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[3-(Sulfinylpropyl)tins and (3-sulfonylpropyl)tins. Studies on intramolecular coordination

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Ph_3PbBr was added. The solution was stirred for 30 min at −78 °C during which time it became red and a white precipitate formed (LiBr). It then was removed from the cold bath and stirred another 3 h at room temperature. After the solution was filtered, the diethyl ether was removed, leaving a red tar. This tar was subjected to filtration chromatography (silicic acid/pentane). Pentane eluted a minor yellow band which was not collected. Pentane/CH_2Cl_2 (9:1, v/v) eluted a red band which gave 0.91 g (71% yield of (μ-Ph_3PbS)(μ-PhC≡CS)$Fe_2(CO)_6$ as a glassy, red solid.

IR ($CHCl_3$): ν(C≡C) 2175; terminal CO, 2079 (s), 2044 (vs), 2007 (vs) cm^{-1}. ^1H NMR (CD_2Cl_2, 90 MHz): δ 7.1–7.8 (complex m, Ph). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 67.9 MHz): δ_C 86.1, 87.0 (alkyne), 122.7 (ipso Ph), 129–132.5 (Ph), 155.5 (J_{C-Pb} = 438 Hz, ipso PbPh), 209.1 (CO). Anal. Calcd for $C_{32}H_{20}Fe_2O_6PbS$: C, 43.50; H, 2.28. Found: C, 43.73; H, 2.44.

Addition of (μ-Ph_3PbS)(μ-PhC≡CS)$Fe_2(CO)_6$ to a THF Solution of Lithium Bromide. A 100-mL, round-bottomed flask was charged with 0.05 g (0.57 mmol) of anhydrous lithium bromide and 10 mL of THF. After this solution was cooled to −78 °C, 0.50 g (0.57 mmol) of (μ-Ph_3PbS)(μ-PhC≡CS)$Fe_2(CO)_6$ in 10 mL of THF was cannulated into it. The mixture became brown. It was stirred at −78 °C for 2 h, then removed from the cold bath, and stirred for another 3 h prior to removal of the solvent. The black tar remaining was extracted with pentane, yielding a red solution which was subjected to filtration chromatography (silicic acid/pentane). Pentane eluted a red band which gave 0.065 g (26% yield) of **8** as a red solid, identified by comparison of its ^1H NMR spectrum with that of an authentic sample.

Addition of (μ-Ph_3SnS)(μ-PhC≡CS)$Fe_2(CO)_6$ to a THF Solution of Lithium Chloride. A 100-mL, round-bottomed flask was charged with 0.02 g (0.46 mmol) of anhydrous lithium chloride and 10 mL of THF. After this solution was cooled to −78 °C, 0.368 g (0.46 mmol) of (μ-Ph_3SnS)(μ-PhC≡CS)$Fe_2(CO)_6$ in 10 mL of THF was cannulated into it. The mixture became brown. It was stirred at −78 °C for 30 min, then removed from the cold bath, and stirred for 4 h at room temperature. Removal of the solvent left a black tar which was extracted with pentane, giving a red solution. This was subjected to filtration chromatography (silicic acid/pentane). Pentane eluted a red band which yielded 0.031 g (0.069 mmol, 15% yield) of **8** as a red solid identified by comparison of its ^1H NMR spectrum with that of an authentic sample.

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Registry No. 2, 14243-23-3; **6** (R = Ph, R′ = Et), 85552-98-3; **6** (R = Ph, R′ = Et) (equatorial/axial isomer), 104011-59-8; **6** (R = Ph, R′ = Et) (equatorial/equatorial isomer), 104011-60-1; **6** (R = Ph, R′ = $PhCH_2$), 103934-15-2; **6** (R = Ph, R′ = $CH_3C(O)CH_2$), 103934-16-3; **6** (R = n-C_4H_9, R′ = Me), 103934-18-5; **6** (R = n-C_5H_{11}, R′ = Me), 103934-19-6; **6** (R = n-C_5H_{11}, R′ = $CH_3C(O)CH_2$), 103934-20-9; **6** (R = n-C_5H_{11}, R′ = $CH_3C(O)CH_2$) (equatorial/axial isomer), 104011-61-2; **6** (R = n-C_5H_{11}, R′ = $CH_3C(O)CH_2$) (equatorial/equatorial isomer), 103934-20-9; **6** (R = CH_2=C(CH_3), R′ = Me), 103934-21-0; **6** (R = Me_3Si, R′ = Me), 103934-22-1; **6** (R = Me_3Si, R′ = Et), 103934-23-2; **6** (R = H, R′ = Me), 103934-24-3; **6** (R = Ph, R′ = Ph_3Sn), 103934-25-4; **6** (R = Ph, R′ = Ph_3Pb), 103958-92-5; **7** (R = Ph, R′ = Me), 85553-00-0; **7** (R = Ph, R′ = Me_3C), 103934-17-4; **8**, 85553-01-1; **9** (R = Me), 85553-20-4; **9** (R = n-C_4H_9), 85553-21-5; **9** (R = n-C_5H_{11}), 85553-22-6; **9** (R = CH_2=C(CH_3), 85553-23-7; **9** (R = H), 12079-70-8; **10** (R = Me_3Si), 85553-04-4; **10** (R = CO_2CH_3), 85553-03-3; **11a**, 85553-18-0; **11b**, 85553-19-1; **11c**, 85553-17-9; **12a**, 85553-02-2; **12b**, 85553-08-8; **12c**, 85553-05-5; **12d**, 85553-09-9; **12e**, 85553-10-2; **12f**, 85553-07-7; **12g**, 85553-12-4; **12h**, 85553-06-6; **12i**, 85553-11-3; **13** (M = Si), 85553-13-5; **13** (M = Sn), 85553-14-6; **16**, 85553-15-7; **17**, 85553-16-8; **24**, 104011-58-7; PhC≡CLi, 4440-01-1; n-C_4H_9C≡CLi, 17689-03-1; n-$C_5H_{11}C$≡CLi, 42017-07-2; CH_2=C(CH_3)C≡CLi, 38341-85-4; $(CH_3)_3SiC$≡CLi, 54655-07-1; HC≡CMgBr, 4301-14-8; MeI, 74-88-4; EtI, 75-03-6; $PhCH_2Cl$, 100-44-7; $CH_3C(O)CH_2Br$, 598-31-2; $CH_3C(O)Cl$, 75-36-5; $Me_3CC(O)Cl$, 3282-30-2; Me_3CCHO, 630-19-3; PhCHO, 100-52-7; CH_3CHO, 75-07-0; Me_3SiCl, 75-77-4; Me_3SnBr, 1066-44-0; Ph_3GeBr, 3005-32-1; Ph_3SnCl, 639-58-7; Ph_3PbBr, 894-06-4; MeHgCl, 115-09-3; PhLi, 591-51-5; S_2, 23550-45-0.

(3-Sulfinylpropyl)tins and (3-Sulfonylpropyl)tins: Studies on Intramolecular Coordination

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A series of sulfoxides of the structures $Me_nX_{3-n}Sn(CH_2)_3SOC_2H_5$ and $Me_nX_{3-n}Sn(CH_2)_3SOC_6H_5$ (X = Cl or Br; n = 1–3) and sulfones $Me_nX_{3-n}Sn(CH_2)_3SO_2C_2H_5$ (X = Cl or Br; n = 1–3) have been prepared and characterized. ^1H, ^{13}C, and ^{119}Sn NMR and IR studies were carried out. These showed that the sulfoxides with n = 1 or 2 are cyclic species with S–O → Sn coordination. The sulfones in chloroform showed evidence of intramolecularly coordinated species in equilibrium with acyclic species. Only the acyclic species were present in acetonitrile which presumably coordinates more strongly to the tin than does the sulfonyl group.

