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Reaction of Tin(II) Hydride with Compounds Containing Aromatic C−F Bonds†

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The reaction of the stable tin(II) hydride LSnH (**1**; L = CH{(CMe)$_2$(2,6-*i*Pr$_2$C$_6$H$_3$N)$_2$}) with fluorinated aromatic compounds is described. The reaction of **1** with equivalent amounts of pentafluorobenzophenone (PhCOC$_6$F$_5$) and perfluorobenzophenone (C$_6$F$_5$COC$_6$F$_5$), respectively, in toluene at room temperature, leads to the nucleophilic addition products LSnOCHPh(C$_6$F$_5$) (**3**) and LSnOCH(C$_6$F$_5$)$_2$ (**4**) as well as to metathesis products PhCO(4-C$_6$F$_4$H) (**5**) and C$_6$F$_5$CO(4-C$_6$F$_4$H) (**6**) with the formation of LSnF (**2**). In contrast, the reactions of 4-fluorobenzophenone (PhCO-4-C$_6$H$_4$F) and pentafluorobenzaldehyde (C$_6$F$_5$CHO) with **1** provide the tin(II) alkoxide products LSnOCHPh(4-C$_6$H$_4$F) (**7**) and LSnOCH$_2$C$_6$F$_5$ (**8**) as a result of nucleophilic addition of hydride to the carbonyl group. Moreover, **1** was treated with C$_6$F$_6$ in C$_6$D$_6$ at room temperature and after 24 h the ^{1}H, ^{19}F, and ^{119}Sn NMR spectra were recorded, which indicated the appearance of LSnF (**2**), C$_6$F$_5$H (**9**), and LSnC$_6$F$_5$ (**10**). Formation of compound **10** was further confirmed by its synthesis from LSnCl and C$_6$F$_5$Li.

Introduction

The breaking of carbon−fluorine bonds is one of the most significant challenges in chemistry, because carbon−fluorine bonds are among the most unreactive single bonds in chemistry,[1] in spite of the fact that fluorine-containing molecules are important in pharmaceutical, agrochemical, and materials science.[2] From a thermodynamic point of view, the C−F bond is the strongest single bond to carbon, and also from a kinetic perspective organic fluorides are modest substrates for nucleophilic substitution reactions or oxidative addition to low-valent metal centers. In the literature, there are numerous reports on the catalytic C−F bond activation of fluorinated compounds by transition-metal catalysts in the presence of silicon(IV) hydride.[3] However, their selective activation and transformation under mild conditions are scarcely known. In 2005, Andersen and co-workers reported the hydrogen for fluorine exchange by cerium hydride.[4] Consequently we became interested in the activation of carbon−fluorine bonds by group 14 hydrides, because one of our research topics involves compounds of group 14 with low-valent and low-coordinate elements.[5] To the best of our knowledge, the hydrodefluorination by group 14 elements was only reported by Ozerov et al. in 2008 using silylium−carborane catalysts in the presence of silicon(IV) hydride.[6] Herein we present our results on the selective breaking of aromatic C−F bonds by the Sn−H bond of LSnH (**1**).[7]

Results and Discussion

In a previous communication we have already discussed the nucleophilic addition reaction of LSnH (**1**) with compounds containing the trifluoroacetyl group (2,2,2-trifluoroacetophenone and 2,2,2-trifluoroacetothiophane).[8] There were no indications that the aliphatic C−F bonds show a metathesis reaction with the Sn−H bond. Moreover, it is worth mentioning that an analogous reaction occurred when these fluorinated compounds were treated with LGeH.[9] Compound

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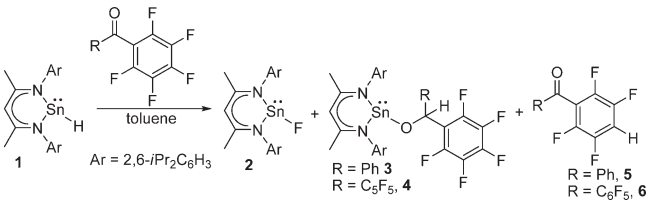
Scheme 1. Preparation of Compounds 2−6



