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Syntheses, Structures, and ^{1}H, ^{13}C{^{1}H} and ^{119}Sn{^{1}H} NMR Chemical Shifts of a Family of Trimethyltin Alkoxide, Amide, Halide and Cyclopentadienyl Compounds†

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The synthesis and full characterization, including Nuclear Magnetic Resonance (NMR) data (^{1}H, ^{13}C{^{1}H} and ^{119}Sn{^{1}H}), for a series of Me_3SnX (X = O-2,6-^{t}Bu$_2$C$_6$H$_3$ (**1**), $(Me_3Sn)_2$N(2,6-^{i}Pr$_2$C$_6$H$_3$) (**3**), NH-2,4,6-^{t}Bu$_3$C$_6$H$_2$ (**4**), N(SiMe$_3$)$_2$ (**5**), NEt$_2$, C$_5$Me$_5$ (**6**), Cl, Br, I, and SnMe$_3$) compounds in benzene–d_6, toluene–d_8, dichloromethane–d_2, chloroform–d_1, acetonitrile–d_3, and tetrahydrofuran–d_8 are reported. The X-ray crystal structures of Me$_3$Sn(O-2,6-^{t}Bu$_2$C$_6$H$_3$) (**1**), Me$_3$Sn(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (**2**), and Me$_3$Sn)(NH-2,4,6-^{t}Bu$_3$C$_6$H$_2$) (**4**) are also presented. These compiled data complement existing literature data and ease the characterization of these compounds by routine NMR experiments.

Introduction

Among main-group organometallics, organotin amide, alkoxide, and halide compounds show a diverse array of applications ranging from all sorts of biological activity,[1] ionophores in sensors,[2] precursors for hybrid organic-inorganic nano and non-linear optical materials,[3] and catalysts for a variety of widely-used organic carbon-carbon coupling processes.[4] Although their use as marine antifoulants is being phased out, new organotin derivatives with N, O and S donating groups are showing promise as antimicrobial, antifungal, and anticancer agents.[5] Despite their broad utility and long-standing history in organometallic and inorganic chemistry, it is surprising that very little solution and solid-state structural information has been reported for even the simple organotin compounds Me$_3$SnX (where X = NR$_2$, OR, halide, C$_5$Me$_5$, and SnMe$_3$).[6] In our own studies, we have found that some of the ^{1}H NMR data of trimethyltin derivatives have been misreported.[7] Herein, we report the synthesis and characterization of a family of trimethyltin amide, alkoxide, and cyclopentadienyl compounds. We show that transmetallation from a potassium amide, alkoxide or cyclopentadienyl reagent and Me$_3$SnCl provides an improved route for accessing the corresponding trimethyltin derivatives and offers an alternative to existing literature procedures. For completeness, we have compiled ^{1}H and ^{13}C{^{1}H} NMR data of eleven Me$_3$SnX compounds in six common deuterated solvents (benzene–d_6, toluene–d_8, dichloromethane–d_2, chloroform–d_1, acetonitrile–d_3, and tetrahydrofuran–d_8). In addition, ^{119}Sn{^{1}H} NMR data is also presented (in benzene–d_6 or chloroform–d_1) for all compounds. We anticipate that these collocated data will serve as a resource for chemists working with trimethyltin compounds.

Results and discussion

Synthesis and solid-state structural characterization

Scheme 1 presents the synthetic methods used and the yields obtained in the preparation of trimethyltin compounds **1**–**6**. All of these compounds were prepared by transmetallation. For example, treatment of a tetrahydrofuran (THF) solution of Me$_3$SnCl with one equivalent of either K(O-2,6-^{t}Bu$_2$C$_6$H$_3$) or K(O-2,6-^{i}Pr$_2$C$_6$H$_3$) at room temperature afforded the corresponding trimethyltin aryloxide compounds Me$_3$Sn(O-2,6-^{t}Bu$_2$C$_6$H$_3$) (**1**) and Me$_3$Sn(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (**2**), in 81% and 86% isolated yields respectively. Following workup by filtration through Celite and recrystallization, both complexes were isolated as white and off-white solids, respectively. The X-ray crystal structures of complexes **1** and **2** are presented in Figures 1 and 2, respectively. Both compounds represent rare examples of structurally characterized trimethyltin aryloxides; they are monomeric in the solid state with similar bond lengths and angles. The tin(IV) atom in both complexes is four-coordinate and possesses a distorted tetrahedral geometry. The Sn–O bond distances, Sn–O–C$_{ipso}$ bond angles, and Sn–C bond distances for complexes **1** (Sn–O = 2.0263(11) Å, Sn–O–C$_{ipso}$ = 133.62(10)^o, Sn–C = 2.1252(17)–2.1264(13) Å) and **2** (Sn–O = 2.032(3) Å, Sn–O–C$_{ipso}$ = 121.20(18)^o, Sn-C = 2.117(3)–2.130(4) Å) are comparable to those reported for the handful of known four-coordinate trialkyltin aryloxide complexes: [1,4-(Et$_3$SnO)$_2$C$_6$Cl$_4$] (Sn–O = 2.08 Å, Sn–O–C$_{ipso}$ = 127^o, Sn–C = 2.15–2.21 Å),[8] (PhMe$_2$CCH$_2$)$_3$Sn(OC$_6$H$_4$-4-NO$_2$) (Sn–O = 2.0454(13) Å, Sn–O–C$_{ipso}$ = 127.98(12)^o, Sn–C = 2.1415(13)–2.1584(18) Å),[9] (CH$_3$)$_3$Sn(O-2,6-^{t}Bu$_2$C$_6$H$_4$-4-Me) (Sn–O = 2.0082(15) Å, Sn–O–C$_{ispo}$ = 133.77(14)^o, Sn–C = 2.127(2)–2.139(3) Å),[10] (CH$_3$)$_3$Sn[OC$_6$H$_4$-4-CMe$_2$-C$_6$H$_4$-4-OH] (Sn–O = 2.094(2) Å, Sn–O–C$_{ipso}$ = 127.60(10)^o, Sn–C = 2.115(3)–2.120(2) Å),[11] and (PhMe$_2$CCH$_2$)$_3$Sn(OC$_6$H$_4$-2-OMe-4-CHO) (Sn–O = 2.038(3) Å, Sn–O–C$_{ipso}$ = 127.1(2)^o, Sn–C = 2.142(4)–2.148(4) Å).[12] The only marked difference between the two trimethyltin aryloxide complexes are in the Sn(1)–O(1)–C(3)/C(4) angle which is larger for **1** (133.62(10)^o) than for **2** (121.20(18)^o) and is attributed to the greater steric interactions between the Me$_3$Sn group and the *ortho* ^{t}Bu versus ^{i}Pr substituents on the aromatic ring.

