Correlation of Structure and Internal Dynamics for (Tris(2,6-dimethoxyphenyl)methyl)tin Trihalides: A Homologous Series of Seven-Coordinate Tin Compounds

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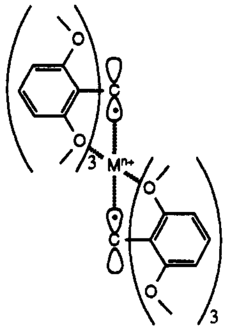
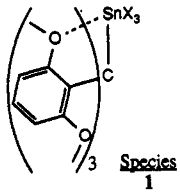
Reaction of tris(2,6-dimethoxyphenyl)methyl cation and the stannous halides produced a series of SnX_3 (**1**, X = F; **2**, X = Cl; **3**, X = Br; **4**, X = I) derivatives of the triarylmethyl. These species constitute a homologous series of heptacoordinate tin compounds. Crystals of **1** are monoclinic, space group $P2_1/c$: $a = 9.8087(5)$ Å, $b = 16.081(3)$ Å, $c = 15.864(2)$ Å, $\beta = 106.120(6)°$, $Z = 4$. Crystals of **2** are orthorhombic, space group $P2_12_12_1$, $a = 11.622(2)$ Å, $b = 15.192(2)$ Å, $c = 33.379(3)$ Å, $Z = 8$. The asymmetric unit contains two independent, heterochiral molecules and one molecule of diethyl ether. Crystals of **3** are triclinic, space group $P\bar{1}$: $a = 10.049(1)$ Å, $b = 10.7709(9)$ Å, $c = 14.996(3)$ Å, $\alpha = 93.18(1)°$, $\beta = 104.77(1)°$, $\gamma = 116.263(9)°$, $Z = 2$. The tin atoms are covalently bound to three halogens and the central carbon of the triarylmethyl unit; their association with the three near methoxy groups raises their coordination number to seven. Methoxy group site exchange barriers were determined for **1**–**4** by variable temperature NMR spectroscopy and/or by the saturation spin transfer method: $\Delta G^{\ddagger}$: **1**, 83 kJ mol^{-1}; **2**, 71 kJ mol^{-1}; **3**, 65/64 kJ mol^{-1} (both methods); **4**, 59 kJ mol^{-1}. Since aryl ring rotation requires concomitant Sn–O bond breaking, the activation energies serve to measure the relative strengths of the Sn ligation by the ether oxygens. The trend observed (F > Cl > Br > I) correlates well with progressive molecular structure changes among **1**, **2**, and **3** and with expectations from the relative Lewis acidities of the tin halides. The order of the ^{119}Sn NMR chemical shifts for **2**–**4** also conforms to expectations based on halide electronegativity, but shows a strong leveling effect which is attributed to coordination by the ether tripods.

Introduction

We have recently proposed a scheme for the assembly of organic-based magnetic systems that relies on complexation of the stable free radical, tris(2,6-dimethoxyphenyl)methyl, with alkali-metal cations, as shown below.[1] Here, a related complexation is unambiguously presented in a series of covalently bonded $-SnX_3$ derivatives of the title radical that exhibit unusual coordination geometries. These compounds were synthesized in the context of a general study of metal binding properties of the per-*o*-methoxytriarylmethyl ligand. They represent what we believe to be the first homologous series of structurally and spectroscopically well-characterized heptacoordinate tin compounds; they are also unique in fixing tin atoms in capped octahedral coordination geometries.



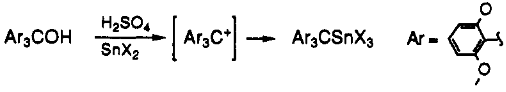


Species	X
1	F
2	Cl
3	Br
4	I

Compounds **1**, **2**, **3**, and **4** were obtained from the reaction of the tris(2,6-dimethoxyphenyl)methyl cation[2] with stannous halides. X-ray crystallographic analyses of the products showed heptacoordinate Sn atoms with three near-ether oxygens participating in their ligation. The degree of coordination by oxygen in this series of organotin halides was investigated by three measures: comparison of the ligand geometries about the Sn atoms, ^{119}Sn NMR spectroscopy, and dynamic NMR examination of the energy required to equate methoxy groups. As X progresses down the group from Cl to I, the large negative ^{119}Sn NMR chemical shifts (for **2**–**4**) move to lower frequency, while for **1**–**4** the barrier to methoxy site exchange, which requires the cleavage of the Sn–O bonds, decreases.

Results and Discussion

Crystal and Molecular Structures of (Tris(2,6-dimethoxyphenyl)methyl)tin Trihalides. The complexes **1**, **2**, and **3** were prepared by reducing tris(2,6-dimethoxyphenyl)methanol with the stannous halide in H_2SO_4 solution as shown in eq 1. Single crystals suitable



$$Ar_3COH \xrightarrow[SnX_2]{H_2SO_4} \left[Ar_3C^+\right] \longrightarrow Ar_3CSnX_3 \qquad Ar = \qquad (1)$$

for X-ray analysis were obtained in each case by slow evaporation of chloroform or ether solutions. The iodide

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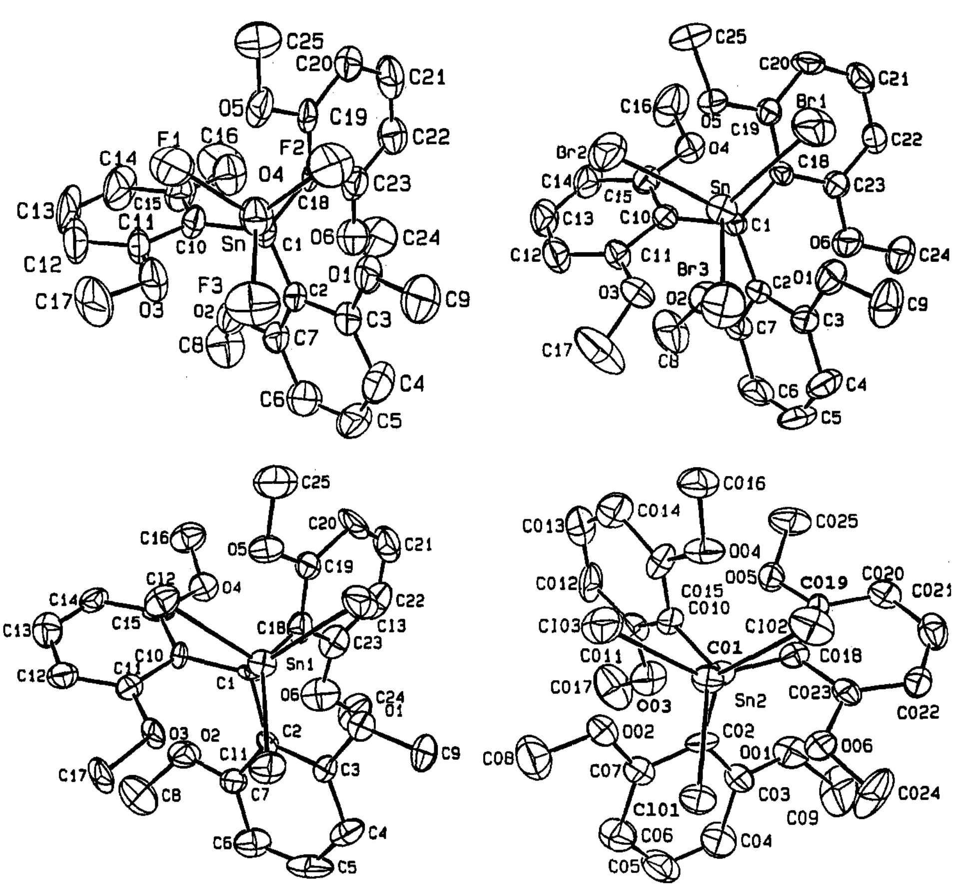

Figure 1. ORTEP representations (50% probability) of 1 (top left), 2 (bottom left), 20 (bottom right), and 3 (top right) with atomic numbering schemes.

