^{119}Sn NMR spectra owing to intramolecular Sn- - -O interactions. Thus, for example, the peak at 41 ppm in **3** moves to 123.0 ppm upon dilution, but in the solid state this peak appears at -61 ppm (Table 1).



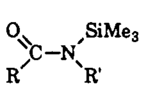
C



D



7



	R	R'
8	H	H
9	Me	Me
10	H	Me
11	Me	H

Our configurational conclusions are corroborated by the solid state structures of **5** and **3** determined by X-ray means. The atom Sn(2) in **5** is seen in Figure 1 to be significantly distorted from tetrahedral toward a TBP geometry in order to accommodate the intermolecular Sn- - -O bond. The average C$_{\text{eq}}$−Sn(2)−C$_{\text{eq}}$ angle is 117.3(2)° in the pseudo-TBP configuration around Sn(2) and the average N$_{\text{ax}}$−Sn(2)−C$_{\text{eq}}$ angle is 99.7(1)°. The intermolecular Sn(2)- - -O bond length of 2.672(3) Å is *ca.* 0.06 Å shorter than the intramolecular Sn(1)- - -O link in which the Sn(1) atom is more tetrahedral, thus reflecting the reduced strength of the intra compared with the intermolecular

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(24) Komoriya, A.; Yoder, C. H. *J. Am. Chem. Soc.* **1972**, *94*, 5285.

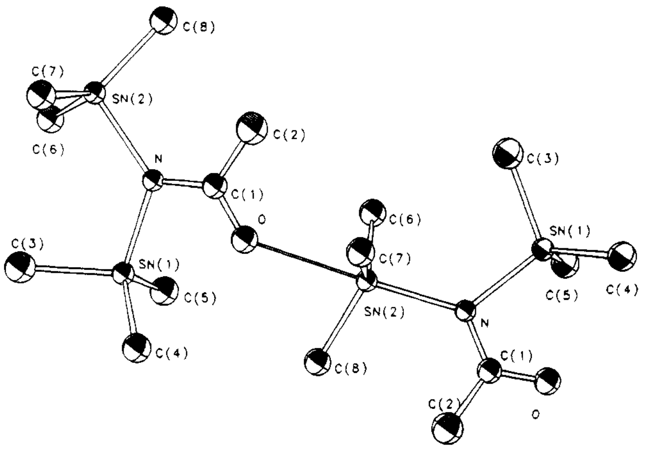

Figure 1. Computer drawing of $CH_3C(O)N(SnMe_3)_2$, **5**, showing the intermolecular Sn(2)- - -O interaction with a second molecule of **5**. Ellipsoids are drawn at the 50% probability level.

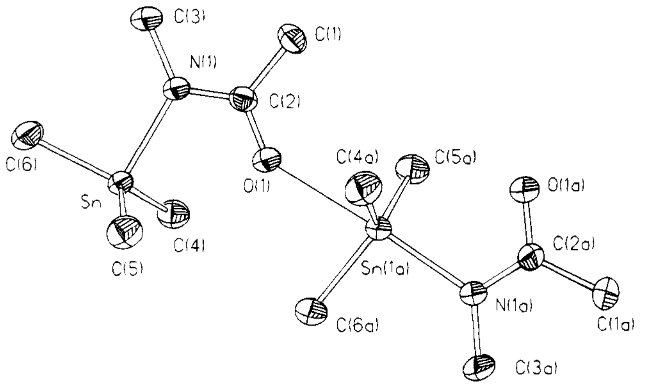

Figure 2. Computer drawing of $CH_3C(O)NCH_3(SnMe_3)$, **3**, showing the intermolecular Sn- - -O interaction with a second molecule of **3**. Ellipsoids are drawn at the 50% probability level.

Sn- - -O interaction as was deduced from the ^{119}Sn NMR experiments described above. Moreover, the Sn(2)-N bond length is *ca.* 0.06 Å longer than Sn(1)-N, which also reflects the stronger Sn(2)- - -O interaction.