The synthesis of molecules bearing functional groups of opposite polarities so disposed that they can undergo intramolecular interaction with each other is of general interest because such interaction may lead to formation of cyclic compounds. The result may be the formation of a new functional group at one extreme or, at the other, a weak donor–acceptor interaction which is quite labile but will nonetheless modify the chemical and physical properties of each group. Compounds bearing Lewis acidic tin atoms and donor organofunctional groups are well-suited for studies of the nature of such donor–acceptor interactions.[1] Donors which have been studied in varying degrees

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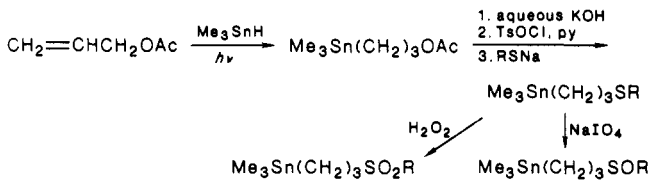
Table I. ^{13}C and ^{119}Sn NMR Parameters[a,b]

no.	compd	solv	a	b	c	d	e	f	^{119}Sn
1	$Me_3SnCH_2CH_2CH_2OCOCH_3$	$CDCl_3$	−10.37 (325.0)	6.25 (354.0)	25.69 (17.0)	67.46 (67.0)	170.76	20.98	2.83
2	$Me_3SnCH_2CH_2CH_2OH$	$CDCl_3$	−10.36 (324.0)	6.10 (359.0)	29.59 (19.0)	65.65 (64.0)			2.32
3	$Me_3SnCH_2CH_2CH_2SCH_2CH_3$	$CDCl_3$	−10.33 (322.0)	10.31 (351.0)	27.02 (19.0)	35.67 (67.0)	25.83	14.87	−0.17
4	$Me_3SnCH_2CH_2CH_2SOCH_2CH_3$	$CDCl_3$	−10.73 (329.0)	9.42 (344.0)	19.68 (19.2)	55.14 (64.0)	45.06	6.28	0.49
		CD_3CN	−9.91 (319.1)	10.74 (350.4)	21.03 (15.7)	56.26 (59.9)	46.70	7.31	0.27
5	$Me_2SnClCH_2CH_2CH_2SOCH_2CH_3$	$CDCl_3$	2.46 (489.0)	22.18 (520.3)	21.65 (29.2)	49.38 (18.0)	45.19	6.76	−21.22
		CD_3CN	1.99 (506.0)	22.49 (551.1)	21.71 (26.5)	48.84 (20.6)	45.09	6.49	−36.37
6	$MeSnCl_2CH_2CH_2CH_2SOCH_2CH_3$	$CDCl_3$	12.59 (668.2)	31.66 (703.0)	21.28 (46.0)	47.1 (27.4)	44.71	7.07	−99.28
		CD_3CN	13.65 (720.7)	32.76 (741.3)	20.48 (44.1)	47.45 (23.5)	44.07	6.31	−130.75
7	$Me_2SnBrCH_2CH_2CH_2SOCH_2CH_3$	$CDCl_3$	3.13 (481.0)	22.12 (510.0)	21.86 (27.0)	49.32 (15.9)	45.31	6.75	−27.31
		CD_3CN	3.16 (498.8)	23.63 (540.0)	21.99 (27.0)	48.64 (13.6)	45.08	6.56	−47.04
8	$MeSnBr_2CH_2CH_2CH_2SOCH_2CH_3$	$CDCl_3$	15.04 (633.0)	33.56 (673.0)	22.31 (46.0)	47.28 (18.0)	44.73	7.23	−136.55
		CD_3CN	17.38 (756.0)	36.8 (736.0)	21.87 (50.2)	46.43 (23.5)	44.22	6.40	−160.17
9	$Me_2SnClCH_2CH_2CH_2SO_2CH_2CH_3$	$CDCl_3$	0.26 (416.0)	19.02 (424.0)	18.72 (21.20)	53.64 (43.03)	47.62	6.58	102.5
		CD_3CN	0.43 (429.0)	19.44 (455.2)	19.44 (21.5)	54.61 (66.5)	47.69	6.76	86.83
10	$MeSnCl_2CH_2CH_2CH_2SO_2CH_2CH_3$	CD_3CN	13.75 (615.8)	31.23 (659.0)	19.05 (38.8)	53.05 (65.0)	47.57	6.50	−17.17
11	$Me_2SnBrCH_2CH_2CH_2SO_2CH_2CH_3$	$CDCl_3$	−0.15 (396.0)	18.55 (409.0)	18.93 (21.5)	53.56 (49.0)	47.48	6.46	90.26
12	$MeSnBr_2CH_2CH_2CH_2SO_2CH_2CH_3$	$CDCl_3$	[c]						−4.75
		CD_3CN	14.92 (560.0)	30.37 (610.0)	19.07 (40.0)	52.29 (75.0)	46.99	5.87	−33.19

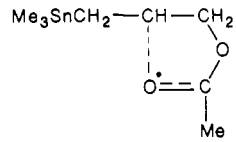
[a] Chemical shifts (δ) vs. internal Me_4Si for ^{13}C and external Me_4Sn for ^{119}Sn. [b] Coupling constants $^nJ(^{13}C-^{119}Sn)$ in hertz given in parentheses after the ^{13}C chemical shift. [c] Not determined.

Scheme I



include the oxygen of a ketone,[2] the carbonyl oxygen of an ester group,[3-6,12] the amide[5] and amino nitrogens,[7,8] the phosphine oxide oxygen,[9] and the sulfoxide oxygen.[10,11] In general, intramolecular coordination occurs when a five- or six-membered ring can be formed. Our own studies have shown that the five-membered ring is more stable than the six-membered ring in the case of organostannyl ketones.[2] On the other hand, sulfoxide was completely coordinated to form the cyclic six-membered ring species in the solid state in compounds bearing two Lewis acidic tins.[11] In this paper we report on the preparation of compounds with a single tin atom separated by three carbons from the sulfoxide or sulfone function, along with the results of ^1H, ^{13}C, and ^{119}Sn NMR and IR studies of these compounds in the noncoordinating solvent chloroform-*d* and the moderately coordinating solvent acetonitrile-d_3.

The procedures used in the synthesis of the 3-stannylpropyl sulfoxides (see Scheme I) followed substantially those used previously for the 3,3-distannylpropyl sulfoxides, in which hydrostannation of propargyl acetate was the initial step.[10,11] In this study allyl acetate was used. Its hydrostannation proceeded with complete regiospecificity to give the adduct in at least 90% yield. We have previously postulated that similar high regiospecificity in the hydrostannation of propargyl acetate is due to stabilization of the radical formed by attack of the trimethylstannyl radical on the terminal unsaturated carbon by a neighboring group interaction of the carbonyl oxygen of the acetoxy group with the radical center. The analogous structure formed from allyl acetate is



Hydrolysis of the acetate by aqueous alcoholic KOH provided 90% of the alcohol. This was treated with *p*-toluenesulfonyl chloride in pyridine yielding 86–90% of the crude tosylate which was treated without further purification with ethanethiol in aqueous NaOH to yield 95% of the ethyl thioether or with thiophenol under similar conditions to provide the phenyl thioether in 95% yield. Oxidation of the sulfides with sodium metaperiodate at 0 °C provided virtually quantitative yields of the ethyl and phenyl sulfoxides. We earlier reported that 3,3-bis(trimethylstannyl)propyl ethyl sulfide could be oxidized to the sulfoxide cleanly with acidic hydrogen peroxide.[10] The 3-(trimethylstannyl)propyl ethyl sulfide provided only the corresponding sulfone in high yield when the same oxidation was conducted with neutral hydrogen peroxide. Yields were high, and the procedure was adopted for this study.

