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Monomeric Triorganotin(IV) Fluorides Containing a C,N-Chelating Ligand

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The set of four triorganotin(IV) fluorides of general formula $\{2\text{-}[(CH_3)_2NCH_2]C_6H_4\}R_2SnF$, where R is Me (**5**), *n*-Bu (**6**), *t*-Bu (**7**), and Ph (**8**), respectively, has been prepared and characterized using NMR and ESI-MS techniques. The structures of crystalline compounds **5** and **8** were determined using X-ray methods. All compounds are monomeric both in solution using different solvents and in the solid state. The tin central atom is five-coordinated with all carbon atoms in equatorial positions and fluorine and nitrogen, from the intramolecularly coordinated dimethylamino group, in the axial positions of the distorted trigonal bipyramid. The ability of compounds **6** and **8** to perform fluorination of organometallic chlorides was tested on titanocene dichloride. A quantitative yield of Cp_2TiF_2 was obtained.

Introduction

At the present time, triorganotin(IV) fluorides are of great interest due to their ability to undergo the metathetical halide for fluoride exchange reactions with different kinds of organometallic halides.[1]

The structures of many triorganotin fluorides have been determined and found to be either oligo- or polymeric with “rod-like” or “zig-zag” F−Sn−F chains.[2] The Sn−F distances in linear polymers such as Ph_3SnF[2e] and cyclohexyl$_3$SnF[2f] were found to be 2.1458(3), 2.051(10), and 2.303(10) Å, respectively. These compounds have relatively high melting points and are rather insoluble in common organic solvents, which was reported many times as a limitation in studies of their structure and reactivity. Only a small number of compounds containing bulky ligands, e.g., $(Sn[C(SiMe_2Ph)_3]Me_2F$, $Sn[C(SiMe_3)_3]Ph_2F$,[3] and $Sn[C_6H_2Me_3\text{-}2,4,6)_3]Me_2F$[4]) with a four-coordinated tin central atom are monomeric with a Sn−F terminal single bond distance of about 1.96 Å.[5] $Sn(CH_2SiMe_3)_3F$ has been found to be monomeric in the solid state with a weak intermolecular Sn···F interaction.[6] $Sn[(CH_2CH_2CH_2)_3N]F\cdot H_2O$ is an example of a compound with an intramolecular Sn−N interaction. The structure of this compound in the solid state has been established as tetrameric due to intermolecular fluorine and hydrogen bridges, respectively, and monomeric in solution.[7]

We described previously that intramolecularly coordinated donor group(s) (via a C,N-chelating ligand) in organotin(IV) compounds may lead to interesting structures and very soluble substances[8] in comparison to compounds without this type of coordination.

We now report the syntheses and structures of four novel triorganotin(IV) fluorides, **5**−**8**, of general formula $\{2\text{-}[(CH_3)_2NCH_2]C_6H_4\}R_2SnF$, which contain one 2-(*N,N*-dimethylaminomethyl)phenyl (L) as a C,N-chelating ligand and two alkyl (Me, *n*-Bu, *t*-Bu) or aryl (Ph) groups of different steric bulk and electronic properties (Scheme 1). The compounds **6** and **8** were preliminarily tested to examine their fluorinating capability in reaction with titanocene dichloride.

Results and Discussion

Synthetic Aspects. Compounds **5**−**8** were prepared by the reaction of the appropriate triorganotin(IV) chlorides **1**−**4** and KF in a water/diethyl ether mixture.

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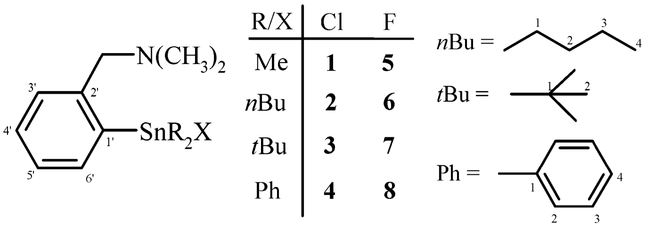
Scheme 1. Numbering of Compounds Studied



R/X	Cl	F
Me	1	5
*n*Bu	2	6
*t*Bu	3	7
Ph	4	8

The purity of the compounds was established by ESI/MS spectrometry, elemental analysis, and multinuclear NMR spectroscopy.

