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Structural and Mechanistic Studies of Halogenation of a Tin(II) N-Functionalized Alkyl

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The halogenation of the tin(II) alkyl SnR^1_2 (**1**) [$R^1 = CH(SiMe_3)C_9H_6N\text{-}8$] to give $R^1_2SnX_2$ [X = F (**2**), Cl (**3**), Br (**4**), I (**5**)] was investigated by reacting **1** with SnX_2 (X = F, Cl, Br, and I), $PbCl_2$, BCl_3, and X_2 (X = Br, I), respectively. ^1H, ^{119}Sn NMR and X-ray analysis showed that the reactions with SnX_2 under a milder experimental condition afforded intermediate compounds, $R^1_2Sn{\rightarrow}SnX_2$ [X = Cl (**6**), Br (**7**)] and R^1SnX [X = Cl (**8**), Br (**9**)]. Further heating gave the final products R_2SnX_2. The X-ray structures of **2**−**6** and **9** have been determined. The dynamic exchange process between diastereoisomers of R^1SnX (X = Cl, Br) has been studied by variable-temperature ^1H and ^{119}Sn NMR spectroscopy.

Introduction

Bivalent group 14 metal alkyls MR_2 (M = Ge, Sn, or Pb) are considered to be carbene analogues, and their reactivities have been reviewed by Lappert and co-workers.[1] For example, the dialkylstannylene $[Sn\{CH(SiMe_3)_2\}_2]$ can behave as (i) a Lewis base or (ii) a Lewis acid or (iii) can undergo oxidative-addition (insertion reactions). In particular, the reaction of SnR_2 and $SnCl_2$ to give SnR_2Cl_2 has been reported.[2] The reaction mechanism of this halogenation of tin(II) alkyls was proposed to involve transition state **A** for R^- capable of functioning in a bridging mode, such as $[C(SiMe_3)_2C_5H_4N\text{-}2]^-$, and transition state **B** if R^- is a nonfunctioning ligand such as $[CH(SiMe_3)_2]^-$ (Figure 1).

We have reported the oxidative-addition reactions of tin(II) alkyls SnR^1_2 (**1**) with chalcogen to form stannachalcogenones.[3] We also communicated the synthesis and structure of $R^1_2Sn{\rightarrow}SnCl_2$ (**6**) [$R^1 = CH(SiMe_3)C_9H_6N\text{-}8$] isolated as the intermediate compound from the reaction between SnR^1_2 and $SnCl_2$.[4] We now report more details of the halogenation reactions of SnR^1_2. By different synthetic routes, we have prepared and structurally characterized a series of dialkyltin dihalides $SnR^1_2X_2$ (X = F, Cl, Br, I) and some of the reaction intermediates.

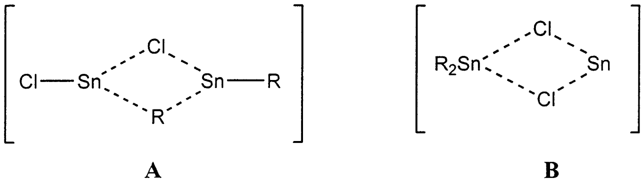

Figure 1.

Results and Discussion

The Reaction of SnR^1_2 (1) with SnX_2 (X = F, Cl, Br, I). Reactions between SnR^1_2 (**1**) and SnX_2 (X = F, Cl, Br, I) have been investigated under different experimental conditions. By heating the reaction mixture for over 2 h, $SnR^1_2X_2$ [X = F (**2**), Cl (**3**), Br (**4**), I (**5**)] and tin metal, respectively, were obtained. This is similar to the results reported by Lappert and co-workers, in whose hands the redistribution reaction of $SnCl_2$ with $[Sn\{CH(SiMe_3)_2\}_2]$ has led to the formation of $[Sn\{CH(SiMe_3)_2\}_2Cl_2]$ and tin metal. The formation of $(RSnCl)_n$ [$R = C(SiMe_3)_2C_5H_4N\text{-}2$, $n = 1$; or $R = N(SiMe_3)_2$, $n = 2$] was also proposed.[2,5] We anticipated to study the redistribution reaction in more detail under various experimental conditions. When the above reaction was carried out at ambient temperature without heating, the reaction products, $R^1_2Sn{\rightarrow}SnCl_2$ (**6**), $R^1_2Sn{\rightarrow}SnBr_2$ (**7**), SnR^1Cl (**8**), and SnR^1Br (**9**), respectively, were isolated in the reactions of **1** with $SnCl_2$ and $SnBr_2$ (Scheme 1). Further heating of compounds **6**, **7**, **8**, and **9** in solvent (THF or toluene) at reflux led to the formation of the final products, $SnR^1_2X_2$ and tin metal. In view of the solid state structure of **6**, it is suggested that the redistribution reaction of **1** and $SnCl_2$ proceeds via the “head-to-head” approach of **1** and $SnCl_2$ to form the donor−acceptor complex **6**, which is a preliminary intermediate to the $(\mu\text{-}Cl)_2$ bridging transition state as proposed earlier.[2] The complex $[R^1_2Sn{\rightarrow}SnX_2]$ will then undergo ligand−halogen exchange to form the subsequent intermediate compound $[SnR^1X]$, which can form $SnR^1_2X_2$ at higher temperature via transition state **A**. Alternatively, at higher temperature the redistribution reaction may proceed via transition state **B** with the dissociation of the Sn−Sn interaction. In the present case, the vacant tin orbitals are conceivably occupied by the nitrogen lone pairs of the quinolyl ligands. Hence, $[SnR^1_2]$ behaves like a Lewis base and favors the formation of a donor−acceptor type complex by donating a lone pair from its

