

## Complexation of Organotin Halides with Ambidentate, S, N, and O Donor Ligands

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Eleven adducts derived from organotin halides of formula  $\text{MeSnCl}_3$  and  $\text{R}_2\text{SnCl}_2$  ( $\text{R} = \text{Me}, \text{Ph}$ ) were prepared with ligands containing N, O, or S as possible bonding sites. X-ray crystal structure analyses for trichloromethyltin(IV)-1-methyl-2-(methylsulfinyl)imidazole ( $\text{MeSnCl}_3\cdot\text{ImSOMe}$ ), trichloromethyltin(IV)-2-(*n*-propylsulfinyl)pyridine ( $\text{MeSnCl}_3\cdot\text{PySOPr}$ ), and dichlorodimethyltin(IV)-1-methyl-2-(methylsulfinyl)imidazole ( $\text{Me}_2\text{SnCl}_2\cdot\text{ImSOMe}$ ) were determined. The  $\text{MeSnCl}_3\cdot\text{ImSOMe}$  complex crystallized in the space group  $P2_1/n$  (No. 14) with  $a = 7.237$  (4) Å,  $b = 14.074$  (5) Å,  $c = 12.725$  (5) Å,  $\beta = 102.83$  (3)°,  $V = 1263.7$  (8) Å<sup>3</sup>,  $Z = 4$ , and final  $R = 0.028$  ( $R_w = 0.032$ ) for 2232 unique reflections. The  $\text{MeSnCl}_3\cdot\text{PySOPr}$  complex crystallized in space group  $P\bar{1}$  (No. 2) with  $a = 7.399$  (2) Å,  $b = 8.740$  (3) Å,  $c = 13.291$  (4) Å,  $\alpha = 95.47$  (2)°,  $\beta = 100.25$  (2)°,  $\gamma = 114.98$  (2)°,  $V = 752.5$  (4) Å<sup>3</sup>,  $Z = 2$ , and final  $R = 0.042$  ( $R_w = 0.049$ ) for 1959 unique reflections. The  $\text{Me}_2\text{SnCl}_2\cdot\text{ImSOMe}$  complex crystallized in space group  $P1$  (No. 1) with  $a = 6.985$  (1) Å,  $b = 7.075$  (1) Å,  $c = 7.320$  (1) Å,  $\alpha = 66.61$  (2)°,  $\beta = 85.42$  (2)°,  $\gamma = 87.94$  (2)°,  $V = 330.9$  (1) Å<sup>3</sup>,  $Z = 1$ , and final  $R = 0.018$  ( $R_w = 0.022$ ) for 1277 unique reflections. Whereas the molecular structures of  $\text{MeSnCl}_3\cdot\text{ImSOMe}$  and  $\text{MeSnCl}_3\cdot\text{PySOPr}$  show hexacoordination about tin, with the ligands binding both through nitrogen and the sulfinyl oxygen in a bidentate mode, in the  $\text{Me}_2\text{SnCl}_2\cdot\text{ImSOMe}$  adduct the ligand is monodentate, forming an N-bonded, 5-coordinate complex. Proton and <sup>13</sup>C NMR data find these structures to be maintained in solution. NMR and IR data are presented for these and eight other adducts, finding that small changes in the Lewis acidity of the organotin chloride govern the coordination number and geometry about tin.

## Introduction

The chemistry of tin is extremely rich and varied.<sup>2</sup> The bonding mode of the tin atom in adducts of its organometallic compounds is dependent upon the charge on the metal and the nature of the ligands.<sup>3</sup> Frequently, more than one product, either with respect to stoichiometry<sup>4</sup> or to geometry,<sup>5</sup> can be obtained.

This work dealt with the preparation and study of several adducts derived from organotin chlorides and potentially chelating ligands possessing one  $\text{X}=\text{O}$  "pointed"<sup>6</sup> donor site and one nitrogen donor site (Figure 1). Most of the ligands were also prepared by us using literature or adaptations of literature methods.<sup>7</sup> The resulting complexes were studied by IR and NMR spectroscopy and X-ray crystallography.

## Experimental Section

**Preparation of the Ligands.** The six ligands used in this work were as follows: 1-methyl-2-(methylsulfinyl)imidazole, ImSOMe; 2-(*n*-propylsulfinyl)pyridine, PySOPr; 2-(methylsulfinyl)pyridine, PySOMe; 2-(methylsulfinyl)pyrimidine, PymSOMe; 2,2'-bis(pyridyl) ketone, Py<sub>2</sub>CO; 2-(methylsulfinyl)benzothiazole, BtSOMe. Except for the Py<sub>2</sub>CO ligand, available commercially, all the others were prepared in the laboratory

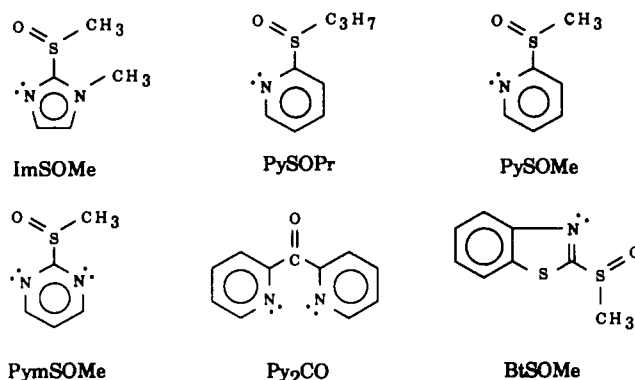
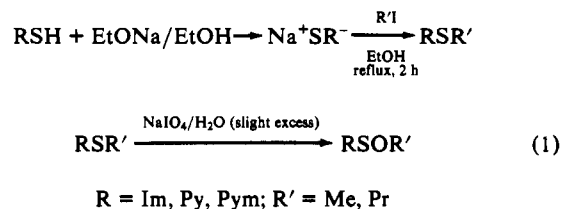


Figure 1. Structural formulas of the ligands: ImSOMe, 1-methyl-2-(methylsulfinyl)imidazole; PySOPr, 2-(*n*-propylsulfinyl)pyridine; PySOMe, 2-(methylsulfinyl)pyridine; PymSOMe, 2-(methylsulfinyl)pyrimidine; Py<sub>2</sub>CO, 2,2'-bis(pyridyl) ketone; BtSOMe, 2-(methylsulfinyl)benzothiazole.

according to literature preparations.<sup>7</sup> The first four ligands were made from the corresponding thiols in the following way:



In the oxidation step, ImSOMe and PymSOMe both demanded 16 h at 5 and 25 °C, respectively, whereas PySOPr and PySOMe took 12 h at 5 °C. The final products were all liquids and were checked for purity by TLC. They were identified by IR and NMR spectroscopies.