1 reacts with equivalent amounts of pentafluorobenzophenone ($PhCOC_6F_5$) and perfluorobenzophenone ($C_6F_5COC_6F_5$), respectively, in toluene at room temperature with the formation of products **2**−**6** (Scheme 1). This is shown from the ^1H, ^{19}F, and ^{119}Sn NMR spectra. One of these species is the metathesis product LSnF (**2**),[10] obtained by cleavage one of the C−F bonds, and the others are the addition products $LSnOCH(C_6F_5)Ph$ (**3**) and $LSnOCH(C_6F_5)_2$ (**4**), which are obtained by nucleophilic hydride addition to the respective carbonyl group.

The formation of LSnF (**2**) and the alkoxide product ratio of **3** and **4** are calculated by integration of the resonances in the respective ^{119}Sn NMR spectrum. In the case of the reaction between LSnH (**1**) and pentafluorobenzophenone, the product ratio is 1.0:0.6, and the ^{119}Sn NMR resonance arises at δ −217 ppm for the compound $LSnOCH(C_6F_5)Ph$ (**3**), and the other one is the doublet for LSnF (**2**) (δ −371.5 ppm, $^2J(Sn-F) = 3100$ Hz). The latter resonance matches well with that of freshly prepared **2** from the reaction of LSnMe with Me_3SnF.[10] For perfluorobenzophenone, the product ratio is 1.0:0.8, with a ^{119}Sn chemical shift (δ −252 ppm) for $LSnOCH(C_6F_5)_2$ (**4**). The ^1H NMR spectrum of **4** shows a singlet (δ 4.77 ppm) for the γ-CH protons and two septets (δ 3.46 and 3.02 ppm) corresponding to the two different types of C*H* protons of the *i*Pr moieties. All the other resonances are as expected. In the ^1H NMR spectrum the quaternary proton from the LSn−O−C*H* moiety appears as a singlet at δ 6.41 and 6.72 ppm for **3** and **4**, respectively, which is comparable with those of analogous compounds.[8] In the EI mass spectrum of **4**, the molecular ion peak is observed at *m*/*z* 900 as the base peak. Moreover, there are no indications that the tin(II) alkoxide products **3** and **4** react further with **1** as a result of fluorine exchange with the aromatic skeleton.

Therefore, LSnF (**2**) can only be formed from the fluorine exchange of pentafluorobenzophenone ($PhCOC_6F_5$) and perfluorobenzophenone ($C_6F_5COC_6F_5$). In addition, we found in both ^1H NMR spectra that there is a triplet of triplets (δ 6.18 and 6.08 ppm) present with coupling constants of $^3J(H-F) = 9.65$ Hz and $^4J(H-F) = 7.30$ Hz for **5** and $^3J(H-F) = 9.56$ Hz and and $^4J(H-F) = 7.45$ Hz for **6** (Figure 1). According to the values of chemical shifts and on the basis of the coupling constant, we conclude that this is due to the selective breaking of the para carbon−fluorine bond, leading to the formation of the two new compounds $PhCO(4\text{-}C_6F_4H)$ (**5**) and $C_6F_5CO(4\text{-}C_6F_4H)$ (**6**).[11] Unfortunately, we cannot assign the ^{19}F chemical shifts, because the resonances overlap with each other. Only in the case of **2** were we able to assign the ^{19}F NMR spectrum Sn−F resonance at δ −125.29 ppm, which is flanked by satellite peaks attributable to $J(^{19}F-^{119}Sn) = 3100$ Hz and $J(^{19}F-^{117}Sn) = 2955$ Hz.