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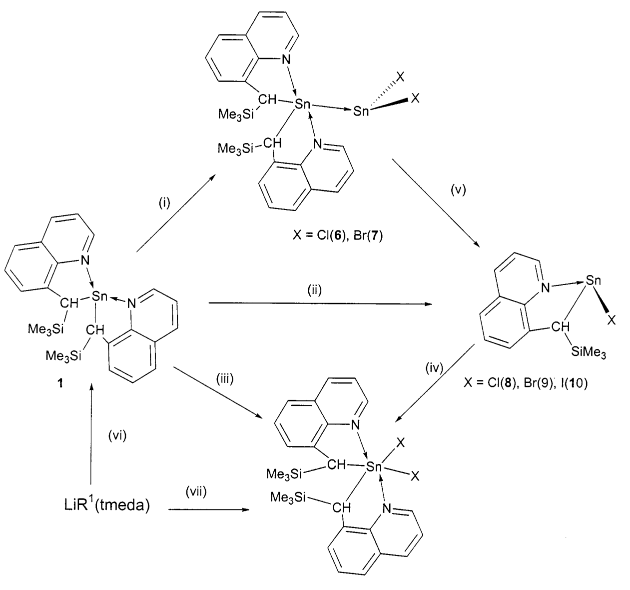
Scheme 1[a]



[a] Regents and conditions: (i) SnX_2, THF, 25 °C, 30 min; (ii) SnX_2, THF, 25 °C, >2 h; (iii) SnX_2, THF, reflux; (iv) THF, reflux; (v) THF, 25 °C, >2.5 h; (vi) $SnCl_2$, THF; (vi) $SnCl_4$, diethyl ether.

sp^2 orbital to the vacant p$_z$ orbital of the Lewis acid $SnCl_2$. The bonding involved differs from the double donor−acceptor double bond as described for $R_2Sn{=}SnR_2$.[1] On the basis of the structural data, compound **6** is best represented as a donor−acceptor complex $R^1{}_2Sn{\rightarrow}SnCl_2$ with a single bond linking the tin atoms.

In a similar reaction of **1** with SnI_2 in THF, the major product isolated was SnR^1I. The ^{119}Sn NMR spectrum of a mixture of **1** and SnI_2 in THF solution showed a signal at δ 386.03 ppm, assignable to $[SnR^1I]$ (**10**). Signals due to the complex $[R^1{}_2Sn{\rightarrow}SnI_2]$ were not observed. This suggests that the donor−acceptor type complex was not formed, perhaps because SnI_2 is a weaker Lewis acid than $SnCl_2$ and $SnBr_2$. However, NMR signals due to the intermediate compounds $[R^1{}_2Sn{\rightarrow}SnF_2]$ and $[SnR^1F]$ have not been observed when **1** and SnF_2 were mixed in THF or toluene at ambient temperature. Heating of the reaction mixture afforded $SnR^1{}_2F_2$.

The stability of $[SnR^1X]$ [X = Cl (**8**), Br (**9**), I (**10**)] is attributed to the sterically hindered N-functionalized alkyl ligand $(R^1)^-$. Compounds of similar nature such as $[Sn\{C(SiMe_3)_2C_5H_4N\text{-}2\}X]$ [X = Cl, $N(SiMe_3)_2$] and $[Me_2Si(NHBu^t)(NBu^t)SnX]$ (X = Cl, Br, I) have been reported.[5,6] In contrast, the three-coordinate silylene [Si(R)Me] [R = 8-(dimethylamino)-1-naphthyl] generated by thermal degradation of $[SiMe(OEt)(SiMePh_2)(R)]$ has only been trapped as a five-coordinate 1,2-disilacyclobut-3-ene.[7]

^1H and ^{119}Sn NMR spectroscopy has been used to study the reactions of **1** with SnX_2. The signals in the ^1H NMR spectrum of the reaction mixture of **1** with $SnCl_2$ were assignable to compounds **6** and **8**. Compounds **6** and **8** were formed in the ratio of 1:3. Two singlets due to $SiMe_3$ from the compounds at δ −0.07 and −0.04, respectively, were observed. The broad signal at δ 2.32 was assigned to a methine proton. Similar signals were also observed in the ^1H NMR spectrum of the reaction mixture of **1** and $SnBr_2$, with δ −0.10, −0.05, and 2.47 assignable to $SiMe_3$ groups and the methine proton, respectively. The inequivalence of the $SiMe_3$ groups and the broad signal of the methine proton were probably due to a fast-exchange process between two stereoisomers in both $[Sn(R^1)Cl]$ (**8**) and $[Sn(R^1)Br]$ (**9**), respectively (Figure 2). A similar process had been reported for the related compound $[Sn\{C(SiMe_3)_2C_5H_4N\text{-}2\}X]$ [X = Cl, $N(SiMe_3)_2$].[5]

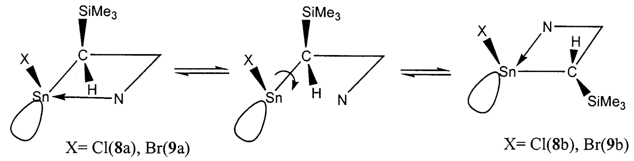


Figure 2. Dynamic exchange process between diastereoisomers of **8** and **9**.