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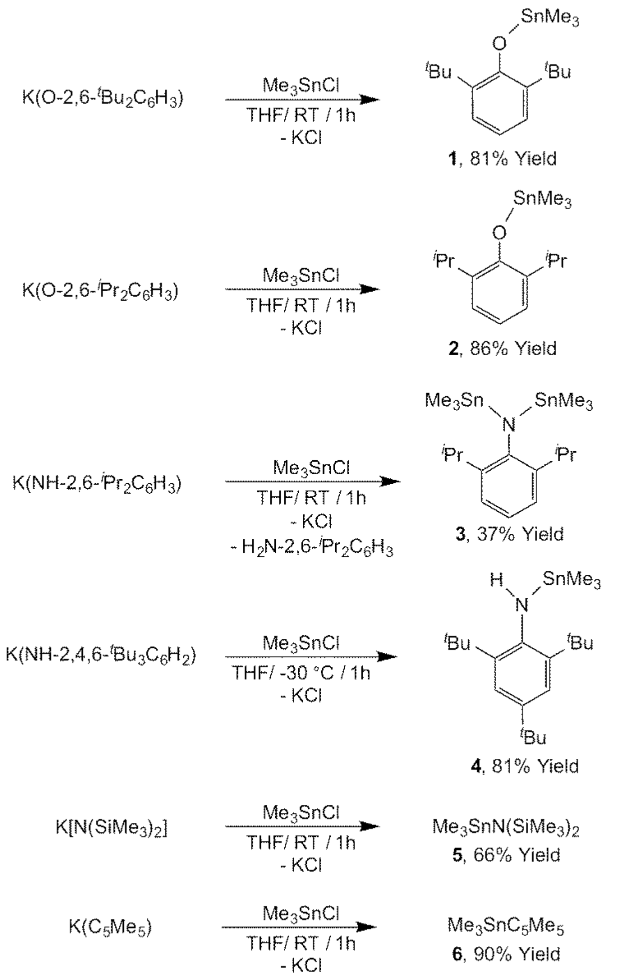
Electronic Supplementary Information (ESI) available: Crystallographic data for compounds **1**-**2** and **4** (CCDC reference numbers XXXXX-XXXXX) in CIF or other electronic format see DOI: 10.1039/x0xx00000x

Scheme 1. Synthetic Routes to Trimethyltin Alkoxide (**1**-**2**), Amide (**3**-**5**) and Cyclopentadienyl (**6**) Compounds



Similarly, reaction of a THF solution of Me$_3$SnCl with one equivalent of K(NH-2,6-^{i}Pr$_2$C$_6$H$_3$)·½THF at room temperature for 1 h afforded the redistribution products (Me$_3$Sn)$_2$N(2,6-^{i}Pr$_2$C$_6$H$_3$) (**3**) and H$_2$N-2,6-^{i}Pr$_2$C$_6$H$_3$. Cooling a saturated 1:5 toluene–acetonitrile solution of this mixture to -30 ^{o}C furnished **3** as a white crystalline solid in 37% isolated yield. Although **3** has been previously reported, the synthesis takes 2–4 days to complete and involved isolation of (Me$_3$Sn)(NH-2,6-^{i}Pr$_2$C$_6$H$_3$).[6f] The authors noted that the monostannylamine (Me$_3$Sn)(NH-2,6-^{i}Pr$_2$C$_6$H$_3$) is not thermodynamically stable; two equivalents of (Me$_3$Sn)(NH-2,6-^{i}Pr$_2$C$_6$H$_3$) similarly yielded a mixture of **3** and H$_2$N-2,6-^{i}Pr$_2$C$_6$H$_3$. The synthesis of Me$_3$Sn(NH-2,4,6-^{t}Bu$_3$C$_6$H$_2$) (**4**) has also been previously reported.[13] The authors reported that compound **4** is obtained by transmetallation from Me$_3$SnCl and Li(NH-2,4,6-^{t}Bu$_3$C$_6$H$_2$) in diethyl ether at room temperature. However, in our hands, this reaction consistently yielded a mixture of the redistribution products, H$_2$N-2,4,6-^{t}Bu$_3$C$_6$H$_2$ and (Me$_3$Sn)$_2$N(2,4,6-^{t}Bu$_3$C$_6$H$_2$). We found that reaction of K(NH-2,4,6-^{t}Bu$_3$C$_6$H$_2$) with Me$_3$SnCl in tetrahydrofuran at -30 ^{o}C, gave **4** in 81% yield following workup. Single crystals suitable for X-ray diffraction were grown from a saturated acetonitrile solution of **4** at -30 ^{o}C. The molecular structure of **4** is shown in Figure 3. Similar to the aryloxide complexes discussed above, the tin(IV) atom in **4** is four-coordinate and possesses a distorted tetrahedral geometry. The most relevant aspects of the structure are the Sn–N bond distance, Sn–N–C$_{ipso}$ bond angle, and the Sn–C bond distances (Sn–N = 2.098(6) Å, Sn–N–C$_{ipso}$ = 125.4(6)^o, Sn–C = 2.098(6)–2.152(11) Å), which compare favorably with those reported for the few structurally characterized four-coordinate trialkyltin arylamide complexes: (Me$_3$Sn)$_2$(NC$_6$H$_5$) (Sn–N = 2.053(3), 2.058(3) Å, Sn–N–C$_{ipso}$ = 119.8(2), 118.7(2)^o, Sn-C = 2.133(4)–2.142(4) Å),[6c] (Me$_3$Sn)$_2$(N-2,6-^{i}Pr$_2$C$_6$H$_3$) (Sn–N = 2.044(3) Å, Sn-N-C$_{ipso}$ = 117.5(2)^o, Sn–C = 2.118(6)–2.122(8) Å),[6f] [1,3-{(Me$_3$Sn)(-2,6-^{i}Pr$_2$C$_6$H$_3$)NCH$_2$}$_2$C$_6$H$_4$] (Sn–N = 2.0454(13) Å, Sn–N–C$_{ipso}$ = 127.98(12)^o, Sn–C = 2.1318(23)–2.1584(18) Å).[14] Finally, preparation of the known compounds Me$_3$SnN(SiMe$_3$)$_2$ (**5**) and Me$_3$Sn(C$_5$Me$_5$) (**6**) is straightforward by reaction of Me$_3$SnCl with K[N(SiMe$_3$)$_2$] or K(C$_5$Me$_5$), respectively, yielding the products in 66% and 90% isolated yields.