4 was prepared similarly, yet well-faceted crystals scattered poorly and were not suitable for X-ray analysis.

The molecular structures of 1, 2, and 3 (Figure 1), as determined from refinements of the single crystal diffraction data, show seven-coordinate Sn atoms. In each case the Sn centers have four formally negative ligands and three neutral ether oxygen atoms that participate in complexation. The geometric figure defined by the ligands can be described as a distorted monocapped-trigonal-antiprism. The oxygen ligands adopt positions *anti* to the halogens while the three aryl rings share similar twists out of their common coordination plane with Sn. Thus, the molecules have propeller conformations with approximate C_3 symmetries. A summary of salient crystallographic data and refinement parameters are presented in Table I. Atomic coordinates for 1, 2, and 3 are listed in Tables II, III, and IV, respectively.

Despite the similar molecular structures of 1, 2, and 3 in the crystals, we have found no isomorphous relationships. The compounds crystallize in three crystal systems: monoclinic, orthorhombic, and triclinic, respectively. Compounds 1 and 3 crystallize in the centrosymmetric space groups $P2_1/c$ and $P\bar{1}$, with molecules in general positions. Compound 2 crystallizes in the chiral group $P2_12_12_1$ with two independent heterochiral molecules and one diethyl ether molecule in the asymmetric unit. Stereoviews comparing the unit cell packing are presented in Figure 2.

In the series 1–3, the average Sn–O distances increase progressively: 1 (2.436(7) Å) < 2 (2.596(7) Å) < 3 (2.653(7) Å). At the same time the average X–Sn–X angles widen with 1 (93.9(3)°) < 2(96.0(3)°) < 3(97.1(3)°). There is a synergistic interaction among the oxygen and halogen ligands which defines the coordination geometry about Sn. This synergy is reflected in the twists of the propellers as defined by the Sn–C_{methyl}–C_{ipso}–C_{ortho} torsion angles.

Table I. Crystallographic Data for Tris(2,6-dimethoxyphenyl)methyltin Trihalides 1–3

compound	1	2	3
formula	$C_{25}H_{27}O_6SnF_3$	$C_{25}H_{27}O_6SnCl_3\cdot 0.5C_4H_{10}O$	$C_{25}H_{27}O_6SnBr_3$
MW, g mol^{-1}	599.18	693.60	781.91
temperature, K	293	173	293
radiation (Å)	Cu Kα (λ = 1.54178)	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)
monochromator	graphite single crystal	graphite single crystal	graphite single crystal
crystal size, mm	0.05 × 0.22 × 0.25	0.13 × 0.15 × 0.24	0.30 × 0.32 × 0.44
crystal color	colorless	yellow	orange
crystal system	monoclinic	orthorhombic	triclinic
space group	$P2_1/c$	$P2_12_12_1$	$P\bar{1}$
lattice constants:			
a, Å	9.8087(5)	11.622(2)	10.049(1)
b, Å	16.081(3)	15.192(2)	10.7709(9)
c, Å	15.864(2)	33.379(3)	14.996(3)
α, deg	–	–	93.18(1)
β, deg	106.120	–	104.77(1)
γ, deg	–	–	116.263(9)
V, Å^3	2403.8(9)	5893(2)	1380.8(8)
Z	4	8	2
d_{calcd}, g cm^{-3}	1.656	1.563	1.881
μ_{calcd}, cm^{-1}	92.05	11.84	52.64
measd reflctns	$\pm h, k \geq 0, l \geq 0$	$h \geq 0, k \geq 0, l \geq 0$	$\pm h, \pm k, l \geq 0$
scan type	ω–2θ	ω–2θ	ω–2θ
2θ range, deg	$4 \leq 2\theta \leq 110$	$4 \leq 2\theta \leq 50$	$4 \leq 2\theta \leq 45$
unique data	3137	5764	3597
no. of obsd data	2264	3463	3074
absorption corr	empirical/ ψ-scans	empirical/ ψ-scans	empirical/ ψ-scans
$R(F_o)$,[a] $R_w(F_o)$[b]	0.056, 0.070	0.038, 0.042	0.037, 0.047
no. of parameters	316	651	316
goodness of fit	1.77	1.17	1.70
residual, e Å^{-3}	0.87	0.80	0.49

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

Table II. Fractional Coordinates (×10^4) and Isotropic Thermal Parameters for (Tris(2,6-dimethoxyphenyl)-methyl)tin Trifluoride (1)[a]

atom	*x*	*y*	*z*	*B* (Å^2)
Sn	0.02840(7)	0.23495(4)	0.01151(5)	3.47(1)
F(1)	0.1225(6)	0.3323(4)	–0.0208(4)	5.2(2)
F(2)	0.1442(6)	0.1581(4)	–0.0341(4)	5.2(2)
F(3)	0.1512(6)	0.2298(5)	0.1334(4)	5.4(2)
O(1)	–0.0307(7)	0.0980(4)	0.0599(4)	3.8(2)
O(2)	–0.4209(7)	0.2595(4)	0.0737(5)	4.2(2)
O(3)	–0.0545(8)	0.3501(4)	0.0861(5)	4.4(2)
O(4)	–0.4691(8)	0.2804(5)	–0.1317(5)	4.9(2)
O(5)	–0.0800(7)	0.2442(4)	–0.1436(4)	3.4(2)
O(6)	–0.4340(8)	0.1070(5)	–0.0530(5)	4.8(2)
C(1)	–0.205(1)	0.2245(6)	–0.0121(6)	3.1(2)
C(2)	–0.222(1)	0.1805(6)	0.0681(6)	3.0(2)
C(3)	–0.130(1)	0.1147(6)	0.1028(6)	3.5(2)
C(4)	–0.139(1)	0.0703(7)	0.1771(8)	4.9(3)
C(5)	–0.239(1)	0.0922(7)	0.2179(7)	4.9(3)
C(6)	–0.335(1)	0.1557(8)	0.1853(7)	4.6(3)
C(7)	–0.327(1)	0.1992(6)	0.1100(6)	3.5(2)
C(8)	–0.546(1)	0.2669(9)	0.0999(9)	5.8(3)
C(9)	0.083(1)	0.0421(8)	0.1011(8)	5.6(3)
C(10)	–0.256(1)	0.3156(6)	–0.0240(6)	3.4(2)
C(11)	–0.175(1)	0.3774(6)	0.0277(7)	4.0(2)
C(12)	–0.215(1)	0.4592(7)	0.0210(9)	5.4(3)
C(13)	–0.339(2)	0.4815(7)	–0.039(1)	6.9(4)
C(14)	–0.423(1)	0.4234(8)	–0.0908(9)	5.9(3)
C(15)	–0.386(1)	0.3404(7)	–0.0833(7)	4.2(3)
C(16)	–0.613(1)	0.296(1)	–0.172(1)	7.7(4)
C(17)	0.046(1)	0.4115(8)	0.1324(9)	6.7(4)
C(18)	–0.248(1)	0.1730(5)	–0.0969(6)	2.6(2)
C(19)	–0.181(1)	0.1851(6)	–0.1609(6)	2.8(2)
C(20)	–0.220(1)	0.1393(7)	–0.2401(7)	4.1(3)
C(21)	–0.325(1)	0.0823(7)	–0.2528(8)	4.8(3)
C(22)	–0.398(1)	0.06990(7)	–0.1921(7)	4.2(3)
C(23)	–0.363(1)	0.1140(6)	–0.1138(7)	3.7(2)
C(24)	–0.572(1)	0.0714(9)	–0.0792(9)	6.4(4)
C(25)	0.011(1)	0.2526(8)	–0.2025(7)	5.0(3)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent temperature factor defined as: $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

The average value of the torsion angles is 39.0(3)° in 1, 47.1(3)° in the two independent molecules of 2, and 48.6(3)° in 3. The smaller torsion angles in the fluoride congener are necessary to achieve the smaller Sn–O distances. Relevant aspects of the molecular geometries are summarized in Table V.