The dynamic exchange process between the diastereoisomers in **8** and **9** has been investigated by variable-temperature ^1H NMR spectroscopy of the reaction mixtures of **1** and SnX_2 (X = Cl, Br). For compound **8**, two well-resolved singlets were observed in a ratio of 1:4 at $T = 298$ K, indicating that the equilibrium favored one of the diastereoisomers of **9**. It is suggested that **9b** is more favorable than **9a** since the $SiMe_3$ group is trans to the large bromine atom, thus has a less hindered environment. With the coalescence temperature (T_c) of 333 K and maximum peak separation ($\delta\nu$) of 24.53 Hz, the energy barrier ($\Delta G^{\ddagger}$) for the dynamic process calculated by the Eyring equation was 16.9 kcal mol^{-1}.[8]

The two well-resolved singlets were believed to correspond to closed three-coordinate diastereoisomers **9a** and **9b**, whereas the equivalence of the $SiMe_3$ signals was attributed to the fast-exchange process between **9a** and **9b** through the open two-coordinate structure which involves breaking of the weaker Sn−N bond. The broad signal of the methine proton sharpened as the temperature increased, showing that the methine protons become equivalent during the fast-exchange process. $^{119}Sn{-}^1H$ coupling ($^2J_{Sn-H}$ =19.8 Hz) due to the methine proton was observed at 338 K, which was smaller than the values of 95.8−116.6 Hz in Sn(IV)−H coupling. It was observed that the ratio of **7** to **9** decreased when the temperature of the experiment was increased, indicating that **7** was converting to **9** at higher temperature, as we proposed earlier. However, the ratio of **7** and **9** increased to 1:4 when the mixture was cooled to room temperature again. This suggested that the process of converting **7** to **9** was reversible. The ^1H NMR spectrum of the mixture of **6** and **8** was similar to that of the mixture of **7** and **9**. It is believed that a similar dynamic process between **8a** and **8b** was taking place in solution state.

The ^{119}Sn NMR spectrum of $R^1{}_2Sn{\rightarrow}SnCl_2$ (**6**) in THF/benzene-d_6 displayed two singlets at δ 1264.44 and −637.19, respectively. The peak at δ 1264.44 is assigned to Sn(1) of the $SnR^1{}_2$ fragment in **6**, which is more downfield than the signal of δ 141.73 for the starting

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compound SnR^1_2 (**1**). This downfield shift is a consequence of reduction of electron density at the Sn(1) center due to its donor bonding to $SnCl_2$. Some π-backbonding from the lone pair of Sn(2) to the vacant d orbital of Sn(1) is also possible. With reference to the ^{119}Sn NMR chemical shift of $SnCl_2$ (δ −388) reported in the literature, the signal at δ −637.19 in **6** is assigned to Sn(2) of the $SnCl_2$ fragment.[9] Furthermore, we have carried out ^{119}Sn NMR experiments to monitor the reaction of SnR^1_2 with $SnCl_2$ in THF solution as mentioned before and found that a peak at δ 327.02 emerged in addition to the peaks due to **6**, after 2 h. This peak is assignable to SnR^1Cl (**8**), when compared with the reported chemical shifts for $[Sn\{C(SiMe_3)_2C_5H_4N\text{-}2\}Cl]$[4] and those of SnR^1Br (**9**) (δ 353.67) and SnR^1I (**10**) (δ 386.03) in this work. In a similar experiment with **1** and $SnBr_2$, peaks at δ 1425.45 and −504.66 assignable to $R^1_2Sn{\rightarrow}SnBr_2$ (**7**) and at δ 353.67 due to SnR^1Br (**9**) were observed. In a similar experiment with **1** and SnI_2, signals corresponding to $R^1_2Sn{\rightarrow}SnI_2$ were not observed, but a peak at δ 386.03 was found which was assignable to SnR^1I (**10**).

Reactions of 1 with Other Halogenated Compounds. Reactions of **1** with some other Lewis acids have also been studied. The reaction of **1** with BCl_3 in THF gave a pale yellow crystalline solid as confirmed to be $SnR^1_2Cl_2$ (**3**) by its ^1H NMR and ^{119}Sn NMR spectra. It has been reported that the reaction of BCl_3 with $[Sn\{CH(SiMe_3)_2\}_2]$ in 1:1 stoichiometric ratio resulted in formation of impure $[Sn\{CH(SiMe_3)_2\}_2Cl_2]$.[1]

The reaction of $[LiR^1(tmeda)]$ with 1 equiv of SnF_2 in toluene followed by refluxing for 4 h afforded $[Sn(R^1)_2F_2]$ (**2**) in 35% yield. On the basis of the above results, the reaction presumably proceeded via the formation of monoalkylfluorostannylene SnR^1F as the intermediate, which then disproportionated to $SnR^1_2F_2$ (**2**) and tin metal. On refluxing the solution of thermally stable monoalkylhalostannylenes SnR^1X (X = Cl, Br, I) in toluene for 18 h, $SnR^1_2X_2$ [X = Cl (**3**), Br (**4**), I (**5**)] and a grayish precipitate of tin metal were formed.