The BtSOMe ligand was prepared by a modification of the final step,

- (1) (a) Universidad Federal de Minas Gerais. (b) Texas A&M University.
- (2) Zubietta, J. A.; Zuckerman, J. J. *Prog. Inorg. Chem.* **1978**, *24*, 251.
- (3) (a) Filgueiras, C. A. L.; Celso, C.; Marques, E. V.; Johnson, B. F. G. *Inorg. Chim. Acta* **1982**, *59*, 71. (b) Filgueiras, C. A. L.; Babá, J. M. K. *Inorg. Chim. Acta* **1981**, *52*, 129.
- (4) Passos, B. F. T.; de Jesus Filho, M. F.; Filgueiras, C. A. L.; Abras, A.; da Silva, E. G. *Hyperfine Interact.* **1990**, *53*, 379.
- (5) Biddle, B. N.; Gray, J. S.; Crowe, A. J. *J. Chem. Soc., Dalton Trans.* **1990**, 419.
- (6) (a) Rheingold, A. L.; Ng, S. W.; Zuckerman, J. J. *Organometallics* **1984**, *3*, 233. (b) Ng, S.-W.; Barnes, C. L.; Hossain, M. B.; van der Helm, D.; Zuckerman, J. J.; Kumar Das, V. G. *J. Am. Chem. Soc.* **1982**, *104*, 5359. (c) Harrison, P. G.; Molloy, K. C. *J. Organomet. Chem.* **1978**, *152*, 63.
- (7) (a) Chia, P. S. K.; Livingstone, S. E.; Lockyer, T. N. *Aust. J. Chem.* **1966**, *19*, 1835. (b) Johnson, C. R.; McCants, D., Jr. *J. Am. Chem. Soc.* **1965**, *87*, 1109. (c) Brown, D. J.; Ford, P. W. *J. Chem. Soc.* **1967**, 568.

Table I. Formulas and Analytical Data for Compounds 1-11

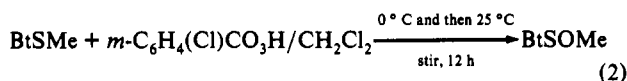
compd	formula	mp, °C	% composition							
			C		H		N		Sn	
			found	calc	found	calc	found	calc	found	calc
1	MeSnCl <sub>3</sub> ·ImSOMe	178 (d)	18.50	18.74	2.85	2.86	7.20	7.29	33.64	32.37
2	MeSnCl <sub>3</sub> ·PySOPr	155-158	26.14	26.39	3.31	3.42	3.33	3.42	28.62	29.00
3	MeSnCl <sub>3</sub> ·PySOMe	158 (subl)	22.01	22.03	2.58	2.62	3.61	3.67	31.61	31.14
4	MeSnCl <sub>3</sub> ·PymSOMe	145 (subl)	19.05	18.84	2.54	2.35	7.49	7.33		
5	MeSnCl <sub>3</sub> ·Py <sub>2</sub> CO	150 (d)	34.95	33.95	2.70	2.60	6.42	6.60	29.04	27.98
6	Me <sub>2</sub> SnCl <sub>2</sub> ·ImSOMe	120 (d)	23.00	23.09	3.71	3.85	7.54	7.70	31.34	32.74
7	Me <sub>2</sub> SnCl <sub>2</sub> ·Py <sub>2</sub> CO	153 (d)	40.40	38.64	3.60	3.47	7.17	6.93	30.70	29.40
8	Ph <sub>2</sub> SnCl <sub>2</sub> ·ImSOMe	125-128	41.11	41.83	3.51	3.69	5.30	5.74		
9	Ph <sub>2</sub> SnCl <sub>2</sub> ·BtSOMe	103-105	44.73	44.39	2.90	3.14	2.51	2.60	22.70	21.95
10	Ph <sub>2</sub> SnCl <sub>2</sub> ·PySOPr	127-130	47.23	46.81	3.89	4.09	2.62	2.73		
11	Ph <sub>2</sub> SnCl <sub>2</sub> ·Py <sub>2</sub> CO	123-125	51.60	52.30	3.30	3.41	5.20	5.31		

Table II. Infrared Absorptions (cm<sup>-1</sup>) (CsI Pellets)

compd	formula	free ligand		organotin precursor		adduct					
		ν <sub>CO</sub>	ν <sub>SO</sub>	ν <sub>SnC</sub>	ν <sub>SnCl</sub>	ν <sub>CO</sub>	ν <sub>SO</sub>	ν <sub>SnC</sub>	ν <sub>SnO</sub>	ν <sub>SnN</sub>	ν <sub>SnCl</sub>
1	MeSnCl <sub>3</sub> ·ImSOMe		1020	560 <sup>a</sup>	382 <sup>c</sup>		970, 940	570	433	340	245
2	MeSnCl <sub>3</sub> ·PySOPr		1050, 1030	560 <sup>a</sup>	382 <sup>c</sup>		955	615	450	335	250
3	MeSnCl <sub>3</sub> ·PySOMe		1040, 1025	560 <sup>a</sup>	382 <sup>c</sup>		970, 950	615	438	335	250
4	MeSnCl <sub>3</sub> ·PymSOMe		1050	560 <sup>a</sup>	382 <sup>c</sup>		915		440	340	235
5	MeSnCl <sub>3</sub> ·Py <sub>2</sub> CO	1685, 1680		560 <sup>a</sup>	382 <sup>c</sup>	<i>d</i>		620		510, 500, 425	245
6	Me <sub>2</sub> SnCl <sub>2</sub> ·ImSOMe		1020	553, 520 <sup>a</sup>	335, 316 <sup>a</sup>		1020	598, 545		340	245
7	Me <sub>2</sub> SnCl <sub>2</sub> ·Py <sub>2</sub> CO	1685, 1680		553, 520 <sup>a</sup>	335, 316 <sup>a</sup>	1685		615, 530		495, 480, 415	235
8	Ph <sub>2</sub> SnCl <sub>2</sub> ·ImSOMe		1020	279, 234 <sup>b</sup>	364, 356 <sup>b</sup>		992		440	343	
9	Ph <sub>2</sub> SnCl <sub>2</sub> ·BtSOMe		1070, 1055	279, 234 <sup>b</sup>	364, 356 <sup>b</sup>		1005		415		260, 250
10	Ph <sub>2</sub> SnCl <sub>2</sub> ·PySOPr		1050, 1030	279, 234 <sup>b</sup>	364, 356 <sup>b</sup>		970		435	380	
11	Ph <sub>2</sub> SnCl <sub>2</sub> ·Py <sub>2</sub> CO	1685, 1680		279, 234 <sup>b</sup>	364, 356 <sup>b</sup>	<i>d</i>				517, 425	240

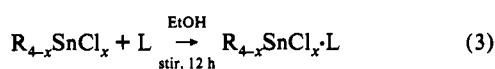
<sup>a</sup> Reference 3b. <sup>b</sup> Reference 19. <sup>c</sup> Reference 20. <sup>d</sup> See text. ν<sub>CO</sub> is not discernible.<sup>17,18</sup>

in which *m*-chloroperbenzoic acid was used as the oxidizing agent:



The CH<sub>2</sub>Cl<sub>2</sub> solution of the product was filtered, and the excess acid in the filtrate was extracted three times with aqueous NaHCO<sub>3</sub>. The organic phase was evaporated under vacuum, and the solid produced was recrystallized from MeOH/H<sub>2</sub>O and dried over MgSO<sub>4</sub>.