Methyl groups on tin were replaced by chlorines by the simple comproportionation reaction with dimethyltin dichloride to form the chlorodimethyl derivatives. The by-

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product trimethyltin chloride could be easily removed from the desired products by gentle heating at low pressure. For replacement of two chlorines tin tetrachloride was used for the comproportionation under mild conditions. Recrystallization of the products gave pure materials. This general procedure was completely selective for the methyl groups: no evidence of exchange of the propyl chain for chlorine was observed.

The bromostannanes were prepared by straightforward brominolysis of the methyl–tin bonds in methanol–carbon tetrachloride. Yields of over 80% of each mono- and dibromostannane indicated high selectivity for cleavage of methyl–tin over propyl–tin bonds.

Carbon-13 NMR spectral parameters are presented in Tables I and II. The tetraalkyltins **1–4** and **13** show the normal shifts near −10 ppm for methyl carbons and 6–10 ppm for methylene carbons bonded to tin. The values are very nearly the same in chloroform and acetonitrile as seen in the case of **4**. The effects of replacement of methyl by halogen can be considered with reference to simple methyl- and ethyltins. For example, replacement of a methyl group by halogen as in the trimethyltin halides normally causes a downfield shift of the carbons of the remaining methyls by about 10 ppm in a poor donor solvent such as methylene chloride.[13] Replacement of an ethyl group of tetraethyltin by chlorine causes a downfield shift of similar magnitude of the methylene carbons of the ethyl groups.[13] In the monohalotin sulfoxides **5**, **7**, **14**, and **16** both the methyl and methylene carbons are shifted downfield by about 12 ppm in chloroform as compared to the tetraalkyl analogues. The corresponding shifts for the triflate **18** are about 2 ppm smaller. Replacement of a second methyl by halogen as in **6**, **8**, **15**, and **17** causes a further downfield shift of about 10 ppm. In pyridine the ^{13}C chemical shift of trimethyltin chloride is 2.1 ppm,[13] reflecting coordination by the pyridine which would cause an upfield shift, but is more than counterbalanced by the downfield shift due to rehybridization of the tin orbitals bonding to carbon from sp^3 to sp^2 of a trigonal bipyramide. Thus the data are consistent with coordination to tin by the sulfoxide. However, it might be argued that this is not a sufficiently sensitive probe to constitute compelling evidence.

The $^1J(^{13}C–^{119}Sn)$ values can be more sensitive to structure than the chemical shifts and, therefore, more informative. For example, the value changes from 340 Hz in tetramethyltin to 386 Hz in trimethyltin chloride in a nondonor solvent; the value for methylene carbon changes from 320 Hz in tetraethyltin to 352 Hz in triethyltin chloride.[13] In the ethyl sulfoxides examined in this study the value of the methyl ^1J changes from 329 Hz for the tetraalkyl derivative **4** to 489 Hz for **5** and to 481 Hz for **7**; in the phenyl sulfoxides the changes are from 327 Hz in **13** to 440 Hz for **14** and to 447 Hz in **16**. The typical dihalotin shows ^1J values in the range 400–440 Hz. The dihalotins among the ethyl sulfoxides show values of 637 Hz for **6** and 633 Hz for **8**; the phenyl sulfoxides show values of 620 Hz for **15** and 617 Hz for **17**. These coupling constants are uniformly larger by 30–40 Hz for the methylene carbons; the changes from the tetraalkyl methylene carbons are also uniformly larger than for the methyl carbons as shown in Tables I and II. These are the results to be expected from an increase in the coordination number of the tin from four to five due to sulfoxide oxygen–tin coordination.

Are the complexes cyclic monomers or polymers? This question can be answered unambiguously from the ^3J-

Table II. ^{13}C and ^{119}Sn NMR Parameters for Phenyl Analogues[a,b]

	compd	solv	a	b	c	d	ipso	aromatic *o*	aromatic *m*	aromatic *p*	^{119}Sn
13	$^{a}Me_3Sn^{b}CH_2^{c}CH_2^{d}SOPh^{e,f}$	$CDCl_3$	−10.47 (327.1)	9.39 (339.4)	19.63 (14.0)	61.04 (62.0)	144.0	128.9	123.56	130.51	0.57
14	$^{a}Me_2SnCl^{b}CH_2^{c}CH_2^{d}SOPh^{e,f}$	$CDCl_3$	2.14 (440.0)	22.18 (480.0)	21.71 (16.1)	56.38 (24.1)	140.70	129.61	124.04	131.83	0.31
		CD_3CN	2.30 (482.3)	22.77 (519.6)	21.79 (24.7)	56.50 (25.6)	142.11	130.40	125.14	132.58	−5.60
15	$^{a}Me_2SnCl_2^{b}CH_2^{c}CH_2^{d}SOPh^{e,f}$	$CDCl_3$	12.95 (649.5)	31.93 (660.8)	21.38 (45.3)	54.44 (25.2)	139.09	129.77	124.47	132.32	−88.22
16	$^{a}MeSnBr^{b}CH_2^{c}CH_2^{d}SOPh^{e,f}$	$CDCl_3$	2.87 (447.2)	22.89 (495.6)	21.83 (25.2)	56.38 (16.1)	*c*	129.67	123.97	131.94	−12.0
			e								−19.70
17	$^{a}MeSnBr_2^{b}CH_2^{c}CH_2^{d}SOPh^{e,f}$	$CDCl_3$	15.19 (616.5)	33.51 (653.7)	21.97 (45.3)	54.23 (21.1)	139.07	129.79	124.49	132.34	−121.14
		CD_3CN	18.62 (683.1)	38.04 (729.4)	22.50 (46.7)	53.92 (24.7)	140.73	130.57	125.70	133.09	−149.19
18	$^{a}Me_2Sn(OTf)^{b}CH_2^{c}CH_2^{d}SOPh^{e,f}$	$CDCl_3$	0.67 (478)[f]	19.66 (500.4)	21.19 (26.2)	55.37 (<76)[d]	137.71	130.00	124.30	132.91	31.33
		CD_3CN	0.88 (478)[f]	20.07 (518.0)	21.34 (36.6)	54.98 (34.2)	139.1	130.98	125.78	133.68	25.75
19	$TfOSn(^{a}CH_2^{b}CH_2^{c}CH_2^{d}CH_3)_3$	$CDCl_3$	21.24 (375.7)	27.34 (28.2)	26.77 (80.6)	13.45					168.43
		CD_3CN	20.64 (422.8)	28.53 (30.2)	27.49 (75.0)	13.98					70.47
20	$ClSn(^{a}CH_2^{b}CH_2^{c}CH_2^{d}CH_3)_3$	$CDCl_3$	17.46 (336.9)	27.82 (29.2)	26.76 (64.8)	13.51					155.06
		CD_3CN	19.66 (369.7)	29.16 (26.2)	27.94 (66.8)	14.49					121.31

[a,b] Same as in Table I. [c] Not detected. [d] Not observed: broadened signal, number indicates line width of signal in Hz as base line. [e] Not determined. [f] ±10 Hz due to broadened signals.