The reaction of **1** with 1 equiv of Br_2 in THF afforded **4** in 85% yield. No reaction occurred between **1** and I_2 at room temperature during 4 h. However, when a solution of **1** and I_2 in toluene was heated at reflux, **5** was formed in 85% yield. It was necessary to reflux the mixture for 18 h, yielding **5** in 85% yield. Halogens are well known to undergo oxidative-addition reactions with dialkylstannylenes to form dialkyltin dihalides.[10]

It was found that dialkyltin dichlorides $SnR^1_2Cl_2$ (**3**) can also be prepared by the reactions of $SnCl_4$ with 2 equiv of $[LiR^1(tmeda)]$. However, the yields obtained in these reactions were relatively low (13 and 56%) when compared with the reactions involving oxidation of Sn(II) species to Sn(IV). Compound **3** was found to be poorly soluble in solvents such as toluene and ether, but soluble in $CHCl_3$ and THF. It has been reported that the reactions of alkyl- and aryllithium with $SnCl_4$ gave $[Sn\{CH(SiMe_3)_2\}_2Cl_2]$[10] and $[Sn\{2,4,6\text{-}(Bu^t)_3C_6H_3\}_2Cl_2]$,[11] respectively.

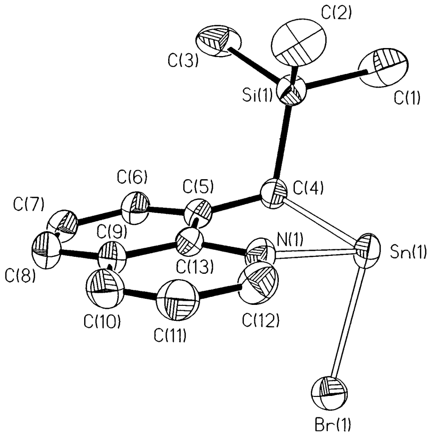

Figure 3. Molecular structure of $[Sn(R^1)Br]$ (**9**). Selected bond distances (Å) and angles (deg): Sn(1)−Br(1), 2.679(1), Sn(1)−N(1), 2.309(5), Sn(1)−C(4), 2.236(5), C(4)−Sn(1)−N(1), 75.8(2), C(4)−Sn(1)−Br(1), 96.9(1), N(1)−Sn(1)−Br(1), 86.4(1).

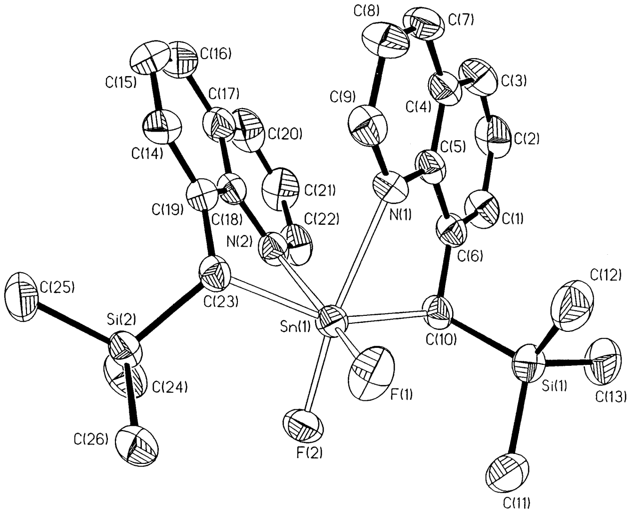

Figure 4. Molecular structure of $[Sn\{CH(SiMe_3)\text{-}C_9H_6N\text{-}8\}_2F_2]$ (**2**).

Molecular Structures

The molecular structure of $[\{CH(SiMe_3)C_9H_6N\text{-}8\}_2\text{-}Sn{\rightarrow}SnCl_2]$ (**6**) has been reported in the previous communication.[4] The molecular structure of $[\{CH(SiMe_3)\text{-}C_9H_6N\text{-}8\}SnBr]$ (**9**) is shown in Figure 3. Compound **9** is an alkyltin(II) bromide with the alkyl ligand $^-R^1$ bonded in a *C*,*N*-chelate fashion to the tin(II) atom and displays a trigonal pyramidal geometry around the tin atom. In the unit cell lattice packing, two independent molecules of **9** are paired up in a "head-to-tail" fashion. The four atoms of Sn and Br from two molecules form a pseudo-four-membered ring. The intermolecular distance of Sn(1a)−Br(1c) is 3.420 Å, which is much longer than the bond length Sn(1a)−Br(1a) of 2.679(1) Å in **9**.

Dialkyltin dihalide compounds **2**−**5** are isostructural. The representative molecular structure of compound **2** is shown in Figure 4. Selected bond distances (Å) and angles (deg) of compounds **2**−**5** are listed in Table 1. The two alkyl ligands $^-R^1$ are bonded to the central tin atom in trans *C*,*N*-chelating fashion. The two halogen atoms are bonded to the central tin atom at the cis position and are both trans to the nitrogen atoms of the alkyl ligands $^-R^1$. The coordination geometry at the tin

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Table 1. Selected Bonds Distances (Å) and Angles (deg) for Compounds 2−5

	$[Sn\{CH(SiMe_3)C_9H_6N\text{-}8\}_2X_2]$			
	X = F (**2**)	X = Cl (**3**)	X = F (**4**)	X = Cl (**5**)
Sn−X(1)	1.981(3)	2.459(1)	2.625(3)	2.818(1)
Sn−X(2)	1.980(5)	2.462(2)	2.630(2)	2.819(1)
Sn−N(1)	2.428(4)	2.436(4)	2.444(4)	2.570(5)
Sn−N(2)	2.492(4)	2.463(4)	2.449(7)	2.559(5)
Sn−C(10)	2.149(6)	2.170(6)	2.211(7)	2.167(6)
Sn−C(23)	2.166(7)	2.161(7)	2.188(7)	2.188(5)
X(1)−Sn−X(2)	92.5(2)	95.4(1)	98.3(1)	96.5(1)
X(1)−Sn−N(1)	92.1(2)	90.8(1)	88.6(2)	85.6(1)
X(2)−Sn−N(1)	168.3(2)	166.7(1)	166.7(2)	166.4(1)
X(1)−Sn−N(2)	169.3(2)	165.2(1)	164.9(2)	166.5(1)
X(2)−Sn−N(2)	93.8(2)	93.9(1)	90.3(1)	85.3(1)
N(1)−Sn−N(2)	83.5(1)	82.6(1)	85.5(2)	95.8(2)