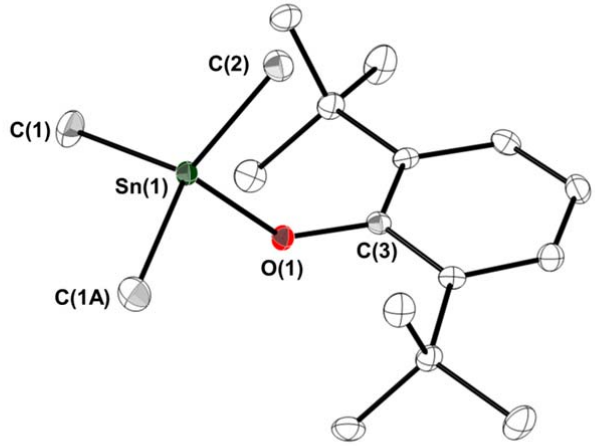


Fig. 1 Molecular structure of Me$_3$Sn(O-2,6-^{t}Bu$_2$C$_6$H$_3$) (**1**) with thermal ellipsoids projected at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (^{o}): Sn(1)–O(1), 2.0263(11); Sn(1)–C(1), 2.1265(13); Sn(1)–C(1A), 2.1264(13); Sn(1)–C(2), 2.1252(17); C(3)–O(1), 1.3536(19); Sn(1)–O(1)–C(3), 133.62(10); C(1)–Sn(1)–C(1A), 107.20(8); C(1)–Sn(1)–C(2), 119.87(4); C(1)–Sn(1)–O(1), 102.89(4).

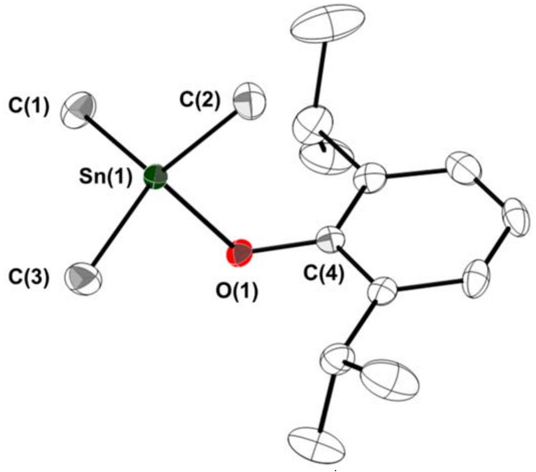


Fig. 2 Molecular structure of Me$_3$Sn(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (**2**) with thermal ellipsoids projected at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (^{o}): Sn(1)–O(1), 2.032(3); Sn(1)–C(1), 2.123(4); Sn(1)–C(2), 2.117(3); Sn(1)–C(3), 2.130(4); C(4)–O(1), 1.364(4); Sn(1)–O(1)–C(4), 121.20(18); C(1)–Sn(1)–C(2), 118.99(16); C(1)–Sn(1)–C(3), 118.69(13); C(1)–Sn(1)–O(1), 101.74(13).

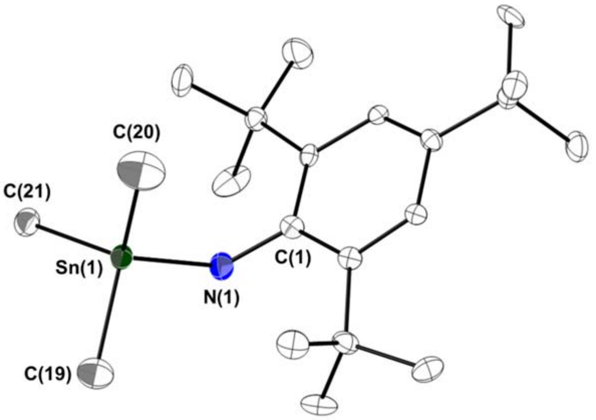


Fig. 3 Molecular structure of $Me_3Sn(NH\text{-}2,4,6\text{-}{}^tBu_3C_6H_2)$ (**4**) with thermal ellipsoids projected at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Sn(1)–N(1), 2.098(6); Sn(1)–C(19), 2.152(11); Sn(1)–C(20), 2.129(12); Sn(1)–C(21), 2.098(6); C(1)–N(1), 1.390(12); Sn(1)–N(1)–C(1), 125.4(6); C(19)–Sn(1)–C(20), 115.6(5); C(19)–Sn(1)–C(21), 106.9(2); C(19)–Sn(1)–N(1), 106.9(2).