**Preparation of the Complexes.** All six ligands yielded adducts obtained according to eq 3. The adducts were filtered out, washed with EtOH and



Et<sub>2</sub>O, and recrystallized from a 1:1 mixture of *n*-hexane and acetone. Table I gives the pertinent analytical data for the 11 complexes obtained.

IR spectra were recorded on a Perkin-Elmer 283B instrument in the 4000-200-cm<sup>-1</sup> range using CsI pellets (Table II). <sup>1</sup>H NMR spectra were obtained on a Bruker 200-MHz instrument for all the complexes soluble in acetone-*d*<sub>6</sub> (Table III). The <sup>13</sup>C NMR spectrum of Me<sub>2</sub>SnCl<sub>2</sub>·ImSOMe was likewise measured in acetone on a Bruker 200-MHz instrument.

**Crystal Structure Determination.** X-ray data were collected on an R3m/V single-crystal X-ray diffractometer. Table IV summarizes the experimental data for the crystallographic analysis. Colorless crystals of 1, 2, and 6 were mounted on glass fibers with epoxy cement, at room temperature. Crystal 1 was cooled to 193 K in a N<sub>2</sub> cold stream (Nicolet LT-2). Preliminary examination and data collection were performed on a Nicolet R3m/V X-ray diffractometer (oriented graphite monochromator: λ(Mo Kα) = 0.710 73 Å radiation). Cell parameters were calculated from the least-squares fitting of the setting angles for 25 reflections for 1, 2, and 6. ω-scans for several intense reflections indicated good crystal quality for all three crystals.

Data were collected for 4.0° ≤ 2θ ≤ 50.0° [ω (Wyckoff) scan for 1 and 6 and θ-2θ scan for 2]. The scan range, on ω, for the data collection was 1.20° plus Kα separation for the θ-2θ scan, with a variable scan rate of 1.50-15.00° min<sup>-1</sup> for all three data collections. Three control reflections, collected every 97 reflections, showed no significant trends for 1, 2, or 6. Background measurements were taken by stationary crystal

Table III. Proton NMR Data: *J*(<sup>119,117</sup>Sn-C-H) Coupling Constants (Hz) and CH<sub>3</sub> Chemical Shifts

compd	<i>J</i> ( <sup>119</sup> Sn-C-H)	<i>J</i> ( <sup>117</sup> Sn-C-H)	δ(Sn-CH <sub>3</sub> )
MeSnClOx <sub>2</sub> <sup>a</sup>	106.6	101.7	
MeSnCl(acac) <sub>2</sub> <sup>a</sup>	120.9	115.5	
MeSnCl <sub>3</sub> ·ImSOMe (1) <sup>b</sup>	128.74	122.86	1.40
MeSnCl <sub>3</sub> ·PySOPr (2) <sup>b</sup>	124.13	118.62	1.30
MeSnCl <sub>3</sub> ·PySOMe (3) <sup>b</sup>	124.38	118.90	1.30
MeSnCl <sub>3</sub> <sup>c</sup>	100.98	96.5-95.5	
Me <sub>2</sub> SnOx <sub>2</sub> <sup>a</sup>	71.2	67.9	
Me <sub>2</sub> Sn(acac) <sub>2</sub> <sup>a</sup>	99.3	95.0	
Me <sub>2</sub> SnClOx <sup>a</sup>	79.9	76.4	
Me <sub>2</sub> SnCl <sub>2</sub> ·ImSOMe (6) <sup>b</sup>	91.54	87.52	1.14
Me <sub>2</sub> SnCl <sub>2</sub> <sup>c</sup>	70.0-69.0	67.0-66.0	
Me <sub>3</sub> SnOx <sup>a</sup>	57.0	54.9-54.6	
Me <sub>3</sub> SnCl <sup>c</sup>	58.5-58.1	56.5	
Me <sub>4</sub> Sn <sup>c</sup>	54.3-53.4	52.5	

<sup>a</sup> Reference 24. <sup>b</sup> This work. <sup>c</sup> Reference 25.

and stationary counter techniques at the beginning and end of each scan for 1/2 of the total scan time.

Lorentz and polarization corrections were applied to all data as were semiempirical absorption corrections (*T*<sub>max</sub>, *T*<sub>min</sub> = 0.981, 0.880; 0.983, 0.757; and 0.946, 0.889 for 1, 2, and 6, respectively). The structures were solved by direct methods [SHELXS, SHELXTL-PLUS program package, Sheldrick (1989)].<sup>8</sup> Full-matrix least-squares anisotropic refinement was used for all non-hydrogen atoms [SHELXLS, SHELXTL-PLUS program package, Sheldrick (1989); quantity minimized Σw(*F*<sub>o</sub>-*F*<sub>c</sub>)<sup>2</sup>; w<sup>-1</sup> = σ<sup>2</sup>*F* + *gF*<sup>2</sup>].<sup>8</sup> The extinction coefficient χ {where *F*\* = *F*<sub>o</sub>/[1 + 0.002χ*F*<sub>o</sub><sup>2</sup>/sin 2θ]<sup>0.25</sup>} was refined for all three structures. For 6 the Rogers absolute configuration parameter η was refined to 0.97 (4), which indicated the correct absolute configuration was chosen.<sup>9</sup> Hydrogen atoms were placed in idealized positions with isotropic thermal parameters fixed at 0.08.<sup>10</sup> Neutral-atom scattering factors and anomalous scattering correction terms

(8) All crystallographic calculations were performed with SHELXTL-PLUS rev 4.11 (G. M. Sheldrick, Institut für Anorganische Chemie der Universität, Tammannstrasse 4, D-3400 Göttingen, Federal Republic of Germany), supplied by Siemens Analytical X-ray Instruments, Madison, WI.

(9) Rogers, D. *Acta Crystallogr.* 1981, A37, 734.

(10) Larson A. C. *Acta Crystallogr.* 1967, A23, 604.