centers of **2**−**5** is most appropriately described as distorted octahedral with X(1), X(2), N(1), and N(2) as the square plane and C(10) and C(23) are in mutual trans positions occupying the apexes of the distorted octahedron. Britton and Dunitz correlated the structural features of $SnC_2X_2Y_2$ ensembles having a C,C-transoid arrangement.[12] It was shown that in such species the C−Sn−C angle is a function of the deviation of the C−X and C−Y distances from the theoretical values. The Sn−N and Sn−X distances in **2**−**5** fit well in the theoretically deduced curve.[12]

Experimental Section

All experiments were performed under a dinitrogen atmosphere using standard Schlenk techniques or in a drybox. Solvents were dried over and freshly distilled under nitrogen, from CaH_2 (hexane), sodium benzophenone ketyl (THF, diethyl ether), and sodium/potassium alloy (pentane, toluene), and degassed twice by a freeze−thaw cycle prior to use. Anhydrous SnF_2, $SnCl_2$, $SnBr_2$, SnI_2, BCl_3, $SnCl_4$, Br_2, and I_2 were purchased from Aldrich Chemical Co. and used without further purification. $GeCl_2\cdot$dioxane,[10] SnR^1_2 (**1**), and $[LiR^1(tmeda)]$ were prepared according to literature procedures.[13]

Synthesis of $[Sn\{CH(SiMe_3)C_9H_6N\text{-}8\}_2F_2]$ (2). Method 1. A solution of $[LiR^1(tmeda)]$ (1.20 g, 3.56 mmol) in toluene (50 mL) was added slowly to a slurry of SnF_2 (0.558 g, 3.56 mmol) in toluene (50 mL) at room temperature. After the resulting mixture was refluxed for 4 h a gray precipitate was obtained. The mixture was filtered, and the greenish-brown filtrate was concentrated and stored at −30 °C to give light brown solids. Recrystallization of the crude product from toluene afforded pale yellow crystals of **2**, 0.365 g (35%); mp 205−206 °C (dec). Anal. Found: C, 53.03; H, 5.41; N, 4.66. Calcd for $C_{26}H_{32}Si_2N_2SnF_2\cdot 1/2THF$: C, 53.34; H, 5.51; N, 4.79. EI-MS: *m/z* 571 $[M - Me]^+$, 334 $[M - R^1 - 2F]^+$, 214 $[R^1]^+$. ^1H NMR (CD_2Cl_2, 250 MHz): δ −0.02 (s, SiMe$_3$, 18H), 1.76−1.80 (m, THF, 2H), 2.73 (s, $^2J_{H-Sn}$ = 116.6 Hz, C*H*Si, 2H), 3.62−3.68 (m, THF, 2H), 6.98 (dd, *J* = 8.2, 4.5 Hz, quinolyl, 2H), 7.17 (dd, *J* = 8.2, 1.4 Hz, quinolyl, 2H), 7.24−7.31 (m, quinolyl, 2H), 7.40 (dd, *J* = 7.8, 1.3 Hz, quinolyl, 2H), 7.78 (dd, *J* = 8.2, 1.6 Hz, quinolyl, 2H), 8.34 (dd, *J* = 4.5, 1.6 Hz, quinolyl, 2H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125.77 MHz): δ −0.01 (SiMe$_3$), 25.71 (THF), 32.55 (t, $^2J_{C-F}$ = 21.3 Hz), 68.88 (THF), 121.77, 123.79, 128.06, 128.51, 131.14, 139.48, 140.91, 143.28, 147.79 (*C*$_9$H$_6$N). ^{119}Sn NMR (CD_2Cl_2, 186.47 MHz, SnMe$_4$ (ext)): δ −323.68 (t, $^1J_{Sn-F}$ = 3073.0 Hz).

Method 2. A solution of SnR^1_2 (**1**) (0.820 g, 1.50 mmol) in THF (30 mL) was added slowly to a slurry of SnF_2 (0.235 g, 1.50 mmol) in THF (30 mL) at room temperature. The resulting orange solution was refluxed for 18 h. The gray precipitate obtained was separated by filtration. The filtrate was concentrated and stored at room temperature. Colorless crystals of **2**, 0.715 g (81%), were isolated.