NMR Studies

The $^{119}Sn\{^1H\}$, ^1H and $^{13}C\{^1H\}$ NMR spectral data for the Me_3SnX (X = $O\text{-}2,6\text{-}{}^tBu_2C_6H_3$ (**1**), $O\text{-}2,6\text{-}{}^iPr_2C_6H_3$ (**2**), $(Me_3Sn)N(2,6\text{-}{}^iPr_2C_6H_3)$ (**3**), $NH\text{-}2,4,6\text{-}{}^tBu_3C_6H_2$ (**4**), $N(SiMe_3)_2$ (**5**), NEt_2, C_5Me_5 (**6**), Cl, Br, I, and $SnMe_3$) compounds are given in Tables 1, 2, and 3, respectively. The ^1H NMR chemical shifts are reported at two concentrations (4–10 mM and 0.3–1.0 M) while the $^{13}C\{^1H\}$ chemical shifts are only reported at the higher concentration in benzene–d_6, toluene–d_8, dichloromethane–d_2, chloroform–d_1, acetonitrile–d_3, and tetrahydrofuran–d_8. The $^{119}Sn\{^1H\}$ chemical shifts are reported at 0.3–1.0 M concentrations in benzene–d_6 and chloroform–d_6. Table 1 shows the $^{119}Sn\{^1H\}$ NMR data in benzene-d_6 for all complexes, except **1**, where chloroform–d_1 was used. The $^{119}Sn\{^1H\}$ resonances in benzene for Me_3SnX (X = halides, NEt_2, $N(SiMe_3)_2$ and $SnMe_3$)[6d, 6e, 6g] have been reported before and are shown here for completion. Thorough reviews discussing trends in $^{119}Sn\{^1H\}$ NMR have been previously reported and it is sufficient to say that resonance shifts are dependent on the electron density of the element attached to tin, the concentration of the sample, and the solvents used.[6e]

Table 2 shows the ^1H NMR data. Me_3SnNEt_2 was unstable in acetonitrile-d_3; hence no data could be obtained in that solvent. The observed $J_{1H\text{-}119Sn}$ constant for the Me_3Sn group of all complexes is measured to be between 49–61 Hz, which is typical of this type of coupling.[6e] In polar solvents the peaks are generally shifted downfield relative to nonpolar solvents, except for those of **3** and **6** where the resonances stay relatively in the same region regardless of solvent used. The difference can be ascribed to the higher steric demands of these complexes, which may prevent direct binding of polar solvent molecules to the tin center. The ^1H NMR trimethyltin resonances of all tin complexes are dependent on concentration of analyte. Dilute samples (4–10 mM) generally shift downfield relative to the higher concentration samples (0.3–1.0 M), but there are notable exceptions. For instance, **2** and Me_3SnX (X = halides) shift upfield when dilute in benzene–d_6 and toluene–d_8. Similarly, an upfield shift of the Me_3Sn proton signal is observed for dilute solutions of **1**, **2** and **4** in chloroform–d_1. In tetrahydrofuran–d_8 the Me_3Sn resonance of **2** is the only one that shifts at different concentrations. In benzene–d_6 and toluene–d_8 the Me_3Sn proton resonances of **4**, **5**, and Me_3SnNEt_2 remain unchanged regardless of concentration.

Table 3 shows ^{13}C NMR data for all complexes. Compound **1** is sparingly soluble in benzene–d_6, toluene–d_8, and acetonitrile–d_3; $^{13}C\{^1H\}$ NMR data could not be obtained in those solvents. Compound **3** is sparingly soluble in acetonitrile–d_3, thus suitable $^{13}C\{^1H\}$ NMR data could not be obtained in this solvent. As observed in Table 2, the Me_3Sn resonance in the $^{13}C\{^1H\}$ NMR shifts farther downfield with solvent polarity. However, there is a difference between the Me_3Sn resonances in dichloromethane-d_2 or chloroform-d_1 and those found in acetonitrile-d_3 or tetrahydrofuran-d_8, with the latter two having the most upfield resonances. The $J_{13C\text{-}119Sn}$ coupling constants for the Me_3Sn resonance reside mostly in the 300-400 Hz range.

Table 1 - ^{119}Sn NMR Data of Organometallic Tin(IV) Compounds.

Compound	δ
$Me_3Sn(O\text{-}2,6\text{-}{}^tBu_2C_6H_3)$ (**1**)	129.9[b]
$Me_3Sn(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ (**2**)	138.2
$(Me_3Sn)_2(N\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ (**3**)	64.2
$Me_3Sn(NH\text{-}2,4,6\text{-}{}^tBu_3C_6H_2)$ (**4**)	63.3
$Me_3SnN(SiMe_3)_2$ (**5**)	46.7[a]
Me_3SnNEt_2	60.0[a]
$Me_3Sn(C_5Me_5)$ (**6**)	48.2
Me_3SnCl	164.2[a]
Me_3SnBr	128.0[a]
Me_3SnI	38.6[a]
$Me_3Sn\text{-}SnMe_3$	-109.0[a]

All NMR resonances are reported in ppm and externally referenced to 20% Me_3SnBr in C_6D_6, unless otherwise noted. Sample concentration range = 0.3–1.0 M. [a]Resonances were previously reported.[6e, 6g] [b]Resonance was measured in $CDCl_3$ with 20% Me_3SnBr as the standard.[6g]

Conclusions

The synthesis and X-ray characterization of complexes **1**,**2** and **4** have been presented and discussed. These data add to the rather small number of trimethyl tin compounds characterized crystallographically in the literature. A modified synthetic route was also presented for complexes **3**–**6** that simplifies purification. The ^1H, $^{13}C\{^1H\}$, and $^{119}Sn\{^1H\}$ NMR data of complexes **1**–**6**, along with Me_3SnX (X = NEt_2, Cl, Br, I, $SnMe_3$) in six common deuterated organic solvents were presented in tabulated form, which we hope will better aid the future researchers to identify tin(IV) compounds present in reactions involving trimethyltin.

Experimental

General Synthetic Considerations

Unless otherwise noted, all reactions and manipulations were performed at 20 °C in a recirculating Vacuum Atmospheres NEXUS 2 model inert atmosphere (N_2) drybox equipped with a 40CFM Dual Purifier NI-Train. Glassware was dried overnight at 150 °C before use. All NMR spectra were obtained using a Bruker Avance 400 MHz spectrometer at room temperature. Chemical shifts for ^1H and $^{13}C\{^1H\}$ NMR spectra were referenced to solvent impurities.[15] $^{119}Sn\{^1H\}$ NMR spectra were referenced to a 20% Me_3SnBr solution in the corresponding deuterated NMR solvent.[6g] Melting points were determined with a Mel-Temp II capillary melting point apparatus equipped with a Fluke 50S K/J thermocouple using capillary tubes flame-sealed under N_2; values are uncorrected. Elemental Analyses were performed by ALS Environmental (Tucson, AZ).