Unfortunately, we have been unsuccessful in crystallographic characterization of 4. Large, brown-red polyhedral crystals diffracted poorly. Some crystallization attempts led to decomposition; we have identified and structurally analyzed single crystals of tris(2,6-dimethoxyphenyl)methyl triiodide in the decomposition products.[3] This salt is very similar to the corresponding triarylmethyl tetrafluoroborate, whose structure we have recently reported.[4]

^{119}Sn and ^{19}F NMR Measurements. Spectra of saturated $CDCl_3$ solutions of 1–4 were obtained at 20 °C. No sensible ^{119}Sn signals could be detected for 1 due to poor solubility, but the ^{19}F spectrum of this compound was readily obtained. The observed ^{19}F and ^{119}Sn chemical shifts of 1–4 are reported in Table VI. The order of the ^{119}Sn chemical shifts is just that expected on the grounds of halide electronegativity. However, the chemical shift range observed for 2–4 is compressed relative to that found for simple alkyltin trihalides. For example, the methyltin trihalides H_3CSnX_3, where X = Cl, Br, I, show a much larger ^{119}Sn chemical shift range (>600 ppm)[5] than we have observed in 2–4 (<50 ppm). We attribute this flattening effect to the presence of the methoxy donor groups in the present system. It is well established that stronger donor ligands (or solvents) and higher coordination numbers shift ^{119}Sn resonances to lower frequency, while increasing ligand electronegativity has the opposite effect.[6] At the same time, the Lewis acidity of the SnX_3 centers is expected to be strongest when X = F and weakest when X = I. The coordination of the Sn atoms by the ether tripods in 1–4 should therefore be tightest in 1 and loosest in 4; these expectations are borne out by the X-ray and dynamic NMR results. Because the Sn atom with the most electronegative halides experiences the strongest tripod complexation, the coordination effect opposes the effect of changing halide electronegativity on ^{119}Sn chemical shift, resulting in a leveling of the shift values.

Although solubility limitations prevented the observation of the ^{119}Sn spectrum of 1, ^{19}F NMR of this compound revealed a single sharp resonance at −13.0 ppm (C_6F_6 reference) with ^{119}Sn and ^{117}Sn satellites. Although the ^{19}F chemical shift is unremarkable for a fluorinated tin compound, the ^{119}Sn–^{19}F coupling constant is 3390 Hz, significantly above the usual range for *J*(Sn–F) values.[7] The origin of this large coupling is unclear at present.

Dynamic NMR Experiments. For compounds 1–4, activation barriers for aryl ring rotation were measured by either variable temperature (VT) or saturation spin transfer (SST) NMR methods. The results are summarized in Table VI. For the VT NMR studies, ^{1}H NMR spectra were recorded in toluene-d_8 as a function of temperature. For compounds 3 and 4, the −80 to 90 °C range accessible in toluene was sufficient to observe two sharp methoxy resonances and, at higher temperature, to observe coalescence of these two signals. These results are consistent with a site-exchange process resulting from the rapid flipping of the aryl rings on the NMR time scale. The activation barriers for aryl ring rotation of 3 and 4 were 63.9 ± 1.3 (T_c = 328 K) kJ mol^{-1} and 58.6 ± 1.3 (T_c = 298 K) kJ mol^{-1}, respectively, as determined by application of the Gutowsky–Holm approximation to the observed methoxy group site exchange at the coalescence temperature (T_c).[8]

Unlike 3 and 4, 1 and 2 showed only broadening; coalescence of the methoxy ^{1}H resonances at 300 MHz was not observed up to 363 K. The saturation spin transfer (SST) method[9] was therefore employed to measure site exchange rates at room temperature; activation barriers of 65.3 ± 0.8, 71.1 ± 0.8, and 82.8 ± 2.5 kJ mol^{-1} were obtained for 3, 2, and 1, respectively. The barrier for 3 determined using the SST method shows good agreement with that obtained from the coalescence measurements. The T_1 values in 3 and 2 (*ca.* 1 s for each) were adequate for accurate determination of the site exchange lifetimes

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Table III. Fractional Coordinates (×10^4) and Isotropic Thermal Parameters for (Tris(2,6-dimethoxyphenyl)methyl)tin Trichloride (2)[a]