Synthesis of $[Sn\{CH(SiMe_3)C_9H_6N\text{-}8\}_2Cl_2]$ (3). Method 1. Anhydrous $SnCl_4$ (4.72 mL, 4.72 mmol) was syringed slowly into a solution of $[LiR^1(tmeda)]$ (3.18 g, 9.45 mmol) in ether (80 mL) at 0 °C. The yellow mixture was slowly warmed to ambient temperature and stirred for 18 h. The precipitate obtained was filtered, and the filtrate was concentrated and stored at −30 °C. A yellow crystalline solid, **3**, was obtained by recrystallization of the crude product from THF, 0.37 g (13%); mp 280−281 °C (dec). Anal. Found: C, 50.79; H, 5.20; N, 4.41. Calcd for $C_{26}H_{32}Si_2N_2SnCl_2$: C, 50.51; H, 5.22; N, 4.53. EI-MS: *m/z* 603 $[M - Me]^+$, 404 $[M - R^1]^+$, 214 $[R^1]^+$. ^1H NMR (CD_2Cl_2, 250 MHz): δ −0.04 (s, SiMe$_3$, 18H), 2.69 (s, $^2J^{119}{}_{Sn-^1H}$ = 116.3 Hz, $^2J^{117}{}_{Sn-^1H}$ = 111.2 Hz, C*H*Si, 2H), 6.98−7.09 (m, quinolyl, 6H), 7.17 (dd, *J* = 8.2, 4.4 Hz, quinolyl, 2H), 7.78 (dd, *J* = 8.2, 1.5 Hz, quinolyl, 2H), 8.60 (dd, *J* = 4.5, 1.6 Hz, quinolyl, 2H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 62.90 MHz): δ −0.19 (SiMe$_3$), 43.96 (*C*SiMe$_3$), 122.07, 123.51, 127.33, 127.83, 129.59, 138.68, 140.12, 143.16, 147.51 (*C*$_9$H$_6$N). ^{119}Sn NMR (CD_2Cl_2, 186.50 MHz, SnMe$_4$ (ext)): δ −248.52 (s).

Method 2. A solution of SnR^1_2 (**1**) (1.32 g, 2.40 mmol) in toluene (30 mL) was added slowly to a slurry of $SnCl_2$ (0.457 g, 2.40 mmol) in toluene (30 mL) at room temperature. The yellow mixture was refluxed for 18 h. The gray precipitate was separated by filtration. The filtrate was concentrated and stored at room temperature to afford colorless crystals of **3**, 0.650 g (44%).

Method 3. A solution of$[SnR^1Cl]$ (**8**) (0.55 g, 1.50 mmol) in toluene was refluxed for 18 h until a gray powder was formed and the yellow color of the mixture faded. The resulting mixture was filtered, and the colorless filtrate was concentrated and stored at −30 °C to give colorless crystals of **3**, 0.26 g (48%).

Synthesis of $[Sn\{CH(SiMe_3)C_9H_6N\text{-}8\}_2Br_2]$ (4). Method 1. A solution of SnR^1_2 (**1**) (0.363 g, 0.614 mmol) in THF (30 mL) was added slowly to a solution of Br_2 (0.106 g, 0.664 mmol) in THF (20 mL) at 0 °C. The resulting yellow mixture was warmed to ambient temperature and stirred for 18 h. It was then concentrated and stored at −30 °C; a white crystalline solid was obtained and washed with cold pentane to yield 0.398 g (85%) of **4**; mp 258−259 °C (dec). Anal. Found: C, 44.20; H, 4.70; N 3.84. Calcd for $C_{26}H_{32}Si_2N_2SnBr_2$: C, 44.16; H, 4.56; N, 3.96. EI-MS: *m/z* 627 $[M - Br]^+$, 492$[M - R^1]^+$. ^1H NMR ($CDCl_3$, 250 MHz): δ 0.30 (s, SiMe$_3$, 18H), 3.03 (s, $^2J_{^1H-^{119}Sn}$ = 109.1 Hz, $^2J_{^1H-^{117}Sn}$ = 103.8 Hz, C*H*Si, 2H), 7.10 (d, *J* = 6.8 Hz, quinolyl, 2H), 7.21−7.32 (m, quinolyl, 4H), 7.55 (dd, *J* = 8.1, 4.2 Hz, quinolyl, 2H), 8.08 (dd, *J* = 8.2, 1.6 Hz, quinolyl, 2H), 9.06 (dd, *J* = 4.5, 1.5 Hz, quinolyl, 2H). ^{13}C NMR ($CDCl_3$, 62.90 MHz): δ −0.75 (SiMe$_3$), 46.12 (*C*SiMe$_3$), 121.26, 122.55, 126.26, 126.78, 127.81, 137.51, 139.72, 142.48, 146.41 (*C*$_9$H$_6$N). ^{119}Sn NMR (THF/C_6D_6, 186.45 MHz, SnMe$_4$ (ext)): δ −302.27 (s).

Method 2. A procedure similar to that described for method 2 used in the synthesis of **3** was used for the preparation of **4**. Starting with SnR^1_2 (**1**) (0.74 g, 1.35 mmol) and $SnBr_2$ (0.47 g, 1.35 mmol), compound **4** was obtained as colorless crystals, 0.40 g (42%).

Method 3. A procedure similar to that described for method 3 used in the synthesis of **3** was used for the preparation of **4**. Starting with complex $[SnR^1Br]$ (**9**) (0.486 g, 1.18 mmol), colorless crystals of **4** were obtained by fractional crystallization in THF, 0.29 g (35%).