Table 2. ^{1}H NMR Data of Organometallic Tin(IV) Compounds.

Compound	Proton	Mult	$J_{^1H-^1H}$	$J_{^1H-^{119}Sn}$	C_6D_6	Tol-d_8	CD_2Cl_2	$CDCl_3$	CD_3CN	THF-d_8
$Me_3Sn(O\text{-}2,6\text{-}{}^tBu_2C_6H_3)$ (**1**)	SnCH_3	s		54.3	(0.32)	(0.33)	0.62 (0.60)	0.62 (0.60)	(0.57)	0.58 (0.56)
	^{t}Bu-CH_3	s			(1.49)	(1.45)	1.41 (1.39)	1.43 (1.41)	(1.38)	1.39 (1.37)
	p-Ar*H*	t	7.84		(6.90)	(6.81)	6.66 (6.65)	6.73 (6.71)	(6.60)	6.52 (6.51)
	m-Ar*H*	d	7.77		(7.35)	(7.26)	7.16 (7.14)	7.21 (7.19)	(7.12)	7.06 (7.04)
$Me_3Sn(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ (**2**)	SnCH_3	s		55.7	0.25 (0.20)	0.20 (0.20)	0.52 (0.54)	0.51 (0.48)	0.44 (0.49)	0.44 (0.49)
	^{i}Pr-CH_3	d	7.98		1.27 (1.30)	1.24 (1.26)	1.23 (1.26)	1.22 (1.19)	1.15 (1.20)	1.15 (1.20)
	^{i}Pr-C*H*	m	6.72		3.38 (3.41)	3.32 (3.35)	3.27 (3.31)	3.27 (3.24)	3.24 (3.31)	3.25 (3.31)
	p-Ar*H*	t	7.45		6.93 (7.00)	6.88 (6.91)	6.82 (6.86)	6.86 (6.83)	6.72 (6.78)	6.63 (6.68)
	m-Ar*H*	d	8.07		7.12 (7.36)	7.06 (7.08)	7.04 (7.08)	7.05 (7.02)	6.97 (7.02)	6.90 (6.95)
$(Me_3Sn)_2(N\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ (**3**)	SnCH_3	s		55.7	0.14 (0.15)	0.12 (0.13)	0.15 (0.22)	0.13* (0.24)	(0.12)	0.15 (0.15)
	^{i}Pr-CH_3	d	7.56		1.19 (1.20)	1.16 (1.17)	1.11 (1.19)	1.10* (1.22)	(1.09)	1.11 (1.12)
	^{i}Pr-C*H*	m	6.99		3.77 (3.78)	3.74 (3.75)	3.68 (3.76)	3.65* (3.77)	(3.70)	3.71 (3.72)
	p-Ar*H*	t	7.84		7.01 (7.01)	6.94 (6.94)	6.87 (6.95)	6.88* (7.01)	(6.84)	6.80 (6.82)
	m-Ar*H*	d	7.37		7.07 (7.09)	7.02 (7.01)	6.98 (7.06)	6.98* (7.10)	(6.98)	6.95 (6.96)
$Me_3Sn(NH\text{-}2,4,6\text{-}{}^tBu_3C_6H_2)$ (**4**)	SnCH_3	s		51.7	0.17 (0.17)	0.16 (0.16)	0.29 (0.39)	0.30 (0.19)	(0.26)	0.24 (0.24)
	p-^{t}Bu-CH_3	s			1.38 (1.38)	1.34 (1.35)	1.28 (1.40)	1.29 (1.21)	(1.26)	1.26 (1.27)
	o-^{t}Bu-CH_3	s			1.56 (1.56)	1.52 (1.53)	1.47 (1.59)	1.49 (1.40)	(1.46)	1.46 (1.47)
	N-*H*	s			2.68 (2.68)	2.62 (2.63)	2.73 (2.84)	2.76 (2.65)	(2.75)	2.76 (2.77)
	m-Ar*H*	s			7.48 (7.48)	7.39 (7.41)	7.21 (7.45)	7.24 (7.04)	(7.22)	7.19 (7.29)
$Me_3SnN(SiMe_3)_2$ (**5**)	SiCH_3	s			0.21 (0.22)	0.17 (0.19)	0.11 (0.21)	0.10 (0.22)	0.10 (0.08)	0.11 (0.12)
	SnCH_3	s		54.7	0.25 (0.25)	0.24 (0.24)	0.33 (0.42)	0.32 (0.43)	0.33 (0.31)	0.34 (0.34)
Me_3SnNEt_2	SnCH_3	s		54.1	0.14 (0.14)	0.12 (0.13)	0.24 (0.29)	0.47 (0.59)	IC	0.17 (0.17)
	NCH_2CH_3	t	7.02		1.06 (1.06)	1.02 (1.04)	1.05 (1.10)	1.08 (1.21)		0.98 (0.99)
	NCH_2	q	7.05		3.00 (2.99)	2.95 (2.97)	2.97 (3.02)	2.62 (2.74)		2.91 (2.93)
$Me_3Sn(C_5Me_5)$ (**6**)	SnCH_3	s		49.6	-0.06 (-0.05)	-0.08 (-0.07)	-0.04(-0.00)	-0.02(-0.02)	-0.08(-0.04)	-0.07 (-0.07)
	$C_5(CH_3)_5$	s		19.7	1.79 (1.83)	1.77 (1.78)	1.80 (1.85)	1.85 (1.89)	1.76 (1.80)	1.76 (1.77)
Me_3SnCl	SnCH_3	s		59.5	0.29 (0.22)	0.28 (0.23)	0.65 (0.70)	0.64 (0.74)	0.60 (0.65)	0.58 (0.59)
Me_3SnBr	SnCH_3	s		56.4	0.40 (0.32)	0.35 (0.33)	0.75 (0.83)	0.75 (0.83)	0.72 (0.77)	0.70 (0.70)
Me_3SnI	SnCH_3	s		61.5	0.48 (0.46)	0.50 (0.48)	0.88 (0.93)	0.87 (0.96)	0.87 (0.91)	0.88 (0.87)
$Me_3Sn\text{-}SnMe_3$	SnCH_3	s		47.8	0.25 (0.25)	0.23 (0.24)	0.22 (0.20)	0.21 (0.20)	0.19 (0.18)	0.21 (0.21)