In **3**, wherein only one tin is available for an oxygen interaction, it is clear from the geometry around the tin atom in Figure 2 that the stronger intermolecular interaction is chosen by the structure even though the intramolecular Sn and O atoms are *cis* to each other. Here the average $C_{eq}-Sn-C_{eq}$ angle is 118.0(2)°, the average $N_{ax}-Sn-C_{eq}$ angle is 98.2(2)° and the intermolecular Sn- - -O distance of 2.564 Å is *ca.* 0.4 Å shorter than the corresponding intramolecular contact.

It has been proposed that electron density donation from oxygen to M in conformation **A** may stabilize this conformer for M = Si,[24] Ge,[7] and Sn.[4] This proposal is not well supported by the solid state structure of **3** wherein this distance (2.925 Å) is 0.8 Å longer than the sum of the covalent radii,[25] although the distance is about 0.5 Å shorter than the sum of the van der Waals radii (see later). The shorter intramolecular Sn- - -O distance in **5** (which is *ca.* 0.6 Å shorter than the sum of covalent radii) is attributable to mutual crowding by the $SnMe_3$ groups. Here the presence of some intramolecular interaction is supported by a distortion of the coordination geometry around Sn(1) from tetrahedral toward TBP in which C(3) and O are pseudo-axial ligands. Thus the average pseudoequatorial bond angle (112.4°) is 3° larger than tetrahedral and the average pseudoapical angle involving C(3) (106.4) is about 3° smaller. The van der Waals radius for Sn is likely to be at least 2 Å, since that for Te is 2.06 Å.[25] Thus the sum of these radii for O and Sn is at least 3.5 Å, which also supports the existence of some bonding in the Sn(1)- - -O link.

A comparison of these metrics with those of **5** given earlier indicates that the distortion of the tin atom toward TBP in **3** is greater than that for Sn(2) in **5** and that the intermolecular contact in **3** is shorter by *ca.* 0.11 Å. This more pronounced TBP geometry in **3** is in accord with its higher-field solid state ^{119}Sn resonance (−61 ppm) compared with that in **5** (−19.35 ppm). The reduced tendency of **5** to form intramolecular links is attributable to steric crowding of the $Me_3Sn(2)$ group by the $Me_3Sn(1)$ substituent which would tend to restrain the C−Sn(1)−C angles toward tetrahedral. Similarly, the steric encumbrance provided by $Me_3Sn(2)$ to $Me_3Sn(1)$ drives the latter tin to an intramolecular Sn- - -O interaction in **5** which is only 0.06 Å longer than the Sn(2)- - -O intermolecular distance.

Compounds **2**−**5** all exhibit IR bands from 1495−1668 cm^{-1} in the solid state which are assigned to the C=O stretching frequency. This range lies at lower frequency, however, than that associated with primary and secondary amides in the solid state (1640−1694 cm^{-1}).[20] Thus the two types of Sn- - -O interactions discussed above (and especially the intermolecular interaction) are expected to weaken the C=O bond and hence lower its stretching frequency. The more normal value of ν(C=O) in **1** (1668 cm^{-1}) could be due to the strong electronegativity of the CF_3 group, which is expected to reduce the donor properties of the carbonyl oxygen.

Conclusions. Spectroscopic data for **1**−**5** and solid state structural dimensions for **3** and **5** provide considerable support for the amidate form for *N*-trialkylstannyl amides. In particular the X-ray structure of **3** gives substantial credence to a dominating *cis* oxygen−tin relationship in this class of compounds, which is probably favored more for steric than electronic reasons. The weaker Sn−O bond strength compared with that of the Si−O bond accounts for the amide form of **5** rather than an imidate configuration as was found in **6**. The solid state structures of **3** and **5** place on a firm basis the suggestion stemming from the results of Moessbauer[8] and infrared[9] experiments that trialkylstannyl amides engage in intramolecular bonding.

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Supporting Information Available: Text detailing the structure solution for **3**, figures showing a different view of **3** and the unit cell of **3**, and tables of complete structural data, bond lengths and angles, and anisotropic thermal parameters, hydrogen atom parameters (16 pages). Ordering information is given on any current masthead page.

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