atom	x	y	z	B (Å^2)	atom	x	y	z	B (Å^2)
Sn(1)	0.21015(7)	0.16230(4)	0.86434(2)	2.10(1)	C(135)	0.123(1)	–0.1762(7)	0.8572(3)	4.1(3)
Sn(2)	0.70670(7)	–0.44998(4)	0.87076(2)	2.27(1)	C(136)	0.068(1)	–0.0966(6)	0.8657(3)	3.0(2)
Cl(11)	0.2230(3)	0.2676(2)	0.91734(7)	2.86(6)	C(211)	0.6105(9)	–0.2708(6)	0.8517(3)	2.2(2)
Cl(12)	0.2384(2)	0.2635(2)	0.81001(8)	2.80(6)	C(212)	0.708(1)	–0.2639(6)	0.8279(3)	2.6(2)
Cl(13)	0.4052(2)	0.1181(2)	0.87079(9)	3.35(6)	C(213)	0.764(1)	–0.1848(8)	0.8191(3)	4.3(3)
Cl(21)	0.7052(3)	–0.5480(2)	0.92685(7)	2.86(5)	C(214)	0.716(1)	–0.1084(7)	0.8355(3)	4.5(3)
Cl(22)	0.7459(3)	–0.5534(2)	0.81906(8)	3.45(6)	C(215)	0.618(1)	–0.1095(7)	0.8581(4)	4.0(3)
Cl(23)	0.9013(3)	–0.4075(2)	0.88289(9)	3.72(7)	C(216)	0.563(1)	–0.1890(6)	0.8656(3)	2.8(2)
O(1121)	–0.0307(6)	–0.0198(5)	0.7869(2)	2.9(2)	C(221)	0.4934(9)	–0.3631(6)	0.8993(3)	2.2(2)
O(1161)	0.0086(6)	0.2418(4)	0.8600(2)	2.3(1)	C(222)	0.556(1)	–0.3495(7)	0.9352(3)	2.6(2)
O(1221)	0.1855(6)	0.0591(5)	0.9242(2)	2.9(2)	C(223)	0.509(1)	–0.3546(8)	0.9731(3)	4.0(3)
C(1261)	–0.1852(6)	0.0899(5)	0.8711(2)	3.4(2)	C(224)	0.395(1)	–0.3728(8)	0.9749(3)	4.6(3)
O(1321)	0.2338(6)	0.0519(5)	0.8057(2)	2.9(2)	C(225)	0.327(1)	–0.3846(9)	0.9415(4)	4.3(3)
O(1361)	–0.0306(8)	–0.0900(5)	0.8875(2)	4.4(2)	C(226)	0.374(1)	–0.3785(8)	0.9035(3)	3.2(3)
O(2121)	0.7453(6)	–0.3434(5)	0.8123(2)	3.3(2)	C(231)	0.4971(9)	–0.4021(6)	0.8246(3)	2.0(2)
O(2161)	0.4630(7)	–0.1951(5)	0.8849(2)	3.9(2)	C(232)	0.4582(9)	–0.3596(7)	0.7899(3)	2.3(2)
O(2221)	0.6702(6)	–0.3377(5)	0.9283(2)	3.3(2)	C(233)	0.405(1)	–0.4045(7)	0.7590(3)	2.9(3)
O(2261)	0.3123(6)	–0.3854(5)	0.8704(2)	3.5(2)	C(234)	0.385(1)	–0.4948(8)	0.7638(3)	3.4(3)
O(2321)	0.4743(7)	–0.2703(5)	0.7884(2)	3.2(2)	C(235)	0.4162(9)	–0.5399(7)	0.7969(3)	2.7(2)
O(2361)	0.5092(7)	–0.5296(4)	0.8620(2)	3.1(2)	C(236)	0.4718(9)	–0.4915(7)	0.8263(3)	2.4(2)
C(10)	0.0581(8)	0.0722(6)	0.8571(3)	1.7(2)	C(1122)	–0.046(1)	–0.0641(8)	0.7502(3)	3.9(3)
C(20)	0.5557(8)	–0.3588(6)	0.8600(3)	2.0(2)	C(1162)	–0.017(1)	0.3336(7)	0.8659(3)	4.1(3)
C(111)	–0.0083(8)	0.1125(6)	0.8230(3)	1.5(2)	C(1222)	0.262(1)	0.0580(8)	0.9581(3)	3.8(3)
C(112)	–0.0455(9)	0.0709(7)	0.7891(3)	2.2(2)	C(1262)	–0.294(1)	0.132(1)	0.8752(4)	6.5(4)
C(113)	–0.106(1)	0.1169(7)	0.7586(3)	2.8(2)	C(1322)	0.334(1)	0.050(1)	0.7806(4)	5.0(3)
C(114)	–0.126(1)	0.2037(8)	0.7634(4)	3.6(3)	C(1362)	–0.075(1)	–0.1660(8)	0.9081(4)	4.9(3)
C(115)	–0.091(1)	0.2487(7)	0.7968(3)	2.8(3)	C(2122)	0.847(1)	–0.3436(9)	0.7877(3)	4.1(3)
C(116)	–0.0332(9)	0.2019(7)	0.8256(3)	2.2(2)	C(2162)	0.420(1)	–0.1188(9)	0.9026(4)	6.0(4)
C(121)	0.0009(8)	0.0788(6)	0.8981(3)	1.6(2)	C(2222)	0.740(1)	–0.3238(9)	0.9633(4)	5.7(4)
C(122)	0.0686(9)	0.0690(7)	0.9324(3)	2.3(2)	C(2262)	0.203(1)	–0.430(1)	0.8716(4)	6.7(4)
C(123)	0.025(1)	0.0686(8)	0.9709(3)	3.2(3)	C(2322)	0.463(1)	–0.2285(8)	0.7508(4)	4.4(3)
C(124)	–0.090(1)	0.079(1)	0.9758(4)	5.2(3)	C(2362)	0.486(1)	–0.6224(7)	0.8678(5)	5.3(3)
C(125)	–0.165(1)	0.0905(8)	0.9425(3)	3.7(3)	O(5000)	0.9596(9)	0.9115(7)	0.4896(3)	6.0(2)*
C(126)	–0.1165(9)	0.0885(7)	0.9044(3)	2.4(2)	C(5001)	0.961(2)	0.764(1)	0.4635(5)	7.9(5)*
C(131)	0.109(1)	–0.0199(7)	0.8494(3)	2.7(2)	C(5002)	0.979(2)	0.819(1)	0.4994(6)	8.6(5)*
C(132)	0.201(1)	–0.0272(7)	0.8229(3)	2.6(2)	C(5003)	0.965(2)	0.977(1)	0.5238(5)	7.9(5)*
C(133)	0.257(1)	–0.1067(8)	0.8156(3)	3.7(3)	C(5004)	0.960(1)	1.062(1)	0.5086(5)	6.9(4)*
C(134)	0.218(1)	–0.1795(7)	0.8333(3)	4.1(3)					

[a] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

(*ca.* 0.1 and 1 s, respectively), but the much slower site exchange lifetime in 1 was roughly 10 times T_1 ($T_1 \approx 10$ s in this system), leading to substantial uncertainty in the barrier determined for this species.

Correlation of Structure and Internal Dynamics. It has been well documented that the predominant process which exchanges aryl ring edges in Ar_3Z and Ar_3ZX molecules is the two-ring flip.[10] Here, two aryl rings turn out of the plane of coordination of the central atom while the third ring turns through it in a disrotatory fashion. The operation of the two-ring flip mechanism in 1, 2, 3, and 4 would enantiomerize these C_3 compounds with concomitant scission of one of the three Sn–O interactions. We surmise that the barrier for methoxy group exchange, and hence for enantiomerization (not directly measurable in the current system), reflects the strength of this bond.[11] The Sn–O interaction would be expected to weaken in response to the decreasing Lewis acidity of the Sn center as the attached halides become less electronegative. Thus, as expected from the trends in our NMR and X-ray studies, the barriers to methoxy group site exchange become lower along the sequence 1–4 as the halides go from F to I in order of decreasing electronegativity.

The structural chemistry of tin has been reviewed by Harrison.[12] Several of the structural features of 1, 2, and 3 may be found in other Sn complexes. A donor heteroatom tethered to a tightly bound (e.g. alkyl or aryl) ligand may participate in intramolecular coordination, thereby increasing the formal coordination number of the Sn.[13] Compounds in which crown ethers form complexes with Sn halides have been reported.[14] Heptacoordinate species have also been described, but the majority of structurally characterized heptacoordinate systems have distorted pentagonal bipyramidal geometries,[15] in contrast to the capped octahedra of ligands found in complexes 1–3. We have found no systematic study on either structure or dynamics of hepatocoordinate tin compounds. In fact, the literature of hypercoordinate tin provides only a few homologous halide series of any kind (vide infra).

Two sequences of pentacoordinate tin halides 5 and 6

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(11) The symmetries of 1–4 preclude direct distinction between enantiomerization and homomerization. Synthesis of less symmetrical derivatives is planned in order to determine the threshold mechanism for aryl ring rotation. In appropriately substituted systems it should also be possible to ascertain whether Sn–C bond rotation is coupled to the aryl ring rotations.