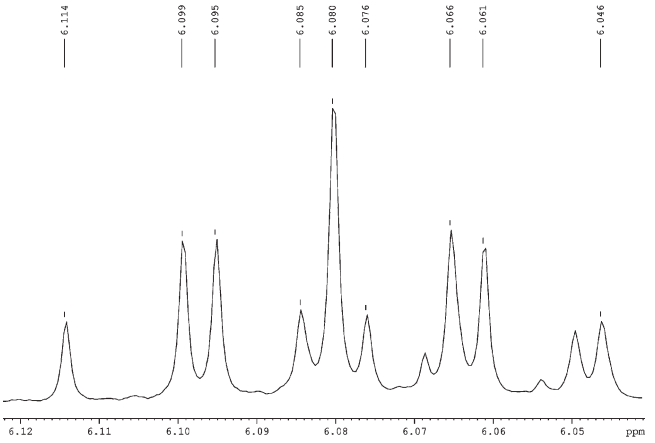
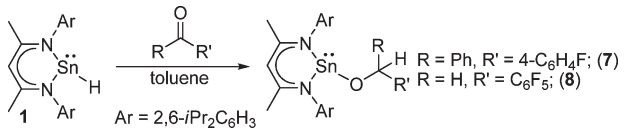


Figure 1. Selected region of the ^1H NMR spectrum of compound **6**, showing the triplet of triplets with coupling constants of $^3J(H-F) = 9.56$ Hz and $^4J(H-F) = 7.45$ Hz.

Scheme 2. Preparation of Compounds 7 and 8



Subsequently, we have selected the substrates 4-fluorobenzophenone ($PhCO4\text{-}C_6H_4F$) and pentafluorobenzaldehyde (C_6F_5CHO) for a better understanding of the reactivity of LSnH (**1**). The reaction of **1** with 4-fluorobenzophenone leads exclusively to the nucleophilic addition product $LSnOCHPh(4\text{-}C_6H_4F)$ (**7**) (Scheme 2). There are no indications that the para fluorine atom is replaced. The ^1H NMR spectrum of **7** exhibits a singlet (δ 5.15 ppm) which corresponds to the quaternary C*H* proton, and the other resonances are as expected.[8] In the ^{19}F NMR spectrum of **7**, the resonance occurs at δ −112.3 ppm as a multiplet. In the ^{119}Sn NMR spectrum, the resonance of **7** exhibits a singlet (δ −212 ppm), which is similar to that of $LSnOCHPh_2$ (δ −218 ppm).[8b] In the EI mass spectrum the molecular ion peak was observed at *m*/*z* 737 with 90% intensity and the base peak occurs at *m*/*z* 652 for $[M^+ - C_6H_4F]$ with 100% intensity.

Treatment of **1** with pentafluorobenzaldehyde leads quantitatively to the stannylene alkoxide $LSnOCH_2C_6F_5$ (**8**), with a $Sn^{II}-O-CH_2$ framework that is formed by nucleophilic hydride addition to the carbon of the carbonyl group (Scheme 2).

Compound **8** is a yellow solid, soluble in benzene, THF, *n*-hexane, and *n*-pentane, and shows no decomposition on exposure to air. The ^1H NMR spectrum of **8** exhibits a singlet (δ 4.81 ppm) which can be assigned to the CH_2 protons and is flanked by Sn satellite lines ($^3J(^{119}Sn-^1H) = 13.5$ Hz). The ^{119}Sn NMR resonance of **8** arises at δ −262 ppm. **8** crystallizes in the triclinic space group $P\overline{1}$ with one monomer in the asymmetric unit (Figure 2). The Sn−O bond length (2.030(1) Å) is comparable with that of compound $LSnOCH_2Fc$ (2.025(1) Å).[8a] The O−C bond distances of **8** and $LSnOCH_2Fc$ are very similar (1.404(2) and 1.411(2) Å).[8a]

From the above reactions we can argue that there is a competition between the metathesis reaction and the nucleophilic addition reaction. The ortho and para C−F bonds are activated in pentafluorobenzophenone and perfluorobenzophenone. Most probably due to steric reasons, the selective C−F bond