Structural Study. The structures of crystalline compounds **5** and **8** were determined by X-ray diffraction. Selected interatomic distances and angles are presented in the appropriate figure caption (Figure 1 (**5**)). Both compounds reveal the monomeric structure without any intermolecular Sn⋯F contacts. The intermolecular Sn⋯F distances are 4.610 and 6.257 Å for **5** and **8**. The sum of the van der Waals radii[9] of Sn and F is 3.63 Å. In both compounds, the geometry of the central tin atom is that of distorted trigonal bipyramid with the electronegative atoms (N, F) in axial positions and all carbon atoms in equatorial positions, which is in accordance with previously published results.[8,10,11] The sum of interatomic angles in the equatorial plane is 358.34° and 357.62° for **5** and **8**, respectively. The extensions of N−Sn−F angles (167.37(5)° for **5** and 166.83(6)° for **8**) are similar to angles observed in the literature for the ligand (L) used.[10] The extralarge torsion angles (C1, C2, C7, N1 32.10° for **5** and C11, C12, C17, N1 34.57° for **8**), which indicate the deviation of the CH_2 ligand group from the plane defined by C1 (C11 in **8**), Sn1, and N1 atoms, are probably caused by different electronic properties of fluorine in comparison with Cl and Br analogues.[12]

The Sn−F bond distances are somewhat longer (2.0384(10) Å (**5**), 2.0242(12) Å (**8**)) than those found in monomeric tetracoordinated species (1.96 Å).[5] Such elongation of these bonds is caused by intramolecular interaction of the amino donor group in the *trans* position to the fluorine atom. The average Sn−F and Sn−F′ distance in polymeric fluorides is 2.15 Å.[2]

The Sn−N distances (Sn1−N1 2.4899(14) Å and Sn1−N1 2.5294(18) Å) lie within the range found in the Cambridge Crystallographic Data Base (2.424−2.548 Å) for triorganotin compounds with L = 2-(*N*,*N*-dimethylaminomethyl)phenyl (for example, $LSnMe_2Cl$[10a] 2.531 Å, $LSnPh_2Cl$[11a] 2.519 Å, $LSnPh_2Br$[13] 2.511 Å). The only rarity from the set of triorganotin compounds containing L as a ligand is compound **3**. It contains tetracoordinated tin atom, and the distance between Sn and N atoms is significantly increased to 2.908 Å.[14]

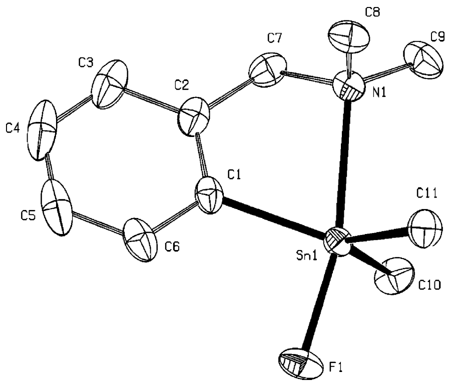


Figure 1. Molecular structure of compound **5** (ORTEP 50% probability). Hydrogens are omitted for clarity. Selected interatomic distances [Å] and angles [deg]: Sn1−F1 2.0384(10), Sn1−C10 2.1248(18), Sn1 C11 2.1261(17), Sn1−C1 2.1313(18), Sn1−N1 2.4899(14), C10−Sn1 C11 115.97(8), C10−Sn1−C1 118.72(7), C11−Sn1−C1 123.65(7), F1−Sn1−N1 167.37(5). For compound **8**: Sn1−F1 2.0242(12), Sn1−C11 2.127(2), Sn1−C31 2.130(2), Sn1−C21 2.134(2), Sn1−N1 2.5294(18), C11−Sn1−C31 117.59(8), C11−Sn1−C21 124.80(8), C31−Sn1−C21 115.34(8), F1−Sn1−N1 166.82(6).