All NMR resonances are reported in ppm. Sample concentration range = 0.3–1.0 M. Values in parenthesis for sample concentration range = 4–10 mM. $J_{^1H-^1H}$ and $J_{^1H-^{119}Sn}$ coupling constants are reported in Hz. Multiplicity listed as singlet (s), doublet (d), triplet (t), quartet (q), or multiplet (m). All resonances are referenced to solvent impurities.[15] IC = incompatible solvent. *Resonances previously reported.[6f]

Table 3. ^{13}C{^{1}H} NMR Data of Organometallic Tin(IV) Compounds.

Compound	Carbon	$J_{^{13}\mathrm{C}\text{-}^{119}\mathrm{Sn}}$	C_6D_6	Tol-d_8	CD_2Cl_2	$CDCl_3$	CD_3CN	THF-d_8
$Me_3Sn(O\text{-}2,6\text{-}{}^tBu_2C_6H_3)$ (**1**)	Sn*C*H$_3$	392	SS	SS	1.02	1.07	SS	1.02
	^{t}Bu-*C*H$_3$				31.45	31.34		31.60
	^{t}Bu-*C*				35.51	35.34		35.58
	Ar-*C*				118.24	118.00		117.81
	Ar-*C*				125.70	125.46		125.48
	Ar-*C*				141.38	141.08		140.95
	Ar-*C*O				160.52	160.17		161.14
$Me_3Sn(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ (**2**)	Sn*C*H$_3$	391	-3.23	-3.48	-2.76	-2.77	-2.13	-2.73
	^{i}Pr-*C*H$_3$		23.76	23.72	23.75	23.67	23.79	23.64
	^{i}Pr-*C*H		27.49	27.50	27.33	26.94	27.58	27.55
	Ar-*C*		119.87	120.07	119.69	119.58	119.64	118.73
	Ar-*C*		123.35	123.33	123.30	123.04	123.68	122.94
	Ar-*C*		139.09	139.04	139.55	139.24	139.94	139.06
	Ar-*C*O		156.25	156.05	155.93	155.18	157.14	157.21
$(Me_3Sn)_2(N\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ (**3**)	Sn*C*H$_3$	368	-4.24	-4.30	-4.18	-4.34*	-4.18	-4.42
	^{i}Pr-*C*H$_3$		24.78	24.74	24.70	24.42*	24.75	24.69
	^{i}Pr-*C*H		27.43	27.44	27.42	26.95*	27.74	27.65
	Ar-*C*	9.8	122.54	122.60	121.81	121.27*	122.33	122.30
	Ar-*C*	9.1	123.17	123.13	122.93	122.46*	123.43	123.13
	Ar-*C*	13.3	146.92	146.88	147.40	146.78*	147.97	147.23
	Ar-*C*N		150.41	150.34	151.00	150.30*	SS	150.99
$Me_3Sn(NH\text{-}2,4,6\text{-}{}^tBu_3C_6H_2)$ (**4**)	Sn*C*H$_3$	376	-3.21	-3.30	-2.88	-2.79	-2.79	-3.34
	^{t}Bu-*C*H$_3$		31.99	31.96	31.82	31.81	31.98	31.91
	^{t}Bu-*C*H$_3$		32.51	32.52	32.31	32.29	32.51	32.54
	^{t}Bu-*C*		34.64	34.63	34.66	34.51	34.99	34.77
	^{t}Bu-*C*		36.30	36.30	36.28	36.11	36.99	36.52
	Ar-*C*		122.43	122.35	122.49	122.26	122.99	122.33
	Ar-*C*		141.05	140.99	140.67	140.43	141.08	140.79
	Ar-*C*		142.69	142.69	142.22	141.79	143.03	142.92
	Ar-*C*N		148.05	147.96	148.32	147.95	149.10	148.52
$Me_3SnN(SiMe_3)_2$ (**5**)	Sn*C*H$_3$	379	-0.89$^+$	-0.92	-0.68	-0.70	-0.73	-0.82
	Si*C*H$_3$		5.66$^+$	5.64	5.57	5.50	5.63	5.63
Me_3SnNEt_2	Sn*C*H$_3$	373	-6.65	-6.67	-6.53	-7.06	IC	-6.89
	NCH$_2$*C*H$_3$		17.51	17.56	17.13	15.49		17.47
	N*C*H$_2$		46.70	46.73	46.70	44.05		46.81
$Me_3Sn(C_5Me_5)$ (**6**)	Sn*C*H$_3$	303	-9.38	-9.46	-9.23	-9.19	-9.38	-9.71
	C$_5$(*C*H$_3$)$_5$		11.92	11.84	11.88	11.72	11.85	11.68
	C$_5$(CH$_3$)$_5$		118.39	118.38	118.50	118.22	118.88	118.58
Me_3SnCl	Sn*C*H$_3$	369	-1.48	-1.69	-0.79	-0.76	0.68	0.07
Me_3SnBr	Sn*C*H$_3$	357	-1.37	-1.81	-0.81	-0.86	1.10	0.47
Me_3SnI	Sn*C*H$_3$	342	-2.09	-2.25	-1.22	-1.24	1.28	0.83
$Me_3Sn\text{-}SnMe_3$	Sn*C*H$_3$	238	-10.08	-10.09	-9.94	-9.99	-10.13	-10.32

All NMR resonances are reported in ppm. Sample concentration range = 0.3–1.0 M. $J_{^{13}\mathrm{C}\text{-}^{119}\mathrm{Sn}}$ coupling constants are reported in Hz. All resonances are referenced to solvent impurities.[15] IC = incompatible solvent. SS = sparingly soluble in solvent. *Resonances previously reported.[6f] $^+$Resonances previously reported.[6d]

Materials.