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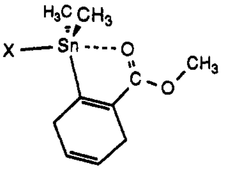
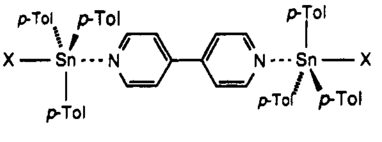
Table IV. Fractional Coordinates (×10^4) and Isotropic Thermal Parameters for (Tris(2,6-dimethoxyphenyl)methyl)tin Tribromide (3)[a]

atom	*x*	*y*	*z*	*B* (Å^2)
Sn	0.33762(4)	0.48097(3)	0.21550(2)	2.638(8)
Br(1)	0.18190(7)	0.29795(6)	0.29830(5)	4.62(2)
Br(2)	0.15911(7)	0.38009(7)	0.04930(5)	5.10(2)
Br(3)	0.51478(7)	0.37739(6)	0.19698(5)	5.34(2)
O(1)	0.5449(4)	0.5741(3)	0.3806(3)	3.40(9)
O(2)	0.6169(4)	0.9979(4)	0.2873(3)	4.4(1)
O(3)	0.5088(4)	0.6700(4)	0.1351(3)	3.9(1)
O(4)	0.2189(4)	0.8563(3)	0.2369(3)	3.51(9)
O(5)	0.0988(3)	0.5432(3)	0.2146(2)	2.98(9)
O(6)	0.5269(4)	0.8452(4)	0.4732(3)	4.0(1)
C(1)	0.4074(5)	0.7109(4)	0.2767(3)	2.2(1)
C(2)	0.5827(5)	0.7790(5)	0.3232(3)	2.3(1)
C(3)	0.6514(5)	0.7047(5)	0.3725(3)	2.8(1)
C(4)	0.8087(6)	0.7575(6)	0.4097(4)	4.1(1)
C(5)	0.9055(6)	0.8880(8)	0.3994(5)	5.3(2)
C(6)	0.8472(6)	0.9708(7)	0.3575(4)	4.8(2)
C(7)	0.6838(6)	0.9178(6)	0.3202(4)	3.3(1)
C(8)	0.7059(9)	1.1194(7)	0.2539(5)	6.2(2)
C(9)	0.6053(7)	0.4918(6)	0.4313(5)	5.2(2)
C(10)	0.3655(5)	0.7634(5)	0.1864(3)	2.4(1)
C(11)	0.4292(5)	0.7454(5)	0.1168(4)	3.0(1)
C(12)	0.4083(7)	0.7946(6)	0.0346(4)	4.3(2)
C(13)	0.3233(7)	0.8660(6)	0.0218(4)	4.7(2)
C(14)	0.2576(6)	0.8861(6)	0.0867(4)	3.9(1)
C(15)	0.2777(5)	0.8339(5)	0.1688(4)	2.9(1)
C(16)	0.1036(7)	0.8988(7)	0.2141(5)	6.2(2)
C(17)	0.6165(8)	0.6810(9)	0.0873(5)	7.7(2)
C(18)	0.3102(5)	0.6926(4)	0.3421(3)	2.1(1)
C(19)	0.1493(5)	0.6060(5)	0.3067(3)	2.5(1)
C(20)	0.0532(5)	0.5830(6)	0.3613(4)	3.6(1)
C(21)	0.1160(6)	0.6500(6)	0.4532(4)	3.6(1)
C(22)	0.2734(5)	0.7373(5)	0.4929(4)	3.3(1)
C(23)	0.3709(5)	0.7579(5)	0.4376(4)	2.7(1)
C(24)	0.5942(7)	0.9084(6)	0.5693(4)	4.2(2)
C(25)	−0.0645(6)	0.4597(7)	0.1685(5)	4.9(2)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.



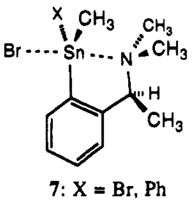
5: X = CH_3, F, Cl, Br, I



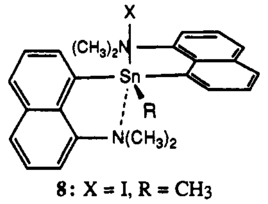
6: X = Cl, Br, I

have been structurally characterized by X-ray diffraction.[16,17] Each system may be described as a triorganotin monohalide to which a neutral nucleophile is coordinated. In 5 the fifth ligand is an endogenous ester carbonyl oxygen, while in 6 it is a pyridine nitrogen. The trends in both of these series are opposite to what we have found for 1–3; specifically, the Sn–O and Sn–N distances in 5 and 6 *decrease* as the attached halides progress from F to I. After a detailed analysis of the geometrical variables in 5, Kolb, Dräger, and Jousseaume suggest that pπ–dπ back donation from the halogen to the tin center in 5 could invert the order of tin Lewis acidities expected on the grounds of simple halogen electronegativity. This suggestion seems weakened, however, by their finding that it is the fluoride 5 (X = F) that self-associates via bridging fluorines to raise the tin coordination number to six. The series 6 provides a more convincing case for the apparent "reverse" trend. These compounds are crystallographically isostructural; furthermore, steric or ring strain effects due to the intramolecular attachment of the nucleophile (as in 5) are impossible as the 4,4′-bipyridine ligands in these complexes are not otherwise linked to the tin centers. However, 5 and 6 show significantly smaller nucleophile–Sn distance variations than do the heptacoordinate trihalides 1–3.

Though neither 5 nor 6 were studied by dynamic NMR methods, van Koten et al. have reported NMR studies of a series of related pentacoordinate[18] and hexacoordinate[19] organotin compounds 7 and 8. However, these workers did not focus on systematic investigations of tin halide sequences obviating a comparison of Lewis acidity trends to halide substituents. There is also limited structural information to correlate with their NMR observations. One message seems clear—two halides confer greater Lewis acidity on Sn than does one. The Sn–N interaction in dibromide 7 (X = Br) is stronger than that in monobromide 7 (X = Ph), as judged by the coalescence of the amine's two methyl group resonances.



7: X = Br, Ph



8: X = I, R = CH_3
X = I, R = C_2H_5
X = Br, R = CH_2Ph
X = Br, R = Br

Further insight into the Lewis acidities of organotin(IV) halides is offered by calorimetric and NMR studies of the 1:1 adduct formation of triphenylphosphine oxide with a series of $(CH_3)_nSnX_{4-n}$ (X = Cl, Br, I) compounds. In this work it was shown that tin's Lewis acidity increases with both the electronegativity and the number of the halogen substituents; thus $(CH_3)_3SnCl$ is more Lewis acidic than $(CH_3)_3SnBr$, but is much less so than $(CH_3)_2SnCl_2$.[20] These ideas are supported by a related but less complete