Table IV. Crystallographic Data

	complex		
	MeSnCl <sub>3</sub> ·ImSOMe (1)	MeSnCl <sub>3</sub> ·PySOPr (2)	Me <sub>2</sub> SnCl <sub>2</sub> ·ImSOMe (6)
chem formula	C <sub>6</sub> H <sub>11</sub> N <sub>2</sub> OSeCl <sub>3</sub> Sn	C <sub>9</sub> H <sub>14</sub> NOSCl <sub>3</sub> S	C <sub>7</sub> H <sub>14</sub> N <sub>2</sub> OSeCl <sub>2</sub> Sn
fw	384.3	409.3	399.3
space group	P2 <sub>1</sub> /n (No. 14)	P1̄ (No. 2)	P1 (No. 1)
a, Å	7.237 (3)	7.399 (2)	6.985 (1)
b, Å	14.074 (5)	8.740 (3)	7.075 (1)
c, Å	12.725 (5)	13.291 (4)	7.320 (1)
α, deg		95.47 (2)	66.61 (2)
β, deg	102.83 (3)	100.25 (2)	85.42 (2)
γ, deg		114.98 (2)	87.94 (2)
V, Å <sup>3</sup>	1263.7 (8)	752.5 (4)	330.9 (1)
Z	4	2	1
T, °C	-80 (±1)	23 (±1)	23 (±1)
λ, Å	0.710 73	0.710 73	0.710 73
ρ <sub>calc</sub> , g cm <sup>-3</sup>	2.02	1.81	1.83
μ, cm <sup>-1</sup>	28.0	23.6	24.7
R <sup>a</sup>	0.028	0.042	0.018
R <sub>w</sub> <sup>b</sup>	0.032	0.049	0.022

$${}^a R = \sum |F_o - F_c| / \sum F_o, {}^b R_w = \{[\sum w(F_o - F_c)^2] / [\sum w(F_o)^2]\}^{1/2}.$$

Table V. Atomic Coordinates ( $\times 10^4$ ) and Equivalent Isotropic Displacement Parameters ( $\text{\AA}^2 \times 10^3$ ) for Compound 1, MeSnCl<sub>3</sub>·ImSOMe

	x	y	z	U(eq) <sup>a,b</sup>
Sn(1)	824 (1)	272 (1)	7374 (1)	20 (1)
Cl(1)	767 (1)	1674 (1)	6190 (1)	35 (1)
Cl(2)	972 (1)	-848 (1)	8868 (1)	34 (1)
Cl(3)	-2346 (1)	-205 (1)	6527 (1)	32 (1)
S(1)	3218 (1)	1682 (1)	9333 (1)	25 (1)
O(1)	3372 (3)	968 (2)	8451 (2)	27 (1)
N(1)	-371 (4)	1281 (2)	8357 (2)	22 (1)
N(2)	-285 (4)	2477 (2)	9483 (2)	22 (1)
C(1)	717 (4)	1821 (2)	9083 (3)	21 (1)
C(2)	-2155 (4)	2325 (2)	8991 (3)	23 (1)
C(3)	-2209 (5)	1593 (2)	8292 (3)	23 (1)
C(4)	406 (5)	3152 (2)	10357 (3)	29 (1)
C(5)	3628 (5)	1036 (3)	10573 (3)	34 (1)
C(6)	2570 (5)	-551 (3)	6586 (3)	36 (1)

<sup>a</sup> Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized *U<sub>ij</sub>* tensor. <sup>b</sup> Estimated standard deviations are given in parentheses.

were taken from refs. 11 and 12. Final atomic coordinates are listed in Tables V–VII.

## Results and Discussion

The tin atom displays a great variety of coordination numbers and bonding modes.<sup>2,13</sup> These features are shown in its extensive organometallic chemistry, which has grown enormously in recent years, especially due to the biological significance of organotin compounds.<sup>14,15</sup> Slight differences in the Lewis acidity of the tin atom, as well as substituent effects, can cause marked differences in the way ligands bond to the metal. Thus, ligands containing more than one basic site can form mono- or bidentate complexes or sometimes a bridge between two tin moieties.<sup>4,16</sup> Theoretical

- (11) Neutral-atom scattering factors were taken from: *International Tables for X-Ray Crystallography*. Ibers, J. A., Hamilton, W. C., Eds.; Kynoch Press. Birmingham, England, 1974; p 99.
- (12) Anomalous scattering correction terms,  $\Delta f'$  and  $\Delta f''$ , were taken from: *International Tables for X-Ray Crystallography*, Ibers, J. A., Hamilton, W. C., Eds.; Kynoch Press: Birmingham, England, 1974; Vol. IV, p 149.
- (13) Davies, A. G.; Smith, P. J. Tin. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon Press: London, 1982.
- (14) (a) *Tin and Malignant Cell Growth*; Zucherman, J. J., Ed.; CRC Press, Inc.: Boca Raton, FL, 1988. (b) *Tin Chemicals-The Formula for Success*; International Tin Research Institute, ITRI: Uxbridge, England, 1990; Publication No. 681. (c) Saxena, A. K.; Huber, F. *Coord. Chem. Rev.* **1989**, *95*, 109.
- (15) Lee, F. L.; Gabe, E. G.; Khoo, L. E.; Eng, G.; Smith, F. E. *Polyhedron* **1990**, *9*, 653.
- (16) Zhu, F. C.; Shao, P. X.; Yao, X. K.; Wang, R. J.; Wang, H. G. *Inorg. Chim. Acta* **1990**, *171*, 85.

Table VI. Atomic Coordinates ( $\times 10^4$ ) and Equivalent Isotropic Displacement Parameters ( $\text{\AA}^2 \times 10^3$ ) for Compound 2, MeSnCl<sub>3</sub>·PySOPr

	x	y	z	U(eq) <sup>a,b</sup>
Sn(1)	-542 (1)	-374 (1)	2453 (1)	40 (1)
Cl(1)	815 (3)	2043 (2)	1583 (1)	60 (1)
Cl(2)	-2683 (3)	786 (2)	3099 (1)	61 (1)
Cl(3)	794 (2)	-1953 (2)	1416 (1)	54 (1)
S(1)	-4552 (2)	-4081 (2)	2309 (1)	41 (1)
O(1)	-2377 (6)	-2805 (5)	2897 (3)	48 (2)
N(1)	-3374 (7)	-1804 (5)	1065 (3)	36 (2)
C(1)	1763 (11)	354 (10)	3840 (6)	70 (3)
C(2)	-3514 (9)	-1209 (7)	163 (5)	46 (3)
C(3)	-5208 (10)	-2044 (8)	-642 (5)	49 (3)
C(4)	-6826 (9)	-3526 (8)	-547 (5)	49 (3)
C(5)	-6685 (9)	-4161 (8)	350 (5)	47 (2)
C(6)	-4947 (8)	-3258 (6)	1139 (4)	37 (2)
C(7)	-6257 (9)	-3650 (8)	2950 (5)	47 (3)
C(8)	-6155 (12)	-4239 (10)	3991 (5)	65 (3)
C(9)	-7690 (16)	-4052 (15)	4521 (8)	111 (7)

<sup>a</sup> Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized *U<sub>ij</sub>* tensor. <sup>b</sup> Estimated standard deviations are given in parentheses.