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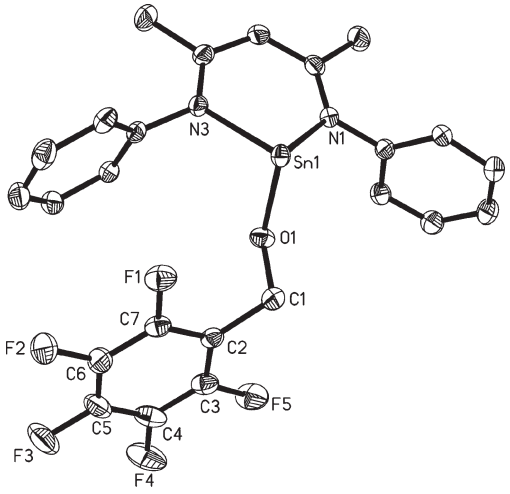
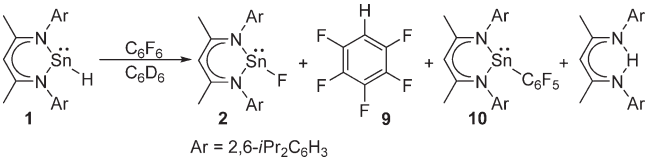


Figure 2. Molecular structure of **8**. Thermal ellipsoids are shown at the 50% probability level. Isopropyl groups and H atoms are omitted for clarity reasons. Selected bond lengths (Å) and angles (deg): Sn1−O1 = 2.030(1), O1−C1 = 1.404(2), Sn1−N1 = 2.191(2), Sn1−N3 = 2.192(1); Sn1−O1−C1 = 120.19(11), N1−Sn1−O1 = 91.85(6), N1−Sn1−N3 = 83.61(6).

Scheme 3. Reaction of LSnH (1) with C_6F_6



cleavage occurs at the para position. Moreover, in the case of 4-fluorobenzophenone and pentafluorobenzaldehyde there are no metathesis reactions. In the former case, the inductive effect dominates compared with the mesomeric effect; therefore, only the addition reaction occurs. In the latter case, the aldehyde group is more reactive in comparison with the ketone group.

Finally, we selected C_6F_6 as a reactant and followed the reaction with LSnH (**1**) (Scheme 3). The ^{1}H NMR spectrum from the crude product showed the formation of four products: one is the free ligand LH, another one is LSnF (**2**), and the third one is C_6F_5H (**9**). We concluded that the last compound is $LSnC_6F_5$ (**10**), because a similar reaction of [1,3,4-$(Me_3C)_3C_5H_2$]$_2$CeH with C_6F_6 leads to the intermediate [1,3,4-$(Me_3C)_3C_5H_2$]$_2$CeC_6F_5, and it decomposes slowly to [1,3,4-$(Me_3C)_3C_5H_2$]$_2$CeF.[4] In the ^{119}Sn NMR spectrum we observed only two resonances, one doublet for LSnF (**1**) and another resonance for the compound $LSnC_6F_5$ (**10**) at δ −176.42 ppm. In the ^{1}H NMR spectrum the resonance for the proton in C_6F_5H was observed at δ 5.95 ppm, which was a triplet of triplets, due to the coupling with the neighboring fluorine atoms.

The ^{1}H NMR data of **2** and **9** match well with those of previously reported values.[10,11] The formation of compound **10** was confirmed by its direct synthesis from LSnCl[12] and C_6F_5Li.[13] The latter was prepared in situ from C_6F_5I and *n*-BuLi (Scheme 4).