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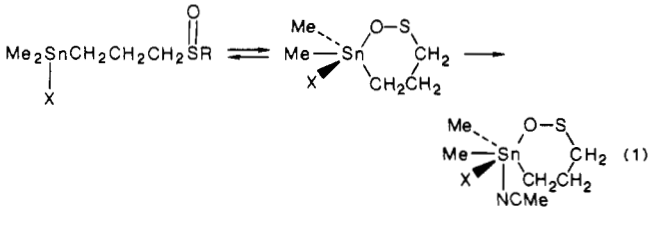
(^{13}C–^{119}Sn) coupling constants. These values have been shown to obey the Karplus equation with a value of around 65 Hz for a 180° dihedral angle, 0–10 Hz for a 90° angle, and 20–30 Hz for a 0° angle.[14] Compounds **1–4** and **13** with values of 62–67-Hz coupling to the low-field carbon of the propyl chain (designated d in the tables) clearly assume conformations with 180° dihedral angles. In the ethyl sulfoxides bearing halotin groups this parameter drops to 16–27 Hz. This indicates dihedral angles less than 180°, but smaller or larger than the 90° minimum, and is entirely consistent with an angle around 60° which would obtain for a six-membered ring structure in a chair conformation. In the present case the chair will be distorted because of differences in bond lengths involving the carbon, sulfur, oxygen, and tin atoms which make up the ring. As expected the phenyl sulfoxides show the same pattern with ^3J values in the range 16–25 Hz.

To test the conclusion that the halotin sulfoxides are monomolecular in solution molecular weights were determined. The isopiestic method, in chloroform at ambient temperature, was used. All of the compounds examined gave values agreeing within six percent of the theoretical, and these were scattered above and below the value for the monomolecular species. This comprises a compelling validation of the use of NMR parameters as described above in establishing structures of organotins.

The triflate **18** which should bear a more electron-deficient carbon than the chloride, for example, does indeed show slightly lower field signals, and the ^1J values are 479 and 500 Hz as comapred to 440 and 480 Hz for **14**. (The ^3J value could not be observed due to broadening of the ^{13}C signal caused by the presence of the (trifluoromethyl)sulfonyl group.)

The ^{13}C spectra of several of the compounds were also taken in acetonitrile because it is a moderately effective donor solvent. Differences in the spectral parameters for the two solvents were slight for the tetraalkyltin **4**. All of the halotins and **18** showed signals at slightly lower fields (0.2–1 ppm) in acetonitrile, and the dihalides show larger shifts up to 3 ppm for both methyl and methylene carbons. The effect of acetonitrile is more evident in the values of ^1J involving both the methyl and methylene carbons. In acetonitrile ^1J values are 17–42 Hz larger for the monohalides and 30–123 Hz larger for the dihalides than in chloroform. The values for the methyl carbon of **18** is uncertain due to substantial line broadening of the signal but the methylene signals are normal. These effects are consistent with further coordination on the tin by acetonitrile showing that, despite the coordination by the strong donor sulfoxide, sufficient residual Lewis acidity remains for coordination with an additional donor molecule to make the tin hexacoordinate. These observations indicate that the equilibrium of eq 1, shown for a monohalotin, may obtain for the halotins with the species in the middle predominating in a noncoordinating solvent like chloroform and that on the right in a donor solvent such as acetonitrile.



(1)

(14) (a) Doddrell, D.; Burfitt, I.; Kitching, W.; Bullpit, Mynott, R. J.; Considine, J. L.; Kuivila, H. G.; Sarma, R. H. *J. Am. Chem. Soc.* **1963**, *85*, 1640. (b) Kitching, W. *Org. Magn. Reson.* **1982**, *20*, 123.

Table III. S–O Stretching Frequencies (cm^{-1}) of Sulfoxides

	in Kbr	5–10% in CH_3CN
4	1046 (neat)	
5	971, 960	962
7	984, 957	964
6	957, 940	962
8	957, 940	961
13	1045 (neat)	
14	985	953
16	970	950
15	970	951
17	980	950
18	965, 948	969, 952

It is unlikely that acetonitrile replaces the sulfoxide as a ligand: the sulfoxide is much stronger and carries an entropic advantage.

Corroboration for this analysis comes from the ^{119}Sn NMR data. The tetraalkyltins show chemical shifts ranging from –0.17 to 2.83 ppm relative to tetramethyltin, along with a minimal solvent effect as seen for **4**. In the ethyl sulfoxide series **5–8** upfield shifts to –2 and –27 ppm occur for the monochlorotins and the monobromotins, respectively. The shifts are –99 and –136 ppm for the corresponding dihalides in chloroform. These are taken to be due to increases in the electron density at tin due to coordination by the sulfoxide oxygen. In inert solvents ^{119}Sn chemical shifts are 160 ppm for trimethyltin chloride and 128 ppm for trimthyltin bromide.[15] Further upfield shifts of 15–31 ppm occur when acetonitrile is the solvent for **5–8** as expected if this solvent also coordinates to tin. In the phenyl sulfoxides **14–17** the shifts are at lower fields: 0.31 to –121 ppm in chloroform. Apparently the phenylsulfinyl group is a less effective donor to tin than is the ethylsulfinyl group. However, the general pattern of substituent effects is the same for both series.

For the phenylsulfinyl triflate **18** the shifts are lower than for the halides: 31 ppm in chloroform and 26 ppm in acetonitrile. However, the behavior is consistent with the others because the chemical shifts are higher than those for tri-*n*-butyltin triflate which are 168.4 ppm in chloroform and 70.5 ppm in acetonitrile.

The IR spectra of the sulfoxides were taken in the solid state (KBr) and in acetonitrile. Results are gathered in Table III. In the tetraalkyltins the S–O stretching frequency appeared at the normal value of 1045 cm^{-1}. All of the halotins showed red shifts of up to 100 cm^{-1}. The shifted band in KBr appeared as a doublet in compounds **5–8**; the triflate **18** showed splitting both in KBr and in acetonitrile. None of the halotins showed any indication of the band at 1045 cm^{-1}, establishing completely coordinated structures in both media.

Sulfones are generally ineffective as donors in intermolecular acid–base interactions. It was of interest to determine whether the decrease in entropy which results when the sulfone group and the tin acceptor center are in the same molecule, separated by an appropriate distance, might facilitate interaction. (Trimethylstannyl)propyl ethyl sulfone and its halotin analogues **9–12** were prepared and examined by NMR and IR spectroscopies.

Carbon-13 NMR parameters for **9–12** are presented in Table II. We can compare the parameters for the methyl carbons of sulfoxide **5** and sulfone **9** in chloroform with those for trimethyltin chloride (**21**) in methylene chloride.[13] The chemical shifts are 2.46, 0.46, and 0.0 ppm, respectively; the ^1J values are 489, 416, and 386 Hz, respectively.

(15) Harris, R. K.; Mann, B. E. *NMR and the Periodic Table*; Academic Press: New York, 1978; p 352.

Table IV. S-O Stretching Frequencies (cm^{-1}) of Sulfones

	in KBr		10% in CH_3CN	
	ν_{as}	ν_s	ν_{as}	ν_s
19[a]	1320	1130 (neat)	1275	1130
9	1312	1115	1275	1130
10	1313	1115	1270	1131
11	1317	1120	1280	1131
12	1310	1114	1272	1129

[a] $Me_3Sn(CH_2)_3SO_2Et$.