Table VII. Atomic Coordinates ( $\times 10^4$ ) and Equivalent Isotropic Displacement Parameters ( $\text{\AA}^2 \times 10^3$ ) for Compound 6, Me<sub>2</sub>SnCl<sub>2</sub>·ImSOMe

	x	y	z	U(eq) <sup>a,b</sup>
Sn(1)	0	0	0	39 (1)
Cl(1)	-2608 (2)	2415 (2)	-1187 (2)	54 (1)
Cl(2)	-1538 (4)	-1764 (4)	3537 (4)	79 (1)
S(1)	4609 (2)	-1025 (2)	-2359 (2)	46 (1)
O(1)	3492 (5)	-1800 (6)	-360 (6)	58 (1)
N(1)	1637 (9)	1760 (9)	-3243 (9)	45 (2)
N(2)	4152 (6)	2839 (6)	-5385 (6)	43 (1)
C(1)	1234 (7)	3669 (7)	-4622 (7)	45 (2)
C(2)	2762 (8)	4354 (7)	-5944 (7)	51 (2)
C(3)	3379 (6)	1301 (6)	-3762 (6)	39 (1)
C(4)	6079 (13)	2959 (14)	-6377 (13)	62 (3)
C(5)	3902 (14)	-2535 (12)	-3626 (15)	65 (3)
C(6)	1813 (11)	1606 (12)	1035 (11)	72 (3)
C(7)	-788 (8)	-2508 (8)	-633 (10)	57 (2)

<sup>a</sup> Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized *U<sub>ij</sub>* tensor. <sup>b</sup> Estimated standard deviations are given in parentheses.

calculations on tin compounds, as well as more experimental data, are needed in order to better understand this behavior. The present study is of the binding of tin in the form of the organotin chlorides, MeSnCl<sub>3</sub>, Me<sub>2</sub>SnCl<sub>2</sub>, and Ph<sub>2</sub>SnCl<sub>2</sub>, to ambidentate ligands containing N, O, or S, defined in Figure 1. Complexes 1–11 were prepared by direct addition of ligand to the appropriate

organotin chloride. As indicated by elemental analyses shown in Table I, all are 1:1 adducts, although with varying structures; vide infra.

**Infrared Spectroscopy.** Table II lists the most important IR data, permitting several conclusions. For the ligands containing the SO group all complexes, except **6**, display a shift of  $\nu_{\text{SO}}$  to lower values as compared to the free ligand, which indicates an SnO bond. For complex **6**, derived from  $\text{Me}_2\text{SnCl}_2$ , the lack of change in the SO stretching frequency precludes any bonding of the SO group to the Sn atom. In contrast, substitution of Me by Ph, forming  $\text{Ph}_2\text{SnCl}_2$ , and reaction with the same ImSOMe ligand leads to a lowering of  $\nu_{\text{SO}}$  from 1020 to 992  $\text{cm}^{-1}$ . This, as well as the appearance of a new band at 343  $\text{cm}^{-1}$ , characteristic of an SnN bond, indicates a bidentate mode of bonding to the  $\text{Ph}_2\text{SnCl}_2$  parent acid.

The CO stretching frequency of  $\text{Py}_2\text{CO}$  is unaltered in complex **7** compared to that of the free ligand, indicating that no bonding occurs between tin and the carbonyl group. The same presumably is the case in complexes **5** and **11** as well, for which it was not possible to ascertain the CO absorption in the spectra of the complexes. This is, however, the behavior of the ligand  $\text{Py}_2\text{CO}$  in many other instances, when it forms N,N-bonded complexes with transition metals.<sup>17,18</sup> The SnC absorption tends to shift to higher values upon complexation, possibly due to rehybridization.<sup>19,20</sup> The SnN absorption appears in general around 400  $\text{cm}^{-1}$ . Although it is difficult to assign values for the SnO and SnN frequencies, it has been shown that they both lie between 600 and 200  $\text{cm}^{-1}$ .<sup>21,22</sup> In complexes **1–4**, **6**, **8**, and **10** a new band which appeared between 335 and 380  $\text{cm}^{-1}$  was assigned to  $\nu_{\text{SnN}}$  by comparison with literature data.<sup>21,22</sup> In the three complexes containing  $\text{Py}_2\text{CO}$ , in which the Sn atom is bonded to two N atoms,  $\nu_{\text{SnN}}$  appears at higher values and splits into two bands, the one of higher frequency being further split in complexes **5** and **7**. The SnO absorptions in the O-bonded adducts are in the range 415–450  $\text{cm}^{-1}$ , quite in accordance with established results.<sup>21,22</sup> The SnCl absorptions of the adducts, characteristically strong bands around 250  $\text{cm}^{-1}$ , are shifted considerably to lower frequencies, compared to the parent acids, as commonly described in other instances.<sup>23</sup>

**NMR Spectroscopy.** Table III presents the  $^2J(^{119,117}\text{Sn}-\text{C}-\text{H})$  coupling constants for the new methyltin complexes whose structures have been determined, as well as for another closely related adduct,  $\text{MeSnCl}_3\cdot\text{PySOMe}$ , measured in acetone- $d_6$ . For comparative purposes, several other compounds are listed;<sup>24,25</sup> extensive lists may be found in the literature.<sup>26–28</sup>

The solid state structures, vide infra, show the  $\text{MeSnCl}_3\cdot\text{ImSOMe}$  and  $\text{MeSnCl}_3\cdot\text{PySOPr}$  complexes to be of octahedral geometry, with a hexacoordinated Sn atom at the center and a N atom trans to the methyl carbon atom. Presumably  $\text{MeSnCl}_3\cdot\text{PySOMe}$  also has a similar structure. For these three complexes the  $^2J(^{119,117}\text{Sn}-\text{C}-\text{H})$  coupling constants are very similar and in the 120–130-Hz range. The experimental ratio

$J(^{119}\text{Sn}-\text{C}-\text{H})/J(^{117}\text{Sn}-\text{C}-\text{H})$  is 1.046, the same as that of the magnetic moments of the two Sn isotopes, as expected.<sup>29</sup> In contrast, the  $^2J(^{119,117}\text{Sn}-\text{C}-\text{H})$  coupling constants for  $\text{Me}_2\text{SnCl}_2\cdot\text{ImSOMe}$  are considerably smaller than those for the former three complexes. Since the IR spectrum suggests pentacoordination, and this is borne out by X-ray structural data (vide infra), the lower  $J$  values correlate with lower coordination numbers.