Unless otherwise noted, reagents were purchased from commercial suppliers and used without further purification. Celite (Aldrich), alumina (Brockman I, Aldrich), and 3 Å molecular sieves (Aldrich) were dried under dynamic vacuum at 250 °C for 48 h prior to use. All solvents (Aldrich) were purchased anhydrous, dried over KH for 48 h, passed through a column of activated alumina, and stored over activated 3 Å molecular sieves prior to use. Benzene–d_6, toluene–d_8, and tetrahydrofuran–d_8 (all Cambridge Isotopes) were dried over KH for 48 h, passed through a column of activated alumina, and stored over activated 3 Å molecular sieves prior to use. Chloroform–d_1, dichloromethane–d_2, and acetonitrile–d_3 (all Cambridge Isotopes) were dried over activated 3 Å molecular sieves for 48 h, passed through a column of activated alumina and stored over fresh 3 Å molecular sieves for one day prior to use. Me$_3$SnCl (Acros), Me$_3$SnBr (Aldrich) and Me$_3$SnI (Gelest) were purchased and used without further purification. K(C$_5$Me$_5$),[16] K(O-2,6-^{i}Pr$_2$C$_6$H$_3$),[16] K(O-2,6-^{t}Bu$_2$C$_6$H$_3$),[16] and Me$_3$SnNEt$_2$,[6i] were prepared according to literature procedures.

Synthesis of K(NH-2,6-^{i}Pr$_2$C$_6$H$_3$)·½THF. This is a modification of a literature procedure.[17] A 20 mL scintillation vial equipped with a stir bar was charged with H$_2$N-2,6-^{i}Pr$_2$C$_6$H$_3$ (0.990 g, 5.58 mmol) and THF (5 mL). K[N(SiMe$_3$)$_2$] (1.14 g, 5.58 mmol) was added as a solid to the resulting solution and the reaction mixture was stirred at room temperature for 2 h. The volatiles were then removed under reduced pressure to give K(NH-2,6-^{i}Pr$_2$C$_6$H$_3$)·½THF as a white solid (1.40 g, 5.56 mmol, 99%). ^{1}H NMR (THF–d_8): δ 6.58 (2H, d, $J_{H,H}$ = 7.3 Hz, *m-H*), 5.84 (1H, t, $J_{H,H}$ = 7.3 Hz, *p-H*), 3.62 (4H, THF), 3.49 (1H, s, N*H*), 3.13 (2H, hept, $J_{H,H}$ = 6.8 Hz, C*H*Me$_2$), 1.77 (4H, THF), 1.16 (12H, d, $J_{H,H}$ = 6.8 Hz, CH(C*H*$_3$)$_2$).

Synthesis of K(NH-2,4,6-^{t}Bu$_3$C$_6$H$_2$). This is a modification of a literature procedure.[18] A 50 mL round bottom flask equipped with a stir bar was charged with H$_2$N-2,4,6-^{t}Bu$_3$C$_6$H$_2$ (4.07 g, 15.5 mmol) and THF (20 mL). While stirring, KN(SiMe$_3$)$_2$ (3.10 g, 15.5 mmol) was added as a solid. The solution became increasingly cloudy, and the white suspension was stirred for 18 h at room temperature. The reaction mixture was filtered through a medium-porosity fritted filter to collect a white powder, which was washed with hexane (3 x 10 mL) and dried under reduced pressure to give K(NH-2,4,6-^{t}Bu$_3$C$_6$H$_2$) as a white powder (4.33 g, 14.4 mmol, 93%). ^{1}H NMR (THF–d_8): δ 6.73 (2H, s, *m-H*), 3.38 (1H, s, N*H*), 1.45 (18H, s, *o*-C(C*H*$_3$)$_3$), 1.17 (9H, s, *p*-C(C*H*$_3$)$_3$).

Synthesis of Me$_3$Sn(O-2,6-^{t}Bu$_2$C$_6$H$_3$) (1). A 20 mL scintillation vial was charged with a stir bar, K(O-2,6-^{t}Bu$_2$C$_6$H$_3$) (0.300 g, 1.23 mmol), Me$_3$SnCl (0.245 g, 1.23 mmol), and THF (5 mL). The reaction mixture was stirred at room temperature for 1 h, after which the volatiles were removed under reduced pressure. The resulting solid was redissolved in toluene (20 mL) and filtered through a Celite-padded coarse-porosity fritted filter. The colorless filtrate was collected and the volatiles were removed under reduced pressure to give Me$_3$Sn(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (**1**) as a white solid (0.370 g, 1.00 mmol, 81%). Crystals suitable for X-ray diffraction were obtained by dissolving compound **1** in hot toluene (100 °C) and then cooling the concentrated solution to room temperature. m.p. 197-199 °C. Anal. Calcd for C$_{17}$H$_{30}$OSn (mol. wt. 369.13 g mol^{-1}): C, 55.31; H, 8.19. Found: C, 55.56; H, 8.66.

Synthesis of Me$_3$Sn(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (2). A 20 mL scintillation vial was charged with a stir bar, K(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (0.300 g, 1.39 mmol), Me$_3$SnCl (0.276 g, 1.39 mmol), and THF (5 mL). The solution was stirred at room temperature for 1 h, after which the volatiles were removed under reduced pressure. The resulting solid was redissolved in toluene (5 mL) and filtered through a Celite-padded coarse-porosity fritted filter. The colorless filtrate was collected and the volatiles were removed under reduced pressure to give Me$_3$Sn(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (**2**) as an off-white pink solid (0.407 g, 1.19 mmol, 86%). Crystals suitable for X-ray diffraction were obtained by dissolving compound **2** in hot toluene (100 °C), cooling the concentrated solution to room temperature, and then storing it at -30 °C for 2 d. m.p. 86-88 °C. Anal. Calcd for C$_{15}$H$_{26}$OSn (mol. wt. 341.08 g mol^{-1}): C, 52.82; H, 7.68. Found: C, 52.20; H, 8.24.