Synthesis of $[Sn\{CH(SiMe_3)C_9H_6N\text{-}8\}_2I_2]$ (5). Method 1. A solution of SnR^1_2 (**1**) (0.845 g, 1.55 mmol) in THF (30 mL) was added slowly to a solution of I_2 (0.392 g, 1.55 mmol) in THF (30 mL). The resulting reddish-brown mixture was refluxed overnight. It was filtered, and the yellow filtrate was concentrated and stored at −30 °C. A pale yellow solid was

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obtained. Recrystallization of the crude product from toluene yielded **5** as pale yellow crystals (1.05 g, 85%); mp 270−271 °C (dec). Anal. Found: C, 38.94; H, 3.92; N, 3.45. Calcd for $C_{26}H_{32}Si_2N_2SnI_2$: C, 38.98; H, 4.03; N, 3.50. EI-MS: *m/z* 675 $[M - I]^+$, 334 $[M - R^1 - 2I]^+$. ^1H NMR (C_6D_6, 250 MHz): δ 0.25 (s, $SiMe_3$, 18H), 2.82 (s, $^2J_{^1H-^{119}Sn} = 95.9$ Hz, $^2J_{^1H-^{117}Sn} = 91.9$ Hz, C*H*Si, 2H), 6.25 (d, $J = 6.5$ Hz, quinolyl, 2H), 6.36 (t, $J = 6.5$ Hz, quinolyl, 2H), 6.49 (dd, $J = 8.2, 1.4$ Hz, quinolyl, 2H), 6.60 (dd, $J = 8.2, 4.4$ Hz, quinolyl, 2H), 7.08 (dd, $J = 8.2, 1.6$ Hz, quinolyl, 2H), 8.64 (dd, $J = 4.4, 1.5$ Hz, quinolyl, 2H). ^{13}C NMR (C_6D_6, 62.897 MHz): δ −0.37 ($SiMe_3$), 47.32 (*C*$SiMe_3$), 121.35, 122.50, 125.74, 126.55, 128.99, 136.71, 141.07, 143.41, 146.38(*C*$_9H_6N$). ^{119}Sn NMR ($CDCl_3$, 186.50 MHz, $SnMe_4$ (ext)): δ −434.18 (s).

Method 2. A procedure identical with that described in method 2 in the synthesis of **3**, starting with SnR^1_2 (**1**) (0.54 g, 0.997 mmol) with SnI_2 (0.371 g, 0.997 mmol), gave compound **5** as pale yellow crystals (0.28 g, 35%).

Method 3. A procedure identical with that described for method 3 for the synthesis of **3** starting with complex $[SnR^1I]$ (**10**) (0.350 g, 0.761 mmol) gave pale yellow crystals of **5**. Recrystallization in THF yielded 0.299 g (49%) of pure product.

Synthesis of $[\{CH(SiMe_3)C_9H_6N\text{-}8\}_2Sn{\rightarrow}SnCl_2]$ (6) and $[Sn\{CH(SiMe_3)C_9H_6N\text{-}8\}Cl]$ (8). A solution of SnR^1_2 (0.61 g, 1.11 mmol) in THF (80 mL) was added slowly to a solution of $SnCl_2$ (0.21 g, 1.11 mmol) in THF (50 mL) at room temperature. The red color of $[Sn(R^1)_2]$ changed to yellow rapidly. The yellow mixture was stirred overnight. It was then concentrated in vacuo to ca. 30 mL and stored at −30 °C for 2 days. A mixture of colorless and yellow crystals of the title compounds (0.29 g), mp 190−191 °C (dec), was obtained. Anal. Found: C, 42.29; H, 4.30; N, 3.69. Calcd for $C_{26}H_{32}Si_2N_2Sn_2Cl_2$: C, 42.37; H, 4.38; N, 3.80. From NMR spectroscopic data, spectra could be assigned to $[(R^1)_2Sn{\rightarrow}SnCl_2]$ and $[Sn(R^1)Cl]$, respectively, as follows:

$[R^1_2Sn{\rightarrow}SnCl_2]$ (6). ^1H NMR (C_6D_6, 250 MHz): δ 0.29 (s, $SiMe_3$, 18H), 1.41 (s, C*H*Si, 2H), 6.56−6.65 (m, quinolyl, 2H), 6.71−6.74 (m, quinolyl, 2H), 6.91−6.98 (m, quinolyl, 4H), 7.35−7.46 (m, quinolyl, 2H), 8.28−8.29 (m, quinolyl, 1H), 9.33−9.35 (m, quinolyl, 1H). ^{119}Sn NMR (THF/C_6D_6, 186.5 MHz, $SnMe_4$ (ext)): δ −637.19 (s, *Sn*Cl_2), 1264.44 (s, $(R^1)_2$*Sn*).

$[SnR^1Cl]$ (8). ^1H NMR (C_6D_6, 250 MHz): δ (−0.07, −0.04, s, $SiMe_3$ of 5**a** and **5b**, 9H), 2.32 (s, C*H*Si, 1H), 6.35 (dd, $J = 8.1, 4.8$ Hz, quinolyl, 1H), 6.73 (d, $J = 7.4$ Hz, quinolyl, 1H), 7.09 (d, $J = 7.3$ Hz, quinolyl, 1H), 7.25 (d, $J = 7.9$ Hz, quinolyl, 1H), 7.30 (d, $J = 8.3$ Hz, quinolyl, 1H), 7.92 (d, $J = 4.7$ Hz, quinolyl, 1H). ^{119}Sn NMR (THF/C_6D_6, 186.5 MHz, $SnMe_4$ (ext)): δ 327.02 (s).