For the methylene carbons using triethyltin chloride as a reference the δ values are 22.18, 19.02, and 9.3 ppm; the ^1J values are 520, 424, and 352 Hz. The value for **9** is intermediate for each parameter, suggesting the possibility of weak coordination. Values of ^3J are 18 Hz for **5** and 43.0 Hz for **9**. This latter value increases to 67 Hz in acetonitrile. Similarly ^3J for **11** in chloroform is 49 Hz, but ^3J in acetonitrile for **10** is 65 Hz, and for **12** it is 75 Hz. The ^{119}Sn chemical shifts are 160 ppm for **21**,[15] −21 ppm for **5**, and 102 ppm for **9** in chloroform. Upfield shifts occur in acetonitrile for **9** and **12** and for **5–8**.

These observations imply that weak coordination occurs in chloroform between the halotin and sulfonyl groups, suggesting an equilibrium between coordinated and uncoordinated species. Weighted means of δ and J values for cyclic and acyclic isomers are observed. When acetonitrile is the solvent, it takes over the role of donor exclusively. This accounts for the upfield ^{119}Sn chemical shifts, and the increase in ^3J values which would result from conversion of the cyclic complexes completely to acyclic structures with acetonitrile coordinating to the tins.

IR data for the sulfones are listed in Table IV. Simple sulfones show stretching frequencies around 1320 (ν_{as}) and 1130 cm^{-1} (ν_s). When one or two methyl groups on tin are replaced by halogen, the 1320 cm^{-1} band undergoes a red shift of 3–10 cm^{-1} and the 1130 cm^{-1} band a shift of 10–15 cm^{-1}. The bands are sufficiently broad that the unshifted band, if present, could be masked. These shifts may be due to the change in medium from the neat liquid of the trimethyltin analogue to the solid of the halo derivatives or to weak coordination to the tin. The 1120 cm^{-1} band shows no detectable shift in acetonitrile, but the 1320 cm^{-1} band is shifted to the red by some 40 cm^{-1}. The unshifted band is not observed. These shifts are clearly due to solvent because the magnitude is the same for the trimethyl analogue as for the halo analogues. Thus the IR data provide no clear evidence concerning the inference that the sulfone group functions as donor to a halotin group to a significant degree. NMR parameters can be more sensitive probes and do provide evidence which suggests that such interaction occurs even though it is weak.

Experimental Section

General Data. Proton nuclear resonance spectra were obtained at 60 MHz by using a Varian EM-360A spectrometer. Chemical shifts are reported in parts per million downfield from internal tetramethylsilane followed in parentheses by the multiplicity, number of protons, coupling constant, and assignment. Proton–tin-119 coupling constants are reported as $^nJ(^{119}Sn–H)$ with the first superscript denoting the number of bonds intervening between nuclei. ^{13}C and ^{119}Sn NMR spectra (at 75.4290 and 111.8620 MHz, respectively) were recorded on a Varian XL300 instrument with a 5-mm tunable probe. Shimming was performed on protons. Typical operating parameters for tetralkyltins were as follows: probe temperature, 23 °C; 32K data points; sweep width, 16 500 Hz; pulse width, 13 μs; acquisition time, 0.97 s; and accumulation of 100–400 transients. The fast relaxation times of the methyl carbons on tin and the tin nuclei in the monchlorotins and dichlorotins allowed the use of acquisition times of 0.3–0.5 s. As a result it was possible to obtain decoupled spectra of moderately concentrated samples involving 10 000 to 20 000 transients in a matter of hours. Chemical shifts (δ) are reported in parts per million downfield from tetramethyltin for ^{119}Sn or tetramethylsilane for ^1H and ^{13}C followed, for example, by $^XJ(^{119}Sn–^{13}C)$ where X denotes the number of bonds intervening between nuclei, and the coupling constants J are reported in hertz. Infrared spectra were obtained on a Beckman IR-10 and Perkin-Elmer 283B infrared spectrometers. Gas chromatographic analyses were performed on a Hewlett Packard Model F & M instrument using a 17 ft × 0.25 in. copper column packed with 15% SE-30 on Chromosorb W, 60–80 mesh, unless otherwise noted. Melting points and boiling points are uncorrected. Carbon–hydrogen analyses were done by Galbraith of Knoxville, TN. Molecular weights were determined by the isopiestic method in chloroform at ambient temperature.[16]

3-(Trimethylstannyl)propyl acetate (1) was prepared by the photoinitiated hydrostannation of allyl alcohol with trimethylstannane. **3-(Trimethylstannyl)propanol (2)** was prepared from the acetate by hydrolysis using ethanol/saturated aqueous KOH (10/1, v/v). **3-(Trimethylstannyl)propyl tosylate** was prepared from the alcohol by reaction with *p*-toluenesulfonyl chloride in pyridine.

3-(Trimethylstannyl)propyl Ethyl Sulfide (3). Into a 500-mL flask equipped with a magnetic stirrer was placed 15.4 g (247.8 mmol) of ethanethiol in 130 mL of ethanol and 10.6 g (265.0 mmol) of NaOH in 65 mL of water, and the mixture was stirred for 15 min. 3-(Trimethylstannyl)propyl tosylate (93.0 g, 246.7 mmol) in 200 mL of ethanol was added. The mixture was refluxed overnight and worked up by addition of 300 mL of hexane and extraction with water (3 × 500 mL). The organic layer was dried and concentrated and the product distilled at 60 °C (0.01 torr) to yield 63.0 g (95%) of 3-(trimethylstannyl)propyl ethyl sulfide: ^1H NMR (neat) δ 0.07 (s, 9 H, $^2J(^{119}Sn–C–H)$ = 50.0 Hz, $SnMe_3$), 1.32 (t, 2 H, CCH_2SnMe_3). Anal. Calcd for $C_8H_{20}SSn$: C, 35.99; H, 7.55. Found: C, 36.13; H, 7.50.

3-(Trimethylstannyl)propyl Phenyl Sulfide. The procedure was the same as that described above for the ethyl analogue: yield, 91%; bp 75 °C (0.05 torr); ^1H NMR (CCl_4) δ 0.05 (s, 9 H, $^2J(^{119}Sn–C–H)$ = 50.0 Hz, $SnMe_3$), 0.73–1.00 (m, 2 H, $SnCH_2$), 1.47–2.06 (m, 2 H, $SnCH_2CH_2$), 2.73 (t, 2 H, $^4J(Sn–CH_2–CH_2–CH_2)$ = 7 Hz), 6.80–7.20 (m, 5 H, C_6H_5). Anal. Calcd for $C_{12}H_{20}SSn$: C, 45.75; H, 6.40. Found, C, 45.55, H, 6.10.