Table 1. Selected NMR Parameters of 5−8

	$LSnR_2F$ (5−8)				
R	$\delta(^{119}Sn)$ [ppm]	$\delta(^{19}F)$ [ppm]	$^1J(^{19}F,^{119}Sn)$[a] [Hz]	$^1J(^{119}Sn,^{13}C)$ [Hz]	angle C−Sn−C[b]
Me	−53.8	−178.8	2023	531.5	127
n-Bu	−77.1	−196.3	2103	515.9	126
t-Bu	−92.1	−207.9	2188	470.1	122
Ph	−198.6	−182.3	2141	792.0	123

[a] Obtained from ^{119}Sn spectra. [b] Calculated from refs 15a,b.

The structure of the studied compounds in chloroform solution at 300 K has been established by various multinuclear NMR techniques. The signals in the ^1H and ^{13}C spectra were assigned on the basis of common 2D NMR techniques (see Experimental Section).

The ^{119}Sn NMR chemical shift values of compounds **5**−**8** are collected in Table 1. Only one signal split to a doublet (due to $^1J(^{119}Sn,^{19}F)$, Table 1) has been observed in all of the ^{119}Sn spectra. The values are shifted a bit upfield but are still in the range for compounds with a five-coordinated tin atom.[15] The values of $\delta(^{119}Sn)$ for insoluble compounds of the R_3SnF type, with oligo- or polymeric structure and five-coordinated tin atoms, obtained in solid state NMR studies, and the compounds of this study are comparable. (For example, $\delta(^{119}Sn)$ for **8** and $\delta(^{119}Sn)_{iso}$ for Ph_3SnF,[16] which is a linear polymer with a rodlike structure with five-coordinated tin atoms,[17] differ by 13.3 ppm.) Similar linear chains were observed in the solid state structure of $PhMe_2SnF$; this compound depolymerizes when dissolved in toluene to give oligomers with 10−50 basic structural units (depending on concentration and temperature).[6] The values

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of $\delta(^{119}Sn)$ for $PhMe_2SnF$ (−49.3 ppm CP/MAS, −53.0 ppm toluene-d_8) differ only slightly from the value observed for compound **5** (−53.8 ppm $LSnMe_2F$). Molecules of compounds $LSn(n\text{-}Bu)_2F$ (**6**) and $LSn(t\text{-}Bu)_2F$ (**7**) obviously have a five-coordinated tin atom, as demonstrated by the upfield shift tendency of $\delta(^{119}Sn)$ in $LSnR_2F$ and R_3SnF, respectively. Similar conclusions can be made from juxtaposition of $\delta(^{119}Sn)$ values of $LSnR_2F$ and $LSnR_2X$ (X = Br, Cl). The five-coordinated geometry of the tin atom in these compounds has been confirmed by X-ray diffraction,[10a,11a] ^{119}Sn CP MAS NMR,[8a] and ^{1}H, ^{13}C, ^{15}N, and ^{119}Sn NMR studies in different solvents,[8c] recently. Differences between extreme $\delta(^{119}Sn)$ values ($LSnR_2F$ vs $LSnR_2X$, ca. 20−30 ppm) are caused by the electronic properties of polar groups, rather than by different coordination numbers (CN) of the tin atom, in contrast to $LSn(n\text{-}Bu)_2Cl$ (−51.7 ppm, CN 5)[8c] and $PhSnMe_2Cl$ (+98.0 ppm, CN 4).[18] On the other hand, the value of $\delta(^{119}Sn)$ in compound **3** does not correlate with the previously found shifts and values obtained from the literature (for example −53.9 ppm for $[(t\text{-}Bu)_2PhSn]_2O$),[19] and is caused by another type of coordination.[14]

The coupling constants $^{1}J(^{119}Sn,^{19}F)$ of the compounds studied are typical for terminal Sn−F bonds, e.g., about 2100 Hz,[6,7] while the oligo- or polymeric compounds R_3SnF with bridging connections[20] Sn−F···Sn have values that are practically half.

Only one sharp signal with resolved $^{1}J(^{19}F,^{119/117}Sn)$ coupling and an integral ratio of signals typical for only one Sn−F interaction has been observed in each ^{19}F NMR spectrum. The ^{19}F NMR chemical shifts of the studied compounds (from −178.8 to −207.9 ppm, see Table 1) are in agreement with a few reported values for the terminal Sn−F bonds in five-coordinated triorganotin(IV) compounds: $(Me_3SiCH_2)_3SnF$ (−207.2 ppm),[6,21] $PhMe_2SnF\cdot$pyridine (−168.6 ppm),[6] and $N(CH_2CH_2CH_2)_3SnF$ (−166.3 ppm).[7]

The measured coupling constants $^{1}J(^{119}Sn,^{13}C)$ and calculated interatomic angles C(1)−Sn−C(1)[15] are collected in Table 1. These values are characteristic for five-coordinated triorganotin(IV) species.