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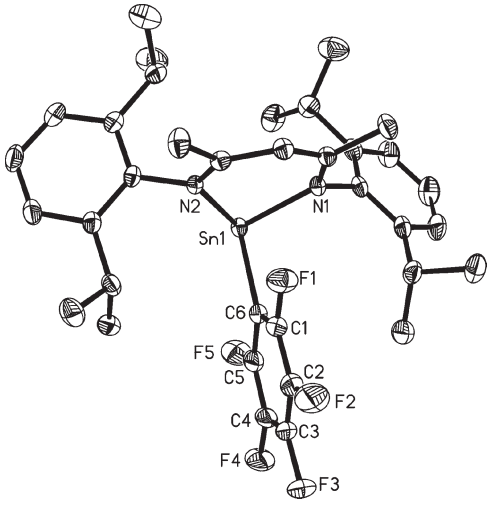
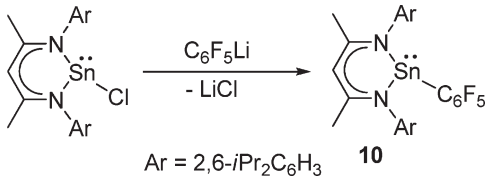


Figure 3. Molecular structure of **10**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity reasons. Selected bond lengths (Å) and angles (deg): Sn1−C6 = 2.3044(17), Sn1−N1 = 2.1861(12); N1−Sn1−C6 = 93.38(5), N1−Sn1−N2 = 86.05(5).

Scheme 4. Preparation of Compound 10



The pale yellow compound **10** was characterized by microanalysis, multinuclear NMR spectroscopy, and EI mass spectrometry. Furthermore, it was characterized by single-crystal X-ray structural analysis. Compound **10** crystallizes in the monoclinic space group $P2_1/n$ with one molecule in the asymmetric unit (Figure 3). **10** is soluble in common organic solvents such as benzene, THF, *n*-hexane, and *n*-pentane. The NMR data are in complete agreement with those obtained from the reaction of **1** with C_6F_6.

Summary and Conclusion

In summary, we have shown the different types of reactions of tin(II) hydride with carbonyl compounds containing aromatic C−F bonds. The reaction of LSnH (**1**) with $PhCOC_6F_5$ and $C_6F_5COC_6F_5$, resulted in the formation of metathesis products by exchange of fluorine by hydrogen and nucleophilic addition of Sn−H to the respective carbonyl group. Moreover, compound **1** reacts with C_6F_6 at room temperature, forming LSnF (**2**), C_6F_5H (**9**), LH, and $LSnC_6F_5$ (**10**). In conclusion, we have reported the cleavage of C−F bonds using LSnH in the absence of additional catalyst. We are currently investigating other main-group reagents for C−F bond activation.

Experimental Section

General Considerations. All manipulations were performed under a dry and oxygen-free atmosphere (N_2) using standard Schlenk techniques or inside a MBraun MB 150-GI glovebox maintained at or below 1 ppm of O_2 and H_2O. Solvents were purified with the M-Braun solvent drying system. The starting

material **1** and LSnCl were prepared using literature procedures.[8a,12] Other chemicals were purchased and used as received. ^{1}H, ^{19}F, and ^{119}Sn NMR spectra were recorded on a Bruker Avance DRX 500 MHz instrument and referenced to the deuterated solvent in the case of the ^{1}H NMR; $CFCl_3$ and $SnMe_4$ were used as references for the ^{19}F and ^{119}Sn NMR spectra, respectively. Elemental analyses were performed by the Analytisches Labor des Instituts für Anorganische Chemie der Universität Göttingen. Infrared spectral data were recorded on a Perkin-Elmer PE-1430 instrument. EI-MS were measured on a Finnigan Mat 8230 or a Varian MAT CH5 instrument. Melting points were measured in sealed glass tubes with a Büchi B 540 melting point instrument.