3-(Trimethylstannyl)propyl Ether Sulfoxide (4). A 200-mL flask was charged with 1.5 g (5.6 mmol) of 3-(trimethylstannyl)propyl ethyl sulfide and 50 mL of methanol and cooled to 0 °C. Sodium metaperiodate (1.3 g, 6.1 mmol) dissolved in 50 mL of water was added dropwise to the reaction flask over a period of 20 min, and the mixture was stirred at 0 °C for 5 h. The ice bath was removed from the reaction flask, and the mixture was stirred at room temperature until the ^1H NMR spectrum indicated that the reaction was complete (18 h). Filtration of the mixture followed by removal of solvent at reduced pressure and distillation yielded 1.61 g (99%) of product: bp 60 °C (0.01 torr); ^1H NMR ($CDCl_3$) δ 0.1 (s, 9 H, $^2J(^{119}Sn–C–H)$ = 51.3 Hz, $SnMe_3$), 1.28 (t, 2 H, CCH_2SnMe_3); IR (neat, KBr) $\nu_{S=O}$ 1046 cm^{-1}. Anal. Calcd for $C_8H_{20}OSSn$: C, 33.95; H, 7.12. Found: C, 33.77; H, 7.09.

3-(Trimethylstannyl)propyl Ethyl Sulfone. A 500-mL flask was charged with 17.0 g (63.7 mmol) of 3-(trimethylstannyl)propyl ethyl sulfide and 330 mL of ethanol and cooled to 0 °C. Hydrogen peroxide (38.5 mL, 30%) was added dropwise to the reaction flask over a period of 20 min, and the mixture was stirrd at 0 °C for 5 h. The solvent was removed on the rotary evaporator. The product was distilled: bp 60 °C (0.01 torr); 17.9 g (94%); ^1H NMR ($CDCl_3$) δ 0.11 (s, 9 H, $^2J(^{119}Sn–C–H)$ = 51.8 Hz, $SnMe_3$), 1.34 (t, 2 H, CCH_2SnMe_3); IR (neat, KBr) ν_{SO_2} 1320, 1130 cm^{-1}; IR (10% in CH_3CN); ν_{SO_2} 1275, 1130 cm^{-1}.

3-(Chlorodimethylstannyl)propyl Ethyl Sulfone (9). Into a 50-mL flask, equipped with a magnetic stirrer, were placed 2.0 g (7.1 mmol) of 3-(trimethylstannyl)propyl ethyl sulfone and 1.6 g (7.1 mmol) of dichlorodimethylstannane in 1 mL of methylene

(16) Pasto, D. J.; Johnson, C. R. *Organic Structure Determination*; Prentice-Hall: Englewood Cliffs, NJ, 1969; p 77.

chloride, and the mixture was refluxed for 12 h. The disappearance of the starting materials was monitored by ^1H NMR analysis. After the reaction was complete, the solvent was removed on the rotary evaporator. The byproduct chlorotrimethylstannane was removed at 0.01 torr and 100 °C, leaving crude product in quantitative yield. Crystallization from methylene chloride and hexane yielded colorless crystals: 2.0 g (89%); mp 86–88 °C; ^1H NMR ($CDCl_3$) δ 0.68 (s, 6 H, $^2J(^{119}Sn-C-H)$ = 59.5 Hz, $SnMe_2Cl$), 1.33 (t, 2 H, CCH_2SnMe_2Cl); IR (KBr) ν_{SO_2} 1315, 1115 cm^{-1}; IR (10% in CH_3CN) ν_{SO_2} 1275, 1130 cm^{-1}. Anal. Calcd for $C_7H_{17}ClO_2SSn$: C, 26.32; H, 5.36; M_r, 363.9. Found: C, 26.14; H, 5.50; M_r, 343.

3-(Chlorodimethylstannyl)propyl Ethyl Sulfoxide (5). The procedure was the same as that described for the sulfone except that refluxing was continued for 48 h. The crude product was recrystallized from hexane yielding colorless crystals: 1.9 g (90%); mp 65–67 °C; ^1H NMR ($CDCl_3$) δ 0.67 (s, 6 H, $^2J(^{119}Sn-C-H)$ = 67.0 Hz, $SnMe_2Cl$), 1.27 (t, 2 H, CCH_2SnMe_2Cl); IR (KBr) ν_{SO_2} 971, 860 cm^{-1}; IR (10% in CH_3CN) ν_{SO_2} 962 cm^{-1}. Anal. Calcd for $C_7H_{17}ClO_2SSn$: C, 27.71; H, 5.65; M_r, 303.2. Found: C, 27.93; H, 5.85; M_r, 320.

3-(Dichloromethylstannyl)propyl Ethyl Sulfone (10). Into a 50-mL flask, equipped with a magnetic stirrer, was added 2.0 g (7.1 mmol) of 3-(trimethylstannyl)propyl ethyl sulfone dissolved in 5 mL of methylene chloride and cooled to 0 °C. To this solution was added 1.9 g (7.1 mmol) of tetrachlorostannane in 10 mL of methylene chloride dropwise while being stirred at 0 °C. After the addition was complete, the reaction mixture was refluxed for 9 days until the starting materials had completely disappeared (^1H NMR analysis). The reaction mixture was subjected to crystallization with methylene chloride and hexane, yielding colorless crystals of 3-(dichloromethylstannyl)propyl ethyl sulfone: 2.0 g (83%); mp 171–173 °C; ^1H NMR (CD_3COCD_3) δ 1.20 (s, 3 H, $^2J(^{119}Sn-C-H)$ = 85.0 Hz, $SnMeCl_2$), 1.30 (t, 2 H, $CCH_2SnMeCl_2$); IR (KBr) ν_{SO_2} 1313, 1115 cm^{-1}; IR (10% in CH_3CN) ν_{SO_2} 1275, 1130 cm^{-1}. Anal. Calcd for $C_6H_{14}Cl_2O_2SSn$: C, 21.21; H, 4.15. Found: C, 21.44; H, 4.23.

3-(Dichloromethylstannyl)propyl Ethyl Sulfoxide (6). The procedure was the same as that for the sulfone except that refluxing was continued for 3 days. Recrystallization of the crude product from methylene chloride/hexane afforded 2.2 g (95%) of product: mp 89–91 °C: ^1H NMR (CD_3COCD_3) δ 1.02 (s, 3 H, $^2J(^{119}Sn-C-H)$ = 91.0 Hz, $SnMeCl_2$), 1.29 (t, 2 H, $CCH_2SnMeCl_2$); IR (KBr) $\nu_{S=O}$ 957, 940 cm^{-1}; IR (10% in CH_3CN) $\nu_{S=O}$ 962 cm^{-1}. Anal. Calcd for $C_6H_{14}Cl_2OSSn$: C, 22.25; H, 4.36; M_r, 323.8. Found: C, 22.09; H, 4.35; M_r, 306.

3-(Bromodimethylstannyl)propyl Ethyl Sulfone (11). Into a 50-mL flask equipped with a magnetic stirrer and cooled in an ice bath were placed 2.0 g (7.1 mmol) of 3-(trimethylstannyl)propyl ethyl sulfone and 10 mL of dry methanol under nitrogen. To this was added dropwise 7.1 mmol of bromine in 7.0 mL of carbon tetrachloride. The flask was warmed to room temperature, the solvent removed on the rotary evaporator, and the product crystallized from methylene chloride/hexane to yield 2.1 g (82%): mp 105–106 °C; ^1H NMR ($CDCl_3$): δ 0.78 (s, 6 H, $^2J(^{119}Sn-C-H)$ = 60.0 Hz, $SnMe_2Br$), 1.33 (t, 2 H, CCH_2SnMe_2Br); IR (KBr) ν_{SO_2} 1317, 1120 cm^{-1}; IR (10% in CH_3CN) ν_{SO_2} 1270, 1131 cm^{-1}. Anal. Calcd for $C_7H_{17}BrO_2SSn$: C, 23.11; H, 4.71; M_r 363.9. Found: C, 22.95; H, 4.72; M_r, 343.