It is instructive to place the carbon-13 NMR data of compound **6** in context with extensive studies which have made remarkably good correlations of Me–Sn–Me bond angles with  $|^1J(^{119}\text{Sn},^{13}\text{C})|$  coupling constants, measured in the solid state.<sup>26–28</sup> In those studies the strictly empirical linear correlation shown in eq 4,  $\theta = \angle\text{Me}-\text{Sn}-\text{Me}$ , was demonstrated.

$$|^1J(^{119}\text{Sn},^{13}\text{C})| = 11.4\theta - 875 \quad (4)$$

In fact the acetone solution NMR data for **6** give a methyl carbon doublet centered at  $\delta$  36.33 with  $^1J(^{119}\text{Sn},^{13}\text{C}) = 888$  Hz. Thus  $\theta$  as calculated from eq 4 and derived from solution NMR data is 154.65°, in excellent agreement with the X-ray crystal structure presented below which finds  $\theta$  to be 154.7°. Hence, there is no structural change on dissolution of **6**.

Table III also shows the  $^2J(^{119,117}\text{Sn}-\text{C}-\text{H})$  coupling constants for complexes of  $\text{R}_{4-x}\text{SnCl}_x$  with 8-hydroxyquinoline (Ox) in its deprotonated form<sup>24</sup> and with acetylacetonate (acac),<sup>24</sup> as well as for all the uncomplexed organotin chlorides.<sup>25</sup> A Fermi contact mechanism governs the coupling between Sn and H;<sup>28</sup> therefore, the more s character with which the Sn atom engages the Me group, the higher the value of  $J$  will be. Thus, the tin–hydrogen coupling constants ( $J(^{119,117}\text{Sn}-\text{C}-\text{H})$ ) can in various cases be correlated semiquantitatively with the s character the Sn atom presents in the Sn–C bond, as long as the hybridization at tin is of the type  $sp^n$  but not  $sp^3 d^n$ .<sup>30</sup> (Even in the latter case, however, some minor correlation between  $J$  and the degree of covalency between the Sn and C atoms can be discerned.) As shown in Table III, the uncomplexed  $\text{Me}_4\text{Sn}$  to  $\text{MeSnCl}_3$  series shows a steady increase in  $J$  values. This is accounted for by the increased covalency of the SnC bond as the number of Cl atoms bonded to Sn increases, since the SnCl bond is more polar than SnC. The increased covalency implies a higher degree of s orbital participation. This interpretation agrees with the fact that the IR spectra also show an increase in  $\nu_{\text{SnC}}$  upon complexation. A similar trend can be seen in the 8-hydroxyquinolinolate and acetylacetonate complexes.<sup>24</sup> The latter are likely to form more polar SnO bonds compared to the SnO, SnN bonds in the former. Thus,  $J$  values for the 8-hydroxyquinolinolate complexes are smaller than those for the acetylacetonate complexes. The data for our adducts show that this trend holds true here also. The three  $\text{MeSnCl}_3$  complexes present similar  $J$  values, which are much higher than that for the  $\text{Me}_2\text{SnCl}_2$  derivative. The trend seems to depend more upon the number of the groups on the Sn atom than on the geometry, as the 6-coordinate Ox and acac complexes also show.

**X-ray Structures.** The molecular structures of  $\text{MeSnCl}_3\cdot\text{ImSOMe}$  (**1**),  $\text{MeSnCl}_3\cdot\text{PySOPr}$  (**2**), and  $\text{Me}_2\text{SnCl}_2\cdot\text{ImSOMe}$  (**6**), respectively, are given in Figures 2–4. Table IV summarizes the crystal data for the three compounds; Table VIII presents selected bond lengths and bond angles for the hexacoordinate compounds **1** and **2**, and Table IX presents bond lengths and bond angles for the pentacoordinate compound **6**.

The geometry about tin in the  $\text{MeSnCl}_3\cdot\text{ImSOMe}$  (**1**) and  $\text{MeSnCl}_3\cdot\text{PySOPr}$  (**2**) adducts is a distorted octahedron with the three chlorides arranged in a meridional fashion and the methyl group trans to N in both complexes (Figures 2 and 3, respectively). The bite angle of the chelating ligand is identical for both and quite acute, 75.3 (2)°. In both cases the “trans” chlorides bend

(17) de Sousa, G. F.; Filgueiras, C. A. L. *Transition Met. Chem.* **1990**, *15*, 286.

(18) de Sousa, G. F.; Filgueiras, C. A. L. *Transition Met. Chem.* **1990**, *15*, 290.

(19) May, J. R.; McWhinnie, W. R.; Poller, R. C. *Spectrochim. Acta* **1971**, *27A*, 969.

(20) Clark, R. J. H.; Davies, A. G.; Puddephatt, R. J. *J. Chem. Soc. A* **1968**, 1828.

(21) Tanaka, T.; Komura, M.; Kawasaki, Y.; Okawara, R. *J. Organomet. Chem.* **1964**, *1*, 484.

(22) Kumar Das, V. G.; Chee-Keong, Y.; Smith, P. *J. Organomet. Chem.* **1987**, *327*, 311.

(23) Alberte, B.; Sánchez González, A.; García, E.; Casas, J. S.; Sordo, J.; Castellano, E. E. *J. Organomet. Chem.* **1988**, *338*, 187.

(24) Kawakami, K.; Okawara, R. *J. Organomet. Chem.* **1966**, *6*, 249.

(25) Lorberth, J.; Vakrenkamp, H. *J. Organomet. Chem.* **1968**, *11*, 111.

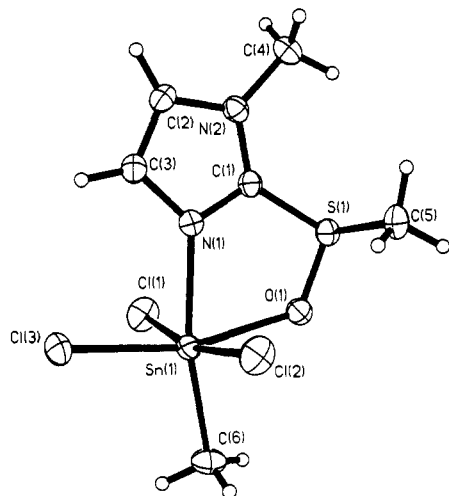
(26) Lockhart, T. P.; Manders, W. F.; Zuckerman, J. J. *J. Am. Chem. Soc.* **1987**, *109*, 7015.

(27) Lockhart, T. P.; Manders, W. F. *J. Am. Chem. Soc.* **1986**, *108*, 892.