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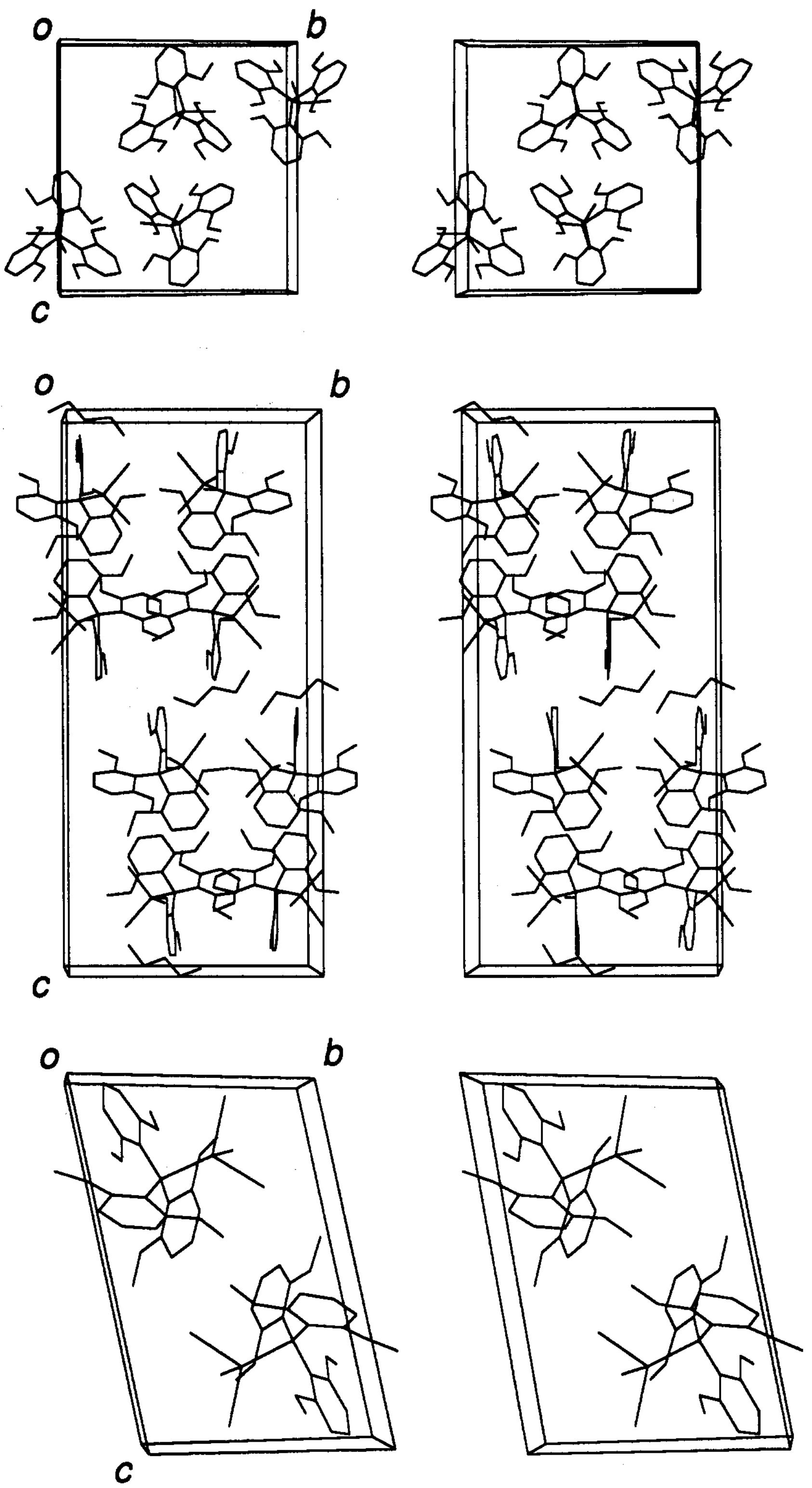

Figure 2. Stereoviews of the unit cells of 1 (top), 2 (middle), and 3 (bottom) each viewed along their respective *a* axis.

calorimetric study of pyridine reacting with $(CH_3)_nSnCl_{4-n}$ and Ph_nSnCl_{4-n}.[21] Why then do 5 and 6 show the observed trends? Detailed examination of the triphenylphosphine oxide complexation data for $(CH_3)_3SnX$ show that the equilibrium constants for binding increase slightly (I: 11; Br: 19, Cl: 21 M^{-1}) from the iodide to the chloride. On the other hand, the *enthalpies* of binding actually become more negative from Cl to I;[20] they are just overbalanced by the increasingly negative entropies of binding. Overall, the monohalides do not vary much in their Lewis acidities. In contrast, the dihalides $(CH_3)_2SnX_2$ show larger binding constants and more variation from one halogen to the next (Br: 108; Cl: 460 M^{-1}). The trihalide CH_3SnCl_3 shows an even larger binding constant to triphenylphosphine oxide ($\geq$566 M^{-1}) and here the data begin to demand that higher coordination numbers be considered as well. It seems reasonable to expect that the Lewis acidity range over halogens will be even more expanded for the trihalides than for the dihalides. It is also clear that organotin trihalides favor more than pentacoordination with nucleophiles. The tin tetrahalides show even greater variation in Lewis acidity and coordination tendencies with increasing electronegativity.[22]

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Table V. Comparison of Salient Features of the Molecular Geometries of (Tris(2,6-dimethoxyphenyl)methyl)tin Trihalides 1–3

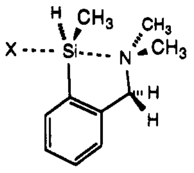
	1	2	2O[a]	3
		Bond Lengths, Å		
Sn–C1	2.22(1)	2.249(9)	2.265(9)	2.312(5)
Sn–O1	2.454(7)	2.555(7)	2.603(7)–O2	2.592(3)
Sn–O3	2.455(8)	2.640(7)	2.576(7)–O4	2.606(4)
Sn–O5	2.399(7)	2.593(7)	2.611(7)–O6	2.760(4)
Sn–X1	1.956(6)	2.390(3)	2.393(2)	2.5316(7)
Sn–X2	1.948(7)	2.400(3)	2.377(3)	2.5110(7)
Sn–X3	1.975(6)	2.374(3)	2.386(3)	2.5430(9)
C1–C2	1.50(1)	1.53(1)	1.50(1)	1.517(6)
C1–C10	1.54(1)	1.50(1)	1.51(1)	1.528(7)
C1–C18	1.54(1)	1.54(1)	1.52(1)	1.516(8)
		Bond Angles, deg		
X1–Sn–X2	92.5(3)	96.99(9)	99.09(9)	99.84(2)
X1–Sn–X3	94.9(3)	93.6(1)	92.4(1)	96.95(3)
X2–Sn–X3	94.4(3)	96.9(1)	96.9(1)	94.36(3)
X1–Sn–O1	165.8(3)	80.7(2)	80.2(2)–O2	82.32(8)
X1–Sn–O3	76.5(3)	77.8(2)	170.3(2)–O4	177.54(9)
X1–Sn–O5	77.8(2)	170.2(2)	78.0(2)–O6	77.64(8)
X1–Sn–C1	123.7(3)	122.5(2)	119.9(3)	114.6(1)
X2–Sn–O1	76.1(3)	177.4(2)	178.2(2)–O2	172.6(1)
X2–Sn–O3	164.3(3)	77.7(2)	80.3(2)–O4	82.09(7)
X2–Sn–O5	78.2(3)	80.2(2)	77.4(2)–O6	77.09(7)
X2–Sn–C1	124.7(3)	114.6(2)	116.0(3)	117.4(1)
X3–Sn–O1	77.8(3)	82.1(2)	81.5(2)–O2	78.3(1)
X3–Sn–O3	75.7(3)	169.1(2)	78.1(2)–O4	81.3(1)
X3–Sn–O5	169.3(2)	77.5(2)	167.8(2)–O6	168.77(6)
X3–Sn–C1	118.8(3)	126.0(3)	126.6(2)	128.3(1)
O1–Sn–O3	112.8(3)	102.9(2)	100.1(2)–O4	95.6(1)
O1–Sn–O5	107.5(2)	101.9(2)	104.0(2)–O6	110.3(1)
O3–Sn–O5	109.6(3)	110.4(2)	111.1(2)	104.3(1)
O1–Sn–C1	70.3(3)	67.8(3)	65.8(3)	67.4(1)
O3–Sn–C1	71.0(3)	64.9(3)	68.3(3)	65.5(2)
O5–Sn–C1	71.9(3)	66.9(3)	65.4(3)	62.8(1)
Sn–C1–C2	103.9(6)	101.8(3)	102.1(3)	104.3(4)
Sn–C1–C10	103.5(6)	103.7(3)	104.1(3)	100.6(3)
Sn–C1–C18	102.0(6)	105.7(3)	101.9(3)	103.0(3)
C2–C1–C10	116.3(8)	115.3(3)	113.8(3)	111.8(4)
C2–C1–C18	114.8(8)	112.0(3)	116.5(3)	116.0(4)
C10–C1–C18	113.9(8)	116.2(3)	115.6(3)	118.3(5)
		Torsion Angles, deg		
Sn–C1–C2–C_{ortho}[b]	–40.96	–48.74	50.54	–38.92
Sn–C1–C10–C_{ortho}	–37.33	–50.81	41.65	–53.15
Sn–C1–C18–C_{ortho}	–38.64	–43.76	50.83	–53.78

[a] **2O** is the second independent molecule in the asymmetric unit. [b] C_{ortho} is the *ortho* carbon atom nearer to Sn.