Synthesis of $[\{CH(SiMe_3)C_9H_6N\text{-}8\}_2Sn{\rightarrow}SnBr_2]$ (7) and $[Sn\{CH(SiMe_3)C_9H_6N\text{-}8\}Br]$ (9). A solution of SnR^1_2 (**1**) (0.930 g, 1.70 mmol) in THF (80 mL) was added slowly to a solution of $SnBr_2$ (0.470 g, 1.70 mmol) in THF (50 mL) at room temperature. The resulting orange mixture was stirred overnight. It was filtered, and the orange filtrate was concentrated in vacuo to ca. 30 mL and stored at room temperature. Orange crystals of title compounds were obtained (0.65 g), mp 185−186 °C (dec). Anal. Found: C, 37.51; H, 3.90; N, 3.42. Calcd for $C_{13}H_{16}SiNSnBr$: C, 37.81; H, 3.91; N, 3.39. From NMR spectroscopic data, spectra could be assigned to $[(R^1)_2\text{-}Sn{\rightarrow}SnBr_2]$ and $[Sn(R^1)Br]$, respectively, as follows:

$[(R^1)_2Sn{\rightarrow}SnBr_2]$ (7). ^1H NMR (C_6D_6, 250 MHz): δ 0.29 (s, $SiMe_3$, 18H), 1.41 (s, C*H*Si, 2H), 6.45−6.51 (m, quinolyl, 2H), 6.69−6.70 (m, quinolyl, 2H), 7.08−7.14 (m, quinolyl, 4H), 7.32−7.44 (m, quinolyl, 2H), 8.31−8.32 (m, quinolyl, 1H), 9.38−9.40 (m, quinolyl, 1H). ^{119}Sn NMR (THF/C_6D_6, 186.5 MHz, $SnMe_4$ (ext)): δ −504.66 (s, *Sn*Br_2), 1425.45 (s, $(R^1)_2$*Sn*).

$[Sn(R^1)Br]$ (9). ^1H NMR (C_6D_6, 250 MHz): δ (−0.10, −0.05, s, $SiMe_3$ of **9a** and **9b**, 9H), 2.47 (s, C*H*Si, 1H), 6.34 (dd, $J = 8.4, 4.8$ Hz, quinolyl, 1H), 6.84 (d, $J = 7.8$ Hz, quinolyl, 1H), 7.23 (d, $J = 7.4$ Hz, quinolyl, 1H), 7.30 (d, $J = 8.3$ Hz, quinolyl, 1H), 7.91 (d, $J = 4.3$ Hz, quinolyl, 1H). ^{119}Sn NMR (THF/C_6D_6, 186.5 MHz, $SnMe_4$ (ext)): δ 353.67 (s).

Synthesis of $[Sn\{CH(SiMe_3)C_9H_6N\text{-}8\}I]$ (10). A solution of SnR^1_2 (**1**) (0.299 g, 0.547 mmol) in THF (50 mL) was added slowly to a solution of SnI_2 (0.204 g, 0.547 mmol) in THF (30 mL) at room temperature. The resulting yellow mixture was stirred overnight. It was filtered, and the yellow filtrate was concentrated in vacuo to ca. 30 mL and stored at −30 °C. A yellowish-orange crystalline solid of the title compound was obtained, 0.167 g (66%); mp 206−207 °C (dec). Anal. Found: C, 33.70; H, 3.56; H, 3.06. Calcd for $C_{13}H_{16}SiNSnI$: C, 33.95; H, 3.51; N, 3.04. EI-MS: *m/z* 459 $[M]^+$, 332 $[M - I]^+$. ^1H NMR (C_6D_6, 250 MHz): δ −0.13 (s, $SiMe_3$, 9H), 2.73 (s, C*H*Si, 1H), 6.27−6.35 (m, quinolyl, 1H), 6.84 (d, $J = 9.0$ Hz, quinolyl, 2H), 7.31 (d, $J = 7.9$ Hz, quinolyl, 2H), 7.93 (d, $J = 5.4$ Hz, quinolyl, 1H). ^{119}Sn NMR (THF/C_6D_6, 186.50 MHz, $SnMe_4$ (ext)): δ 386.03 (s).

Reaction of SnR^1_2 with BCl_3. A red solution of $[Sn(R^1)_2]$ (**1**) (1.66 g, 3.03 mmol) in THF (50 mL) was added slowly to a solution of BCl_3 (3.03 mL, 1.0 M in heptane, 3.03 mmol) in THF (30 mL) at 0 °C. The resulting pale yellow mixture was stirred overnight. The mixture was then filtered, and the yellow filtrate was concentrated and stored at −30 °C. Needle-shaped pale yellow crystals of $[SnR^1_2Cl_2]$ (**3**) were obtained. (0.64 g, 34%). Anal. Found: C, 50.66; H, 4.86; N, 4.13. Calcd for $C_{26}H_{32}Si_2N_2SnCl_2$: C, 50.79; H, 5.20; N, 4.41. ^1H NMR ($CDCl_3$, 250 MHz): δ −0.01 (s, $SiMe_3$, 18H), 2.68 (s, $^2J_{H-Sn} = 109.7$ Hz, C*H*Si, 2H), 6.94−6.68 (m, quinolyl, 4H), 7.02−7.04 (m, quinolyl, 2H), 7.15 (dd, $J = 8.2, 4.5$ Hz, quinolyl, 2H), 7.75 (dd, $J = 8.3, 1.5$ Hz, 2H), 8.63 (dd, $J = 4.5, 1.5$ Hz, quinolyl, 2H). ^{119}Sn NMR (THF/C_6D_6, 186.50 MHz, $SnMe_4$ (ext)): δ −246.12 (s).

Full details of the crystallographic analysis of **2**−**5** are given in the Supporting Information.

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Supporting Information Available: Details about the X-ray crystal structures, including ORTEP diagrams and tables of crystal data and structure refinement, atomic coordinates, bond lengths and angles, and anisotropic displacement parameters for **2**−**5** and **8**, are available free of charge via the Internet at http://pubs.acs.org.

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