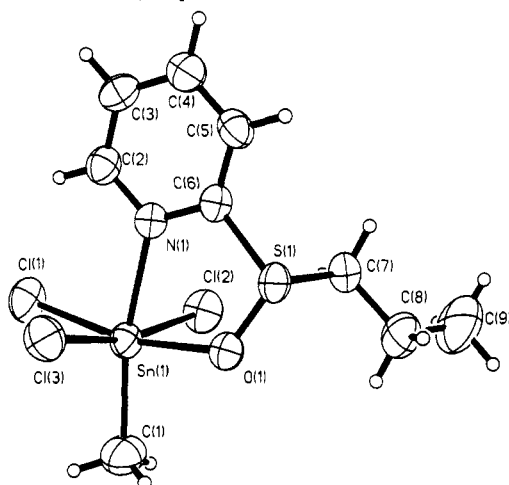
(28) Lockhart, T. P.; Manders, W. F. *J. Am. Chem. Soc.* **1987**, *109*, 7015.

(29) Table of the Isotopes. *CRC Handbook of Chemistry and Physics*, 62nd ed.; CRC Press, Inc.: Boca Raton, FL, 1981.

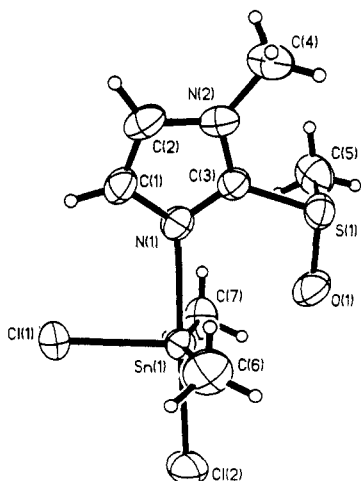
(30) van den Bergh, E. V.; van der Kelen, G. P. *J. Organomet. Chem.* **1966**, *6*, 515.



**Figure 2.** Thermal ellipsoid plot (50% probability) of the trichloromethyltin(IV) adduct of 1-methyl-2-(methylsulfinyl)imidazole,  $\text{MeSnCl}_3 \cdot \text{ImSOMe}$  (compound 1).



**Figure 3.** Thermal ellipsoid plot (50% probability) of the trichloromethyltin(IV) adduct of 2-(*n*-propylsulfinyl)pyridine,  $\text{MeSnCl}_3 \cdot \text{PySOPr}$  (compound 2).



**Figure 4.** Thermal ellipsoid plot (50% probability) of the dichlorodimethyltin(IV) adduct of 1-methyl-2-(methylsulfinyl)imidazole,  $\text{Me}_2\text{SnCl}_2 \cdot \text{ImSOMe}$  (compound 6).

toward the nitrogen donor of the imidazole or pyridine rings generating a  $\text{Cl}-\text{Sn}-\text{Cl}$  angle of  $167.1(1)^\circ$  in the case of **1** and  $164.7(1)^\circ$  for **2**. There are minor but statistically significant differences in bond distances in the  $\text{Sn}-\text{N}$  bond lengths with the tin to pyridine nitrogen distance being slightly greater than that for the tin to imidazole nitrogen. The tin to sulfinyl oxygen is slightly longer in the imidazole complex ( $2.262(2) \text{ \AA}$  in **1** vs

**Table VIII.** Selected Bond Lengths ( $\text{\AA}$ ) and Bond Angles ( $^\circ$ ) for Hexacoordinate Compounds **1** (Figure 2) and **2** (Figure 3) with Estimated Standard Deviations Given in Parentheses

$\text{MeSnCl}_3 \cdot \text{ImSOMe}$ ( <b>1</b> )		$\text{MeSnCl}_3 \cdot \text{PySOPr}$ ( <b>2</b> )	
Bond Lengths			
$\text{Sn}-\text{C}(6)$	2.122 (4)	$\text{Sn}-\text{C}(1)$	2.110 (7)
$\text{Sn}-\text{O}(1)$	2.262 (2)	$\text{Sn}-\text{O}(1)$	2.191 (4)
$\text{Sn}-\text{Cl}(1)$	2.477 (1)	$\text{Sn}-\text{Cl}(1)$	2.427 (2)
$\text{Sn}-\text{Cl}(2)$	2.454 (1)	$\text{Sn}-\text{Cl}(2)$	2.440 (3)
$\text{Sn}-\text{Cl}(3)$	2.403 (1)	$\text{Sn}-\text{Cl}(3)$	2.460 (2)
$\text{Sn}-\text{N}(1)$	2.194 (3)	$\text{Sn}-\text{N}(1)$	2.309 (4)
$\text{S}-\text{O}(1)$	1.530 (3)	$\text{S}-\text{O}(1)$	1.522 (4)
Bond Angles			
$\text{C}(6)-\text{Sn}-\text{N}(1)$	166.9 (1)	$\text{C}(1)-\text{Sn}-\text{N}(1)$	166.0 (2)
$\text{C}(6)-\text{Sn}-\text{Cl}(1)$	94.5 (1)	$\text{C}(1)-\text{Sn}-\text{Cl}(1)$	102.9 (2)
$\text{C}(6)-\text{Sn}-\text{Cl}(2)$	95.0 (1)	$\text{C}(1)-\text{Sn}-\text{Cl}(2)$	98.4 (3)
$\text{C}(6)-\text{Sn}-\text{Cl}(3)$	104.2 (1)	$\text{C}(1)-\text{Sn}-\text{Cl}(3)$	96.5 (3)
$\text{C}(1)-\text{Sn}-\text{O}(1)$	91.8 (1)	$\text{C}(1)-\text{Sn}-\text{O}(1)$	91.0 (2)
$\text{O}(1)-\text{Sn}-\text{N}(1)$	75.3 (1)	$\text{O}(1)-\text{Sn}-\text{N}(1)$	75.3 (2)
$\text{O}(1)-\text{Sn}-\text{Cl}(1)$	85.7 (1)	$\text{O}(1)-\text{Sn}-\text{Cl}(1)$	166.1 (1)
$\text{O}(1)-\text{Sn}-\text{Cl}(2)$	85.4 (1)	$\text{O}(1)-\text{Sn}-\text{Cl}(2)$	88.3 (1)
$\text{O}(1)-\text{Sn}-\text{Cl}(3)$	164.0 (1)	$\text{O}(1)-\text{Sn}-\text{Cl}(3)$	87.5 (1)
$\text{Cl}(1)-\text{Sn}-\text{Cl}(3)$	93.7 (1)	$\text{Cl}(1)-\text{Sn}-\text{Cl}(3)$	90.5 (1)
$\text{Cl}(1)-\text{Sn}-\text{Cl}(2)$	167.1 (1)	$\text{Cl}(1)-\text{Sn}-\text{Cl}(2)$	90.0 (1)
$\text{Cl}(2)-\text{Sn}-\text{Cl}(3)$	92.3 (1)	$\text{Cl}(2)-\text{Sn}-\text{Cl}(3)$	164.7 (1)