3-(Bromodimethylstannyl)propyl Ethyl Sulfoxide (7). The same procedure as that described above was used, yielding 2.1 g (82%) of product: mp 105–106 °C; ^1H NMR ($CDCl_3$) δ 0.78 (s, 6 H, $^2J(^{119}Sn-C-H)$ = 67.0 Hz, $SnMe_2Br$), 1.29 (t, 2 H, CCH_2SnMe_2Br); IR (KBr) $\nu_{S=O}$ 984, 957 cm^{-1}; IR (10% in CH_3CN) $\nu_{S=O}$ 964 cm^{-1}. Anal. Calcd for $C_7H_{17}BrOSSn$: C, 24.17; H, 4.93; M_r, 347.9. Found: C, 24.14; H, 4.76; M_r, 333.

3-(Dibromomethylstannyl)propyl Ethyl Sulfone (12). Into a 50-mL flask equipped with a magnetic stirrer were placed 2.0 g (7.1 mmol) of 3-(trimethylstannyl)propyl ethyl sulfone and 10 mL of dry methanol, and the flask was cooled to 0 °C under nitrogen. To this was added dropwise 14.2 mmol of bromine in 14.0 mL of carbon tetrachloride. After the addition of bromine was complete, the reaction mixture was stirred for 2 h. The reaction mixture was examined by ^1H NMR to follow the disappearance of the starting material. It was treated with Norite to decolorize the solution and filtered. The solvent was removed on the rotary evaporator to give a quantitative yield of crude product which was crystallized from methylene chloride/hexane to yield 2.4 g (79%) of product: mp 158–160 °C; ^1H NMR ($C-D_3COCD_3$) δ 1.41 (s, 3 H, $^2J(^{119}Sn-C-H)$ = 81.0 Hz, $SnMeBr_2$), 1.28; IR (KBr) ν_{SO_2} 1317, 1120 cm^{-1}; IR (10% in CH_3CN) ν_{SO_2} 1280, 1131 cm^{-1}. Anal. Calcd for $C_6H_{14}BrO_2SSn$: C, 16.81; H, 3.29; M_r, 412.8. Found: C, 16.62; H, 3.45; M_r, 395.

3-(Dibromomethylstannyl)propyl Ethyl Sulfoxide (8). Using the above procedure with 6 h of reflux provided 2.5 g (85%) of product: mp 108–109 °C; ^1H NMR (CD_3COCD_3) δ 1.23 (s, 3 H, $^2J(^{119}Sn-C-H)$ = 90.0 Hz, $SnMeCl_2$), 1.29 (t, 2 H, $CCH_2SnMeCl_2$); IR (KBr) $\nu_{S=O}$ 957, 940 cm^{-1}; IR (10% in CH_3CN) $\nu_{S=O}$ 961 cm^{-1}. Anal. Calcd for $C_6H_{14}Br_2OSSn$: C, 17.46; H, 3.42; M_r, 412.8. Found: C, 17.47; H, 3.41; M_r, 395.

Preparation of 3-(Trimethylstannyl)propyl Phenyl Sulfoxide (13). A solution of 11.6 g (36.8 mmol) of 3-(trimethylstannyl)propyl phenyl sulfide in 25 mL of dichloromethane was cooled to 0 °C (ice bath). To this solution was added dropwise, over 30 min, a solution of 8.85 g (38.66 mmol) of *m*-chloroperbenzoic acid in 250 mL of dichloromethane. After the addition was complete, the reaction mixture was warmed to room temperature and stirred for 15 min. The reaction mixture was then suction filtered, and the filtrate was washed with (3 × 100 mL) of saturated aqueous solution of sodium bicarbonate, 2 × 130 mL of water, dried ($MgSO_4$) and filtered. The filtrate was concentrated to give an orange oil which was purified by silica gel column chromatography (80/20 hexanes/acetone) to afford 11.5 g (94%) of **13** as a clear colorless oil: IR (neat film) $\nu_{S=O}$ 1045 cm^{-1}; ^1H NMR (CCl_4) δ 0.11 (s, 9 H, $^2J(^{119}Sn-C-H)$ = 51.5 Hz, SnMe), 0.63–0.98 (m, 2 H, $SnCH_2$), 1.47–2.07 (m, 2 H, $SnCH_2CH_2$), 2.46–2.72 (m, 2 H, $SnCH_2CH_2CH_2$), 7.03, (m, 5 H, C_6H_5). Anal. Calcd for $C_{12}H_{20}OSSn$: C, 43.35; H, 6.09. Found: C, 43.70; H, 6.34.

3-(Chlorodimethylstannyl)propyl Phenyl Sulfoxide (14). The reaction of 3-(trimethylstannyl)propyl phenyl sulfoxide with dichlorodimethylstannane was conducted in the same way as that for the ethyl analogue. Reaction was complete in 20 h providing 53% of product after recrystallization from hexane: mp 108–110 °C; IR (KBr) $\nu_{S=O}$ 985 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.75 (s, 6 H, $^2J(^{119}Sn-C-H)$ = 66.0 Hz, $SnMe_3$), 1.40–1.70, (m, 2 H, $SnCH_2$), 1.97–2.59, m, $SnCH_2CH_2$), 2.63–3.07 (m, 2 H, $SnCH_2CH_2CH_2$), 7.37 (s, 5 H, C_6H_5). Anal. Calcd for $C_{11}H_{17}ClOSSn$: C, 37.59; H, 4.87; M_r, 351.5. Found: C, 37.21; H, 4.56; M_r, 358.

3-(Dichloromethylstannyl)propyl Phenyl Sulfoxide (15). This procedure was the same as that for the ethyl analogue, but the reaction required only 20 h at reflux. Recrystallization from dichloromethane/hexane yielded 87% of product: mp 118–120 °C; IR (KBr) $\nu_{S=O}$ 970 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.28 (s, 3 H, $^2J(^{119}Sn-C-H)$ = 86.0 Hz, $SnMe_3$), 1.82–2.15, (m, 2 H, $SnCH_2$), 2.28–2.72, (m, $SnCH_2CH_2$), 2.82–3.15 (m, 2 H, $SnCH_2CH_2CH_2$), 7.48 (s, 5 H, C_6H_5). Anal. Calcd for $C_{10}H_{14}Cl_2SOSn$: C, 32.30; H, 3.79; M_r, 371.9. Found: C, 31.98; H, 3.59; M_r, 350.

Preparation of 3-(Bromodimethylstannyl)propyl phenyl sulfoxide (16): A solution of 2.634 g (7.96 mmol) of 3-(trimethylstannyl)propyl phenyl sulfoxide in 10 mL of anhydrous methanol was cooled to 0 °C and treated with a solution of 1.272 g (7.96 mmol) of bromine in 25 mL of carbon tetrachloride over a period of 50 min. After the addition, the solution was warmed to room temperature and a clear colorless solution was obtained. The solvents were rotary evaporated, and the residual viscous oil was dissolved in dichloromethane and treated with decolorizing carbon. The solution was gravity filtered, and the filtrate was concentrated to give a white solid. This was dissolved in a 1:1 mixture of dichloromethane and hexanes and let stand at room temperature overnight to afford 2.6 g (84%) of **16** as colorless crystals: mp 129.5–30.5 °C; IR (KBr) $\nu_{S=O}$ 970 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.87 (s, 6 H, $^2J(^{119}Sn-C-H)$ = 65.0 Hz, $SnMe_2$), 1.43–1.73, (m, 2 H, $SnCH_2$), 2.00–2.53 (m, 2 H, $SnCH_2CH_2$), 2.60–3.00 (m, 2 H, $SnCH_2CH_2$), 7.30 (s, 5 H, C_6H_5). Anal. Calcd for $C_{11}H_{17}BrOSSn$: C, 33.37; H, 4.33; M_r, 396.0. Found: C, 33.47; H, 4.35; M_r, 374.