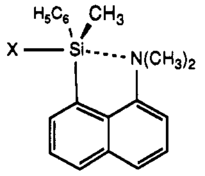
Table VI. NMR Results for (Tris(2,6-dimethoxyphenyl)methyl)tin Trihalides 1–4

	1	2	3	4
δ_{Sn} (ppm)[a]	*b*	–344	–387	–393
$\Delta G^{\ddagger}$ (kJ mol^{-1})	82.8 ± 2.5[c]	71.1 ± 0.8[c]	65.3 ± 0.8[c] 63.9 ± 1.3[d]	58.6 ± 1.3[d]
$1/T_1$ (s^{-1})	0.14[e]	1.00[f]	0.82[g]	
k_{ex} (s^{-1})	0.01[e]	1.2[f]	14.0[g]	
T_c (K)			328	298
k_c (s^{-1})[h]			448	362
δ_H (CH_3O, ppm)	2.96, 3.70[i]	2.53, 3.24[j]	2.79, 3.46[j]	2.74, 3.28[j]
T (K)[k]	293	193	193	193
$\Delta\nu$ (Hz)	222	213	202	163

[a] Spectra measured in $CDCl_3$ and referenced to neat Me_4Sn at 20 °C. [b] No ^{119}Sn resonance was observed for **1** due to poor sample solubility. However, ^{19}F NMR ($CDCl_3$) gave $\delta_F = -13.0$ ppm (referenced to neat hexafluorobenzene) at 20 °C, with ^1J (^{119}Sn–^{19}F) = 3390 Hz and ^1J (^{117}Sn–^{19}F) = 3238 Hz. [c] Calculated from the exchange rate constant (k_{ex}) in toluene-d_8 obtained by SST method at 293 K. [d] Calculated from the coalescence rate constant (k_c) in toluene-d_8 obtained by VT ^{1}H NMR at the coalescence temperature (T_c). [e] Delay times used after 180° pulse: 0, 1, 2, 4, 8, 16, 32, 64 s. [f] Delay times used after 180° pulse: 0, 0.1, 0.2, 0.4, 0.8, 1.2, 2.4, 4.8 s. [g] Delay times used after 180° pulse: 0, 1, 5, 10, 20, 30, 40, 60 ms. [h] $k_c = 2.22\Delta\nu$; see ref 8c. This is converted to $\Delta G^{\ddagger}$ via the Gutowsky–Holm approximation: $\Delta G^{\ddagger}$ (J mol^{-1}) = $19.14T_c[10.32 + \log(T_c/k_c)]$. [i] The linewidths at half-height in the nonexchange region were ca. 3–3.5 Hz. [j] The linewidths at half-height in the nonexchange region were ca. 2–2.5 Hz. [k] Temperature at which δ_H (CH_3O) is obtained.



9: X = F, Cl, Br



10: X = F, Cl

Like (triphenylphosphine oxide)·$(CH_3)_3SnX$, the pentacoordinate tin monohalides **5** and **6** have a small and delicately balanced Lewis acidity variation whereas the trihalides **1–4** belong to an unsubtle family of tin trihalides where Lewis acidity increases rapidly with halide electronegativity. Consistent with these remarks, we note that the variations in O–Sn distances seen in **1–3** are substantially larger than those seen in **5** or the N–Sn changes seen in **6**.

It appears that organosilicon systems analogous to the triorganotin monohalides are likewise tenuously balanced. Corriu et al. have studied the silicon-centered framework **9**, closely related to **7** and **8** above, by dynamic ^{1}H NMR.[23] In this case, the three organosilicon monohalides **9** showed increasing barriers to *N*-methyl group site exchange, in line with the reports from the Jousseaume (**5**) and Bajue (**6**) groups. Such behavior is unfortunately not general; the closely related halides **10** show the opposite trend, albeit measured for only two cases.[24]

Although the exercise raises some interesting and fundamental bonding questions about hypercoordinate Sn(IV) species, it is not clear that tin halides of different coordination number and/or halide content may be comparably analyzed. The tin and silicon species **5–10** differ from compounds **1–4** in at least two significant ways: their coordination numbers are different, and they are all monohalides, except for **7** (X = Br). Furthermore, the nucleophiles coordinated to tin in **1–4** are aromatic ether oxygens which differ substantially from the carbonyl oxygen in **5** and from the amine nitrogens in **6–8**. Thus, it is difficult to judge whether compounds **1–4** behave in accord with expectations based on previous work.

Experimental Section

General. Commercial chemicals were used as supplied: SnF_2 and $SnBr_2$ (Aldrich); $SnCl_2$ (Baker); and SnI_2 (Johnson Matthey Electronics). Tris(2,6-dimethoxyphenyl)methanol was prepared by the method of Martin and Smith.[25] ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Gemini 200 FT/NMR spectrometer; details of other NMR experiments (VT, SST, ^{119}Sn, ^{19}F) are given below. IR spectra were recorded on a Perkin-Elmer Model 1800 FTIR spectrometer. UV-vis spectra were obtained using a Hewlett-Packard 8451A diode array spectrophotometer. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

(Tris(2,6-dimethoxyphenyl)methyl)tin Trifluoride. Tris(2,6-dimethoxyphenyl)methanol (0.5 g, 1.1 mmol) was dissolved

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in 10% H_2SO_4 (30 mL). The filtered solution was added slowly to a solution of SnF_2 (0.34 g, 2.2 mmol) in 10% H_2SO_4 (50 mL). The solution was stirred for 3 h and filtered. The resulting lavender solid was washed with aqueous Na_2CO_3 and dried under vacuum to yield 0.45 g of crude product. The solid was then dissolved in $CHCl_3$ and passed through basic alumina. Slow evaporation of the $CHCl_3$ gave colorless crystals (0.39 g, 59%): mp 219 °C; ^1H NMR ($CDCl_3$) δ 7.18 (t, J = 8.3 Hz, 3 H), 6.58 (d, J = 7.9 Hz, 3 H), 6.56 (d, J = 8.4 Hz, 3 H), 3.96 (s, br, 9 H), 3.19 (s, br, 9 H); $^{13}C\{^1H\}$ NMR δ 160.1 (br), 154.0 (br), 127.8, 120.6, 108.5 (br), 103.4 (br), 57.1 (br); remaining ^{13}C resonances were not observable; ^{19}F NMR ($CDCl_3$, 20 °C) δ −13.0 ($J(^{119}Sn)$ = 3390 Hz; $J(^{117}Sn)$ = 3238 Hz); IR(KBr): 3002, 2948, 2838, 1892, 1582, 1476, 1424, 1282, 1250, 1180, 1016, 910, 898, 878, 778, 768, 736, 706, 610, 582, 566, 546, 506 cm^{-1}. Anal. Calcd for $C_{25}H_{27}O_6F_3Sn$: C, 50.12; H, 4.54; F, 9.51. Found: C, 49.64; H, 4.53; F, 9.78.