Synthesis of LSnOCHPh(C_6F_5) (3; L = HC{(CMe)(2,6-*i*Pr$_2$-C_6H_3N)}$_2$) and PhCO(4-C_6F_4H) (5). In a NMR tube loaded with $PhCOC_6F_5$ (0.136 g, 0.50 mmol) and LSnH (**1**; 0.270 g, 0.50 mmol) was added 1 mL of C_6D_6 at room temperature. After 24 h, the NMR spectrum was measured, showing the formation of compounds **3** and **5** in a ratio of 0.6:1.0. Data for **3**: ^{1}H NMR (200 MHz, C_6D_6) δ 6.85−7.65 (m, 6H, Ar-*H*), 6.41 (s, 1H, C*H*), 4.78 (s, 1H, γ-C*H*), 3.56 (sept, 2H, C*H*(CH_3)$_2$), 3.13 (sept, 2H, C*H*(CH_3)$_2$), 1.53 (s, 6H, CH_3), 1.44 (d, 6H, CH(CH_3)$_2$), 1.23 (d, 6H, CH(CH_3)$_2$), 1.11 (d, 6H, CH(CH_3)$_2$), 0.90 (d, 6H, CH(CH_3)$_2$); ^{119}Sn{^{1}H} NMR (186.46 MHz) δ −217 ppm. Data for **5**: ^{1}H NMR (200 MHz, C_6D_6) δ 6.18 (tt, ^{3}J(F−H) = 9.65 Hz, ^{4}J(F−H) = 7.30 Hz, 1H, 4-*H*) ppm.

Synthesis of LSnOCH(C_6F_5)$_2$ (4; L = HC{(CMe)(2,6-*i*Pr$_2$C$_6$-H$_3$N)}$_2$) and C_6F_5CO(4-C_6F_4H) (6). A solution of $C_6F_5COC_6F_5$ in toluene (0.360 g, 1.00 mmol, 10 mL of toluene) was added by cannula to a solution of LSnH (**1**) in toluene (0.54 g, 1.00 mmol in 20 mL of toluene) at room temperature. After 24 h, all volatiles were removed in vacuo, and the remaining residue was extracted with *n*-hexane (25 mL). The ^{1}H NMR spectrum showed the formation of compounds **4** and **6** in a ratio of 0.8:1.0. Data for **4**: ^{1}H NMR (500 MHz, C_6D_6) δ 6.99−7.13 (m, 15H, Ar-*H*), 6.72 (s, 1H, C*H*), 4.77 (s, 1H, γ-C*H*), 3.46 (sept, 2H, C*H*(CH_3)$_2$), 3.02 (sept, 2H, C*H*(CH_3)$_2$), 1.48 (s, 6H, CH_3), 1.17 (d, 6H, CH(CH_3)$_2$), 1.14 (d, 6H, CH(CH_3)$_2$), 1.08 (d, 6H, CH(CH_3)$_2$), 1.06 (d, 6H, CH(CH_3)$_2$); ^{119}Sn{^{1}H} NMR (186.46 MHz) δ −252 ppm; EI-MS (70 eV) *m*/*z* (%) 900 (100) [M$^+$]. Data for **6**: ^{1}H NMR (500 MHz, C_6D_6) δ 6.08 (tt, ^{3}J(F−H) = 9.56 Hz, ^{4}J(F−H) = 7.45 Hz, 1H, 4-*H*) ppm.

Synthesis of LSnOCHPh(4-C_6H_4F) (7; L = HC{(CMe)(2,6-*i*Pr$_2$C$_6$H$_3$N)}$_2$). A solution of PhCO(4-C_6H_4F) (0.200 g, 1.00 mmol; 10 mL of toluene) was added by cannula to a solution of LSnH (**1**) in toluene (0.54 g, 1.00 mmol in 20 mL of toluene) at room temperature. After 24 h, all volatiles were removed in vacuo, and the remaining residue was extracted with *n*-hexane (25 mL). Compound **7** was obtained after evaporation of the solvent. Yield: 0.605 g (82%). Mp: 130 °C. ^{1}H NMR (300 MHz, C_6D_6): δ 6.65−7.63 (m, 15H, Ar-*H*), 5.88 (s, 1H, C*H*), 4.75 (s, 1H, γ-C*H*), 3.63 (sept, 2H, C*H*(CH_3)$_2$), 3.11 (sept, 2H, C*H*(CH_3)$_2$), 1.55 (s, 6H, CH_3), 1.20 (d, 3H, CH(CH_3)$_2$), 1.18 (d, 3H, CH(CH_3)$_2$), 1.13 (d, 3H, CH(CH_3)$_2$), 1.12 (d, 3H, CH(CH_3)$_2$), 1.11 (d, 3H, CH(CH_3)$_2$), 1.10 (d, 3H, CH(CH_3)$_2$), 1.08 (d, 3H, CH(CH_3)$_2$), 1.07 (d, 3H, CH(CH_3)$_2$). ^{19}F NMR (188.29 MHz, C_6D_6): δ −112.3 (m, 1F, *p*-F). ^{119}Sn{^{1}H} NMR (186.46 MHz): δ −212 ppm. EI-MS (70 eV): *m*/*z* (%) 737 (90) [M]$^+$, 652 (100) [M$^+$ − C_6H_4F]. Anal. Calcd for $C_{42}H_{51}FN_2OSn$ (738.30): C, 68.39; H, 6.97; N, 3.80. Found: C, 68.75; H, 7.16; N, 3.62.