3-(Dibromomethylstannyl)propyl Phenyl Sulfoxide (17). Using the procedure described for the ethyl analogue 3-(trimethylstannyl)propyl phenyl sulfoxide yielded 42% of the sulfoxide after crystallization from dichloromethane/hexane: mp 110–112 °C; IR (KBr) $\nu_{S=O}$ 980 cm^{-1}; ^1H NMR δ 1.50 (s, 3 H,

$^2J(^{119}Sn-C-H)$ = 80.0 Hz, SnMe), 1.97-2.70 (m, 4 H, $SnCH_2CH_2$), 2.73-3.20 (m, 2 H, Sn $CH_2CH_2CH_2$), 7.33 (s, 5 H, C_6H_5). Anal. Calcd for $C_{10}H_{14}Br_2OSSn$: C, 26.07; H, 3.06; M_r, 460.5. Found: C, 26.02; H, 3.18; M_r, 466.

3-(Dimethyl((trifluoromethyl)sulfonyl)stannyl)propyl Phenyl Sulfoxide (18). Into a three-necked 50-mL flask fitted with a dry ice-acetone cold finger was placed 1.133 g (2.862 mmol) of 3-(bromodimethylstannyl)propyl phenyl sulfoxide. The reaction flask was cooled to -78 °C, and about 35 mL of sulfur dioxide was condensed. To the clear solution was added 0.7335 g (2.862 mmol) of silver trifluoromethanesulfonate, the cooling bath was removed, and the mixture was stirred at the SO_2 reflux temperature for 1 h. The solution was then suction filtered under nitrogen, and the clear colorless filtrate was transferred to a 50-mL flask. The sulfur dioxide gas was allowed to evaporate, and the residual volatiles were removed by stirring at 58 °C (oil bath) under 0.05 torr for 3.5 h to give 1.01 g (75%) of **18** as a clear colorless gum: ^{1}H-NMR ($CDCl_3$) δ 0.76 (s, 6, $^2J(^{119}Sn-C-H)$ = 68.0 Hz, $Sn(CH_3)_3$), 1.63 (m, 2, $Sn(CH_3)_3CH_2$), 2.37 (m, 2, $Sn(CH_3)_3CH_2CH_2$), 3.04 (ddd, J_{gem} = 14.3 Hz, J_{AX} = 9.7 Hz, J_{AY} = 1.9 Hz, *H*CHSOPh), 3.36 (ddd, J_{gem} = 14.1 Hz, J_{AX} = 2.2 Hz, HC*H*SOPh), 7.67 (br s, 5, SO*Ph*); IR (KBr plate) 965 cm^{-1} (strong, S=O). Anal. Calcd for $C_{12}F_3H_{17}O_4S_2Sn$: C, 30.99; H, 3.69. Found: C, 30.91; H, 3.49.

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Communications

Reaction of (Pentamethylcyclopentadienyl)(*tert*-butylimino)-phosphane with Tris(acetonitrile)tricarbonylmolybdenum(0): Evidence for a Metalloiminophosphane Intermediate

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Summary: (η^1-Me_5C_5)P=N(*t*-Bu) (**1**) was prepared in a two-step synthesis from $Me_5C_5PCl_2$. Reaction of **1** with $(MeCN)_3Mo(CO)_3$ affords the spirocyclic compound (η^1-$Me_5C_5PN(t\text{-Bu})PN(t\text{-Bu})C(O)Mo(CO)_2(\eta^5\text{-}C_5Me_5)$ (**5**), whose structure was determined by X-ray crystallography. A metalloiminophosphane, (η^5-Me_5C_5)$(CO)_3$MoP=N(*t*-Bu) (**7**), is proposed to be the key intermediate in the formation of **5**.

The use of phosphorus(III) pπ systems as ligands in transition-metal complexes is well-established, and a vast number of such species is known.[1] Only recently this chemistry has been further expanded by incorporating organometallic substituents. New types of compounds include C- and P-metalated phosphaalkenes[2] and metallodiphosphenes,[3] as well as terminal and bridging phosphavinylidene complexes.[4] Here, we report on attempts to synthesize a metalloiminophosphane via the shift of a Me_5C_5 ligand from phosphorus to the transition metal, which has proven to be a convenient route to P-metalated phosphaalkenes.[5]

Me_5C_5P=N(*t*-Bu) (**1**) was prepared in a two-step synthesis starting from $Me_5C_5PCl_2$ (**2**):[6] addition of 0.1 mol of *t*-$BuNH_2$ to a CH_2Cl_2 solution (200 mL) of **2** (0.1 mol) and Et_3N (0.1 mol) during 1 h at room temperature, filtration, and distillation gave the aminochlorophosphane **3**.[7] Metalation of **3** (50 mmol) in THF at -70 °C (10 min), followed by elimination of LiCl on warming to -30 °C (1 h), produced **1**. The product was purified by evacuation of the solvent, extraction of the residue with hexane, filtration, and distillation. **1** was obtained as a yellow, thermally stable liquid that could be identified on the basis of analytical and spectroscopic data.[8] Reaction of **1** with $(MeCN)_3Mo(CO)_3$ (**4**)[9] was found to proceed in a 2:1 molar

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(7) **3**: bp 80-90 °C (0.1 torr); yield 75-80%; $^{31}P\{^1H\}$ NMR ($CDCl_3$, 28 °C) δ 142.9 (s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 28 °C) δ 10.9 (br) and 14.8 (br) H_3CC (ring), 31.4 (d, 9.3 Hz, $NCCH_3$), 51.5 (d, 12.1 Hz, NC), 62.0 (br, (PC ring), 136.7 (br, C ring); ^{1}H NMR ($CDCl_3$, 28 °C) δ 2.87 (br d, 15.4 Hz, 1 H, NH), 1.9-1.7 (br m, 15 H, CCH_3 ring), 1.09 (d, 1.1 Hz, 9 H, $NCCH_3$). Anal. Calcd for $C_{14}H_{25}ClNP$: C, 61.42; H, 9.20; N, 5.11. Found: C, 61.24; H, 9.31, N, 5.15.

(8) **1**: bp 50-54 °C (0.1 torr); yield 72-75%; MS (EI, 70 eV), *m/e* (relative intensity) 237 (10, M^+). $^{31}P\{^1H\}$ NMR (C_6D_6, 28 °C) δ 283.2 (s); $^{13}C\{^1H\}$ NMR (C_6D_6, 28 °C) δ 10.6 (d, 0.9 Hz, CCH_3 ring), 34.4 (d, 10.4 Hz, $NCCH_3$), 59.2 (s, NC), 124.1 (d, 5.3 Hz, C ring); ^{1}H NMR (C_6D_6, 28 °C) δ 1.39 (d, 1.4 Hz, 9 H, $NCCH_3$), 1.81 (d, 1.5 Hz, 15 H, CCH_3 ring). Anal. Calcd for $C_{14}H_{24}NP$: C, 70.85; H, 10.19; N, 5.90. Found: C, 69.33; H, 9.99; N, 5.72.

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