**Table IX.** Selected Bond Lengths ( $\text{\AA}$ ) and Bond Angles ( $^\circ$ ) for the Pentacoordinate Compound **6**,  $\text{Me}_2\text{SnCl}_2 \cdot \text{ImSOMe}$  (Figure 4)

Bond Lengths			
$\text{Sn}-\text{C}(6)$	2.100 (9)	$\text{Sn}-\text{Cl}(2)$	2.550 (2)
$\text{Sn}-\text{C}(7)$	2.105 (7)	$\text{Sn}-\text{N}(1)$	2.411 (6)
$\text{Sn}-\text{Cl}(1)$	2.417 (1)	$\text{S}-\text{O}(1)$	1.504 (4)
Bond Angles			
$\text{C}(6)-\text{Sn}-\text{N}(1)$	86.6 (3)	$\text{C}(7)-\text{Sn}-\text{N}(1)$	93.8 (2)
$\text{C}(6)-\text{Sn}-\text{Cl}(1)$	102.5 (2)	$\text{C}(6)-\text{Sn}-\text{C}(7)$	154.5 (3)
$\text{C}(6)-\text{Sn}-\text{Cl}(2)$	89.2 (2)	$\text{N}(1)-\text{Sn}-\text{Cl}(1)$	86.8 (1)
$\text{C}(7)-\text{Sn}-\text{Cl}(1)$	103.0 (2)	$\text{N}(1)-\text{Sn}-\text{Cl}(2)$	175.7 (2)
$\text{C}(7)-\text{Sn}-\text{Cl}(2)$	89.7 (2)	$\text{Cl}(1)-\text{Sn}-\text{Cl}(2)$	94.9 (1)

$2.191(4) \text{ \AA}$  in **2**), whereas the  $\text{S}=\text{O}$  distances ( $1.530(3) \text{ \AA}$  in **1** vs  $1.522(4) \text{ \AA}$  in **2**) are not significantly different in the two complexes.

In contrast the  $\text{Me}_2\text{SnCl}_2$  adduct of ImSOMe finds the tin in a 5-coordinate geometry, described either as a distorted trigonal bipyramid or a distorted square pyramid. As the former, the axial positions would be occupied by the nitrogen of the imidazole ring and a chloride, at  $\angle \text{N}(1)-\text{Sn}-\text{Cl}(2) = 175.7(2)^\circ$ , while the equatorial plane is distorted significantly from  $120^\circ$  angles, i.e.,  $\angle \text{C}(6)-\text{Sn}-\text{C}(7) = 154.5(3)^\circ$  and  $\angle \text{Cl}(1)-\text{Sn}-\text{C}(7) = 102.5(2)^\circ$ . As a square pyramid, Cl(1) would occupy the axial site while the two methyl groups, Cl(2), and the imidazole nitrogen define the distorted base of a square pyramid. In either view, the sulfinyl oxygen would appear to have no real steric barrier to fulfilling a hexacoordinate structure, and indeed the oxygen is oriented toward the expected potential sixth site. The tin to sulfinyl oxygen distance of  $2.75(1) \text{ \AA}$  is however significantly beyond that of a covalent bond distance (as shown above to be ca.  $2.2 \text{ \AA}$ ) and can be considered no more than a long-range interaction. The  $2.7\text{-}\text{\AA}$  distance is, nevertheless, much shorter than the sum of the van der Waals radii of the two atoms,  $r_{\text{Sn}} = 2.2$ ,  $r_{\text{O}} = 1.5 \text{ \AA}$ .<sup>31</sup> This and the greatly expanded  $\text{Me}-\text{Sn}-\text{Me}$  angle (from  $120$  to  $154^\circ$ ) suggest the type of contact described as charge-transfer interaction or secondary bonding frequently found in solid-state structures such as in  $\text{SnF}_2 \cdot \text{AsF}_5$ .<sup>32</sup> Interestingly the  $\text{Sn}-\text{N}$  distance of  $2.411(6) \text{ \AA}$  is also longer than either of the two derivatives discussed above.

In order to determine whether an intermolecular interaction might account for the loss of the  $\text{Sn}-\text{O}$  bond in compound **6**, a

(31) Huheey, J. E. *Inorganic Chemistry-Principles of Structure and Reactivity*, 3rd ed.; Harper & Row: New York, 1983.

(32) Sawyer, J. F.; Gillespie, R. J. *Prog. Inorg. Chem.* **1986**, *34*, 65.

distance parameter search showed the closest oxygen to adjacent molecule contact to be 3.3 Å, for O-C(2); no other intermolecular contacts were shorter. This, as well as inspection of the packing diagram, suggests that the pentacoordination is not due to intermolecular interactions. Furthermore, the fact that the solution NMR data (*vide supra*) confirms that pentacoordination of complex **6**, as well as the hexacoordination of complexes **1** and **2**, are maintained even in the polar solvent acetone supports the conclusion that the structural differences are not solely due to crystal packaging forces.

Although conclusions are drawn with caution, it would appear most reasonable that the disparate bonding mode of the ImSOMe ligand with  $\text{MeSnCl}_3$  vs  $\text{Me}_2\text{SnCl}_2$  is due to the difference in acidity or  $\delta^+$  of the Sn atom. The former, of higher acidity, forms a hexacoordinated adduct and an N, O-bonded chelate, whereas the latter, of lower acidity and lower  $\text{Sn}^{\delta+}$ , forms a monodentate, N-bound pentacoordinated adduct. Consistent with this conclusion were the several attempts to react the ImSOMe ligand with  $\text{Me}_3\text{SnCl}$ , where, even under different reaction conditions (varying the solvent and using reflux), no product was obtained. One might argue that the direction of steric crowding about Sn also increases as the  $\text{Sn}^{\delta+}$  diminishes in the series, and steric rather than electronic effects govern the coordination

number difference. However, the counter argument is that the sterically similar, if not more demanding,  $\text{Ph}_2\text{SnCl}_2$  adduct of ImSOMe is, according to the  $\nu_{\text{SO}}$  infrared results, demonstrably 6-coordinate. The enhanced electrophilicity of the tin in  $\text{Ph}_2\text{SnCl}_2$  as opposed to  $\text{Me}_2\text{SnCl}_2$  readily accounts for the observation.

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**Supplementary Material Available:** Table SI, listing experimental crystallographic data, Tables IIS, VIS, and XS, listing complete bond lengths and angles, and Tables IIIS, IVS, VIIS, VIIIS, XIS, and XIIS, listing anisotropic displacement parameters, H-atom coordinates, and isotropic displacement parameters (10 pages); Tables VS, IXS, and XIIIS, listing observed and calculated structure factors (22 pages). Ordering information is given on any current masthead page.