(Tris(2,6-dimethoxyphenyl)methyl)tin Trichloride. Tris(2,6-dimethoxyphenyl)methanol (0.5 g, 1.1 mmol) was dissolved in 10% H_2SO_4 (30 mL). The filtered solution was added slowly to a solution of $SnCl_2$ (0.49 g, 2.2 mmol) in 10% H_2SO_4 (50 mL). After stirring for 30 min, the solution was extracted with Et_2O (3 × 40 mL). The extracts were combined, dried over Na_2SO_4, and filtered, and the solvent was evaporated completely to yield 0.4 g of yellow product. Recrystallization from Et_2O gave yellow crystals (0.3 g, 42%): mp 203 °C (turned red at 150 °C); ^1H NMR ($CDCl_3$) δ 7.21 (t, J = 8.3 Hz, 3 H), 6.58 (d, J = 8.4 Hz, 6 H), 3.80 (s, br, 9 H), 3.20 (s, br, 9 H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 159.2 (br), 155.1 (br), 128.3, 127.6, 119.3, 107.1 (br), 103.1 (br), 56.3 (br), 55.5 (br); ^{119}Sn NMR ($CDCl_3$, 20 °C) δ −344; UV-vis (Et_2O): λ_{max} [nm] (ϵ) = 330 (54500); IR (KBr) 3034, 2942, 2834, 1580, 1474, 1428, 1280, 1250, 1198, 1170, 1102, 1022, 920, 792, 780, 758, 734, 688, 630, 606, 504 cm^{-1}. Anal. Calcd for $C_{25}H_{27}O_6Cl_3Sn$: C, 46.30; H, 4.16; O, 14.80; Cl, 16.40; Sn, 18.30. Found: C, 46.70; H, 4.58; O, 14.09 (by difference); Cl, 16.52; Sn, 18.11.

(Tris(2,6-dimethoxyphenyl)methyl)tin Tribromide. Tris(2,6-dimethoxyphenyl)methanol (0.5 g, 1.1 mmol) was dissolved in 10% H_2SO_4 (30 mL). The filtered solution was added slowly to a solution of $SnBr_2$ (0.65 g, 2.2 mmol) in 10% H_2SO_4 (50 mL). After stirring for 30 min the solution was extracted with Et_2O (3 × 40 mL). The extracts were combined, dried over Na_2SO_4, and filtered, and the solvent was evaporated completely to yield 0.5 g of product. Recrystallization from Et_2O gave yellow-orange crystals (0.4 g, 46%): mp 180 °C; ^1H NMR ($CDCl_3$) δ 7.23 (t, J = 8.4 Hz, 3 H), 6.56 (d, J = 8.4 Hz, 6 H), 3.47 (s, 18 H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 157.0 (br), 127.7, 119.5, 105.2 (br), 55.7; remaining ^{13}C resonance was not observable; ^{119}Sn NMR ($CDCl_3$, 20 °C) δ −387; UV-vis (Et_2O) λ_{max} [nm] (ϵ) = 370 (133 000); IR (KBr) 3450, 2934, 2832, 1594, 1580, 1426, 1280, 1198, 1170, 1022, 920, 788, 734, 670, 642, 504 cm^{-1}. Anal. Calcd for $C_{25}H_{27}O_6Br_3Sn$: C, 38.40; H, 3.48; Br, 30.66. Found: C, 39.04; H, 3.48; Br, 31.23.

(Tris(2,6-dimethoxyphenyl)methyl)tin Triiodide. Tris(2,6-dimethoxyphenyl)methanol (0.5 g, 1.1 mmol) was dissolved in 10% H_2SO_4 (30 mL). The filtered solution was added slowly to a solution of SnI_2 (0.80 g, 2.2 mmol) in 10% H_2SO_4 (50 mL). After stirring for 30 min, the solution was extracted with Et_2O (3 × 40 mL). The extracts were combined, dried over Na_2SO_4, and filtered, and the solvent was evaporated to yield a rust-colored product (0.6 g, 59%): mp 137 °C; ^1H NMR ($CDCl_3$) δ 7.26 (t, J = 8.3 Hz, 3 H), 6.53 (d, J = 8.4 Hz, 6 H), 3.41 (s, 18 H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 156.8 (br), 128.1, 120.8, 105.9 (br), 56.6; remaining ^{13}C resonance was not observable; ^{119}Sn NMR ($CDCl_3$, 20 °C) δ −393; UV-vis (Et_2O) λ_{max} [nm] (ϵ) = 426 (146 000); IR (KBr) 3444, 2934, 2828, 1592, 1578, 1470, 1424, 1278, 1248, 1104, 1028, 920, 786, 734, 660, 640, 470 cm^{-1}.

X-ray Crystallography. Crystals of **1** were obtained from $CHCl_3$ by slow evaporation. Crystals of **2** and **3** were obtained from ether by slow evaporation. All X-ray intensities were measured with an Enraf-Nonius CAD4 Kappa axis diffractometer. No decay corrections were applied because standard reflections measured periodically showed constant intensities. Lorentz and polarization corrections were applied. Empirical absorption corrections were applied.[26] The space groups for **1** and **2** were determined from the limiting conditions to be $P2_1/c$ ($h0l$, $l = 2n$ and $0k0$, $k = 2n$) and $P2_12_12_1$ ($h00$, $h = 2n$; $0k0$, $k = 2n$, $00l$; $l = 2n$), respectively. From the E-statistics, the space group of **3** was determined to be centrosymmetric, $P\bar{1}$. Crystallographic calculations employed the MolEN package of programs.[27] Atomic scattering factors[28] and anomalous dispersion terms $\delta f'$ and $\delta f''$[29] were taken from the tables of Cromer. Each structure was solved using the direct methods employed in SHELX86.[30] Models were built by locating atoms in successive difference Fourier syntheses. Hydrogen positions were identified in this way but their positions were not optimized. The structures were refined by the full-matrix least-squares procedure.

NMR Methods. Hexafluorobenzene (99.9%) and Me_4Sn (99+%) reference compounds were obtained from Aldrich and used as received.

NMR measurements were performed on a Varian VXR-300 spectrometer. Sample solutions were placed in 5-mm tubes fitted with coaxial inserts for the reference compounds. The ^{19}F spectrum was recorded in $CDCl_3$ (20 °C) at 282.20 MHz and is referenced to neat hexafluorobenzene. The ^{119}Sn spectra were obtained in saturated $CDCl_3$ (20 °C) solutions at 111.86 MHz and are referenced to neat Me_4Sn.

Variable temperature (VT) ^1H NMR spectra were recorded in toluene-d_8 at 299.95 MHz. The temperature was controlled to within ±0.1 °C by an Oxford Instruments Model VTC 4 temperature controller. The rotational barriers of **3** and **4** were determined from the Gutowsky–Holm approximation.[8]

In the cases of **1** and **2**, where coalescence of the methoxy signals was not observed, the saturation spin transfer (SST) technique[9] was used to obtain exchange rate constants. For a comparison of the VT and SST methods, the rotational barrier for **3** was also determined with this method. Experiments were carried out in toluene-d_8 at 293 K by delivering a selective 180° pulse on the higher frequency methoxy signal, followed by a nonselective 90° pulse after increasingly longer delay times. In each case, the methoxy resonance at lower frequency was the only signal to show a diminution of intensity as a result of transfer of saturation from the irradiated signal. Treatment of the change of intensities[9] of the methoxy signals as a function of time afforded the exchange rate constants, and the rotational barriers were calculated from the Eyring equation assuming a transmission coefficient of unity.

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Supplementary Material Available: Listings of anisotropic thermal parameters, bond lengths, valence angles, and hydrogen atom positions (50 pages). Ordering information is given on any current masthead page.

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