Synthesis of (Me$_3$Sn)$_2$(NH-2,6-^{i}Pr$_2$C$_6$H$_3$) (3). This is a modification of a literature procedure.[6f] A 20 mL scintillation vial was charged with a stir bar, K(NH-2,6-^{i}Pr$_2$C$_6$H$_3$)·½THF (0.500 g, 1.99 mmol), Me$_3$SnCl (0.396 g, 1.99 mmol), and THF (5 mL). The solution was stirred at room temperature for 1 h, after which the volatiles were removed under reduced pressure. The resulting solid was redissolved in toluene (60 mL) and filtered through a Celite-padded coarse-porosity fritted filter. The colorless filtrate was collected and the volatiles removed to yield an oily residue (mixture of **3** and H$_2$N-2,6-^{i}Pr$_2$C$_6$H$_3$). The residue was dissolved in a 1:5 toluene:acetonitrile solution and stored at -30 °C overnight to give (Me$_3$Sn)$_2$(N-2,6-^{i}Pr$_2$C$_6$H$_3$ (**3**) as a white crystalline solid, which was collected by filtration and dried under reduced pressure (0.184 g, 0.366 mmol, 37%).

Synthesis of Me$_3$Sn(NH-2,4,6-^{t}Bu$_3$C$_6$H$_2$) (4). This is a modification of a literature procedure.[13] A 20 mL scintillation vial was charged with K(NH-2,4,6-^{t}Bu$_3$C$_6$H$_2$) (0.100 g, 0.332 mmol) and THF (15 mL) and cooled to -30 °C. A 50 mL round bottom flask was charged with a stir bar, Me$_3$SnCl (0.069 g, 0.332 mmol), and THF (5 mL), and cooled down to -30 °C. The cooled K(NH-2,4,6-^{t}Bu$_3$C$_6$H$_2$)/THF solution was added dropwise with stirring over the course of 10 min to the cooled Me$_3$SnCl/THF solution. The reaction mixture was warmed to room temperature and stirred 1 h, after which the volatiles were removed under reduced pressure. The resulting solid was redissolved in toluene (10 mL) and filtered through a Celite-padded coarse-porosity fritted filter. The filtrate was collected and the volatiles were removed under reduced pressure to yield a white solid powder containing Me$_3$Sn(NH-2,4,6-^{t}Bu$_3$C$_6$H$_2$) (**4**) (0.114 g, 0.269 mmol, 81%). Crystals of **4** suitable for X-ray diffraction were grown by dissolving this white solid in acetonitrile and storing at -30 °C for two days.

Synthesis of Me$_3$SnN(SiMe$_3$)$_2$ (5). This is a modification of a literature procedure.[19] A 20 mL scintillation vial was charged with a stir bar, KN(SiMe$_3$)$_2$ (0.300 g, 1.50 mmol), Me$_3$SnCl (0.300 g, 1.50 mmol), and THF (5 mL). The reaction mixture was stirred at room temperature for 1 h, after which the volatiles were removed under reduced pressure. The resulting solid was redissolved in toluene (5 mL) and filtered through a Celite-padded coarse-porosity fritted filter. The colorless filtrate was collected and the volatiles were removed under reduced pressure to yield Me$_3$SnN(SiMe$_3$)$_2$ (**5**) as an oil (0.323 g, 0.995 mmol, 66%). NOTE: It is important not to leave this product under vacuum for prolonged periods of time (after solvent removal) because the product is slightly volatile.

Synthesis of Me$_3$Sn(C$_5$Me$_5$) (6). This is a modification of a literature procedure.[6h] A 20 mL scintillation vial was charged with a stir bar, K(C$_5$Me$_5$) (0.100 g, 0.574 mmol), Me$_3$SnCl (0.114 g, 0.574 mmol), and THF (5 mL). The reaction mixture was stirred at room temperature for 1 h, after which time the volatiles were removed under reduced pressure. The resulting solid was redissolved in toluene (5 mL) and filtered through a Celite-padded coarse-porosity fritted filter. The colorless filtrate was collected and the volatiles were removed under reduced pressure to yield $Me_3Sn(C_5Me_5)$ (**6**) as an oil (0.154 g, 0.515 mmol, 90%). NOTE: It is important not to leave this product under vacuum for prolonged periods of time (after solvent removal) because the product is slightly volatile.

X-ray Crystallography.

Crystals of **1**-**4** were mounted in nylon cryoloops from Paratone-N oil. The data were collected on a Bruker D8 diffractometer, with APEX II charge-coupled-device (CCD) detector, and Bruker Kryoflex liquid N_2 low temperature device (140 K). The instrument was equipped with graphite monochromatized MoKα X-ray source (λ= 0.71073 Å) and a 0.5 mm monocapillary. A hemisphere of data was collected using ω scans, with 10-second frame exposures and 0.5º frame widths. Data collection and initial indexing and cell refinement were handled using APEX II software.[20] Frame integration, including Lorentz-polarization corrections, and final cell parameter calculations were carried out using SAINT+ software.[21] The data were corrected for absorption using redundant reflections and the SADABS program.[22] Decay of reflection intensity was not observed, as monitored by analysis of redundant frames. The structures were solved using direct methods and difference Fourier techniques. Unless otherwise noted, non-hydrogen atoms were refined anisotropically and hydrogen atoms were treated as idealized contributions. For compound **4**, the tin atom and two methyl groups (C(19) and C(20)) reside on a mirror plane, with the third methyl group, C(21), and the aryl amine group disordered across the mirror plane. The amine nitrogen atom, N(1) and methyl group, C(21), were each refined at one half-occupancy, with coordinates and temperature factors constrained to be identical. Hydrogen atom positions were not included in the model due to the disorder. Structure solution, refinement, graphics, and creation of publication materials were performed using SHELXTL.[23]

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