Synthesis of LSnOCH$_2$$C_6F_5$ (8; L = HC{(CMe)(2,6-*i*Pr$_2$C$_6$-H$_3$N)}$_2$). A solution of C_6F_5CHO in toluene (0.196 g, 1.00 mmol in 5 mL of toluene) was added by cannula to a solution of LSnH (**1**) in toluene (0.54 g, 1.00 mmol in 20 mL of toluene) at room temperature. After 24 h all volatiles were removed in vacuo, the remaining residue was extracted with *n*-hexane (25 mL), and the extract was concentrated to about 15 mL and stored in a −30 °C freezer. After 4 days yellow crystals of **8** were formed. Yield: 0.600 g (82%). Mp: 138 °C. ^{1}H NMR (300 MHz, C_6D_6): δ 6.95−7.13 (m, 6H, Ar-*H*), 4.80 (s, 1H, γ-C*H*), 4.67 (t, ^{4}J(F−H) = 4.18 Hz, 2H, CH_2), 3.57 (sept, 2H, C*H*(CH_3)$_2$), 3.13 (sept, 2H, C*H*(CH_3)$_2$), 1.58 (s, 6H, CH_3), 1.31 (d, 6H, CH(CH_3)$_2$), 1.24 (d, 6H, CH(CH_3)$_2$), 1.20 (d, 6H, CH(CH_3)$_2$), 1.09 (d, 6H, CH(CH_3)$_2$). ^{19}F NMR (188.29 MHz, C_6D_6): δ −143.9 (dd, 2F, *o*-F), −158.95 (t, F, *p*-F), −163.95 (td, 2F, *m*-F). ^{119}Sn{^{1}H} NMR (186.46 MHz): δ −262 ppm. EI-MS (70 eV): *m*/*z* (%) 537 (100) [M$^+$ − OCH$_2$-C_6F_5]. Anal. Calcd for $C_{36}H_{43}F_5N_2OSn$ (734.23): C, 58.95; H, 5.91; N, 3.82. Found: C, 58.24; H, 5.90; N, 3.72.

Table 1. Summary of Crystal Data and Refinement Results for Compounds 8 and 10

	8	10
empirical formula	$C_{36}H_{43}F_5N_2OSn$	$C_{35}H_{41}F_5N_2Sn$
CCDC no.	745457	759435
T (K)	133(2)	133(2)
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$
a (Å)	12.074(2)	13.351(3)
b (Å)	12.398(3)	18.698(4)
c (Å)	12.821(3)	13.566(3)
α (deg)	82.25(3)	90
β (deg)	72.91(3)	102.84(3)
γ (deg)	71.68(3)	90
V (Å^3)	1739.6(7)	3301.8(11)
Z	2	4
D_{calcd} (g cm^{-3})	1.400	1.415
μ (mm^{-1})	0.791	0.828