The ^{1}H and ^{119}Sn NMR spectra in different solvents and at variable temperature (VT) were measured in order to detect previously described (e.g., ionization of compounds or weakening of the Sn−N bond) intramolecular processes.[8c,d] Because compounds **5**−**8** reveal similar behavior in all measured spectra, only compound **5** was selected for this investigation. The VT spectra were measured in the range 185−300 K. Chloroform (as a noncoordinating solvent), acetone (as a coordinating solvent), and methanol (as a coordinating solvent with an acidic hydrogen atom) were selected for these purposes. The values of $\delta(^{1}H)$ for all signals in all spectra differ by a few hundredths of ppm. The values of $\delta(^{119}Sn)$ are similar with the decrease in temperature. The coupling constant $^{1}J(^{119}Sn,^{19}F)$ decreases by 50−70 Hz with decreasing temperature; this indicates only slight weakening of the Sn−F bond. The values of $\delta(^{119}Sn)$ for **5** vary slightly (−64.9 to −46.0 ppm) in all solvents used and are in the previously mentioned range for five-coordinated triorganotin(IV) species with terminal and covalent Sn−X bonds.

Fluorinating Ability. The potential use of compounds **5**−**8** as fluorinating agents[1,22] was tested with **6** and **8** in reaction with titanocene dichloride. Two equivalents of compound **6** or **8**, respectively, were mixed with 1 equiv of titanocene dichloride, and the mixture was stirred in dichloromethane at 35 °C in air. Within 3 h the color changed from orange to yellow, and the solvent was evaporated in vacuo. The ^{1}H and ^{119}Sn NMR spectra of the crude product were recorded, and no trace of starting material was observed. In the ^{119}Sn NMR spectra, only the singlets at −47.1 and −177.2 ppm were observed, which we assigned to compound **2** and **4** ($LSnR_2Cl$), respectively. Also, the ^{1}H NMR and IR spectra revealed the presence of only **2** or **4** ($LSnPh_2Cl$)[8c] and **9** (Cp_2TiF_2).[23] Compound **2** was separated in quantitative yield from **9** by washing the crude product with cold pentane. The same separation procedure did not work quantitavely for a mixture of **8** and **9** because of their similar solubilities in common solvents.

We made two competitive experiments for juxtapossition of the fluorinating power of the commonly used Me_3SnF and **6** as well. Two equivalents of both Me_3SnF (freshly sublimed and finely powderized) and **6** were mixed together with 1 equiv of Cp_2TiCl_2 in both methylene dichloride (40 °C, 3 h) and toluene (80 °C, 10 min). In both experiments the conversion of Cp_2TiCl_2 to Cp_2TiF_2 was quantitative and no trace of Me_3SnCl was detected; only the signal at −47.1 ppm due to **2** was detected in the ^{119}Sn NMR spectra of both reaction crudes. The reaction in toluene was finished in less than 10 min and seems to be much faster than that published (Me_3SnF, 4 h).[22]

Concluding Remarks. From the findings described above, we can conclude that compounds **5**−**8** are easily accessible monomeric triorganotin(IV) fluorides that exhibit the same structure in the solid state and in solutions in different solvents at variable temperature. The tin atom is five-coordinated with three carbons in axial positions and fluorine and nitrogen ($-CH_2N(CH_3)_2$) in equatorial positions of a slightly distorted trigonal bipyramid. Compounds **6** and **8** are able to fluorinate titanocene dichloride essentially quantitatively, and they have better fluorination efficiency than commonly used organotin fluoride, due to their monomeric structure and Sn−F bond activation by Sn−N coordination.