Reaction of C_6F_6 and LSnH (1) with the Formation of LSnF (2), C_6F_5H (9), LSnC_6F_5 (10), and LH. In a NMR tube C_6F_6 (0.095 g 0.50 mmol) and LSnH (**1**; 0.270 g, 0.50 mmol) were loaded, and 1 mL of C_6D_6 was added at room temperature. After 24 h the ^{1}H NMR spectrum was recorded and showed the formation of compounds **2**, **9**, LH, and **10**. Data for **2**: yield 0.13 g (50%), with respect to LSnH; ^{119}Sn{^{1}H} NMR (186.46 MHz) δ −371.5 ppm. Data for **9**: yield 0.04 g (46%), with respect to LSnH; ^{1}H NMR (200 MHz, C_6D_6) δ 5.95 (m, 1H, Ar-*H*) ppm; ^{19}F NMR (188.29 MHz, C_6D_6) δ −139.4 (m, 2F, *o*-F), −154.0 (t, 1F, *p*-F), −162.7 (m, 2F, *m*-F). Data for **10**: yield 0.056 g (17%), with respect to LSnH; ^{119}Sn{^{1}H} NMR (186.46 MHz) δ −176.42 ppm. Data for LH: yield 0.071 g (34%), with respect to LSnH; ^{1}H NMR (200 MHz, C_6D_6) δ 12.45 (s, 1H, N-*H*) ppm.

Synthesis of LSnC_6F_5 (10; L = HC{(CMe)(2,6-*i*Pr$_2$C$_6$H$_3$N)}$_2$). To a stirred solution of C_6F_5I (0.795 g, 2.70 mmol) in diethyl ether (30 mL) was added dropwise 1.70 mL of *n*BuLi (1.6 M, in *n*-hexane, 2.70 mmol) at −78 °C. The reaction mixture was stirred for an additional 1 h at this temperature. This mixture was transferred directly to the solution of LSnCl (1.54 g, 2.70 mmol) in diethyl ether (30 mL) at −78 °C. The resulting reaction mixture was then warmed to room temperature. After 6 h all volatiles were removed in vacuo, and the remaining residue was extracted with *n*-hexane (35 mL) and the extract was concentrated to about 15 mL and stored in a −30 °C freezer. After 2 days, pale yellow block-shaped crystals of **10** were formed. Yield: 1.15 g (60%). Mp: 173 °C. ^{1}H NMR (300 MHz, C_6D_6): δ 6.89−7.15 (m, 6H, Ar-*H*), 5.08 (s, 1H, γ-C*H*), 3.22 (sept, 2H, C*H*(CH_3)$_2$), 2.89 (sept, 2H, C*H*(CH_3)$_2$), 1.55 (s, 6H, CH_3), 1.27 (d, 6H, CH(CH_3)$_2$), 1.11 (d, 6H, CH(CH_3)$_2$), 0.96 (d, 6H, CH(CH_3)$_2$), 0.52 (d, 6H, CH(CH_3)$_2$). ^{19}F NMR (188.29 MHz, C_6D_6): δ −117 (br, 2F, *o*-F), −155.0 (t, 1F, *p*-F), −161 (m, 2F, *m*-F). ^{119}Sn{^{1}H} NMR (186.46 MHz): δ −176.42 ppm. EI-MS (70 eV): *m*/*z* (%) 704 (100) [M]$^+$. Anal. Calcd for $C_{35}H_{41}F_5N_2Sn$ (704.22): C, 59.76; H, 5.87; N, 3.98. Found: C, 59.73; H, 6.11; N, 3.97.

Crystallographic Details for Compounds 8 and 10. Suitable crystals of **8** and **10** were mounted on a glass fiber, and data were collected on an IPDS II Stoe image-plate diffractometer (graphite-monochromated Mo Kα radiation, λ = 0.710 73 Å) at 133(2) K. The data were integrated with X-area. The structures were solved by direct methods (SHELXS-97)[14] and refined by

full-matrix least-squares methods against F^2 (SHELXL-97).[14] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically on calculated positions using a riding model. Crystal data and refinement results for **8** and **10** are given in Table 1.

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Supporting Information Available: CIF files giving X-ray data for **8** and **10** and figures giving ^{119}Sn NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.