Experimental Part

General Remarks. The preparations of compounds **1**−**4** were carried out in an argon atmosphere. *N*,*N*-Dimethylben-

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zylamine, *n*-butyllithium, appropriate diorganotin dihalides, titanocene dichloride, and anhydrous potassium fluoride were obtained from Sigma-Aldrich. Benzene, *n*-hexane, and *n*-pentane were dried over and distilled from sodium wire; chloroform and dichloromethane were dried over and distilled from P_2O_5 and CaH_2.

Compounds **1**,[10a] **2**,[8b] **3**,[14] and **4**[8a] were obtained by published methods. Compounds **5**−**8** were prepared via the typical procedure described below for **5**. The single crystals of **5** and **8** were grown from ca. 5% CH_2Cl_2 solution of the appropriate compound, into which hexane was charged via slow vapor diffusion.

The solution state ^{1}H (500.13 MHz), ^{13}C (125.76 MHz), ^{119}Sn (186.50 MHz), and ^{19}F (470.59 MHz) NMR spectra of the studied compounds were measured on a Bruker Avance 500 spectrometer equipped with a 5 mm broadband probe with *z*-gradient in the temperature range 170−360 K. The solutions were obtained by dissolving 50 mg of each compound in 0.5 mL of deuterated solvents. The ^{1}H chemical shifts were calibrated relative to the signal of residual $CHCl_3$ ($\delta = 7.25$), acetone ($\delta = 2.01$), and methanol ($\delta = 3.31$), respectively. The ^{13}C chemical shifts were referred to the signal of $CDCl_3$ ($\delta = 77.0$), the ^{119}Sn chemical shifts are referred to external neat tetramethylstannane ($\delta = 0.0$), and the ^{19}F chemical shifts are referred to external Cl_3FC ($\delta = 0.0$). Positive chemical shift values denote shifts to higher frequencies relative to the standards. Two-dimensional *gs*(gradient selected)-H,H-COSY, *gs*-^{1}H−^{13}C-HSQC, and *gs*-^{1}H−^{13}C-HMBC[24,25] spectra were recorded using standard microprograms provided by Bruker. ^{119}Sn NMR spectra were measured using the inverse gated-decoupling mode. ^{1}H and ^{13}C chemical shifts were assigned from *gs*-H,H-COSY, *gs*-^{1}H−^{13}C, and *gs*-^{1}H−^{13}C-HMBC spectra (optimized for $^1J(^{13}C,^1H)$ ca. 150 Hz and $^3J(^{13}C,^1H)$ ca. 8 Hz, respectively).

Positive-ion electrospray ionization (ESI) mass spectra were measured on an Esquire3000 ion trap analyzer (Bruker Daltonics, Bremen, Germany) in the range *m*/*z* 50−1000. The ion trap was tuned to yield an optimum response for *m*/*z* 350. The samples were dissolved in acetonitrile and analyzed by direct infusion at a flow rate of 1 μL/min. The IR measurements were performed on a Perkin-Elmer 684 apparatus in Nujol mulls (cm^{-1}).

2-[(*N*,*N*-Dimethylaminomethyl)phenyl]dimethylstannylfluoride (5). To a solution of 0.76 g of **1** (2.4 mmol) in 50 mL of diethyl ether (a 250 mL conical flask) was added 1.36 g (24 mmol) of KF in 75 mL of distilled water, and the mixture was stirred for 2 days. The water phase was separated and washed twice with 10 mL of Et_2O, and ethereal washings were combined. Another 1.36 g of KF in 30 mL of water was added to the ethereal phase and again stirred for 2 days. After this procedure the water phase was separated and washed twice with 10 mL of Et_2O. The combined ethereal extracts were dried over sodium sulfate and filtered, and the filtrate was evaporated to dryness. The resulting white crystals were washed with cold pentane. Mp: 86−89 °C. Yield: 0.60 g (82%). ^{1}H NMR ($CDCl_3$, 300 K, ppm): 7.09 (d, 1H, H(3′)), $^3J(^1H(4'),^1H(3')) = 6.43$ Hz; 7.30 (m, 2H, H(4′,5′)); 7.95 (d, 1H, H(6′)), $^3J(^1H(6'),^1H(5')) = 8.49$, $^3J(^{119}Sn, ^1H) = 43.3$ Hz; 3.57 (s, 2H, NCH_2); 2.26 (s, 6H, $N(CH_3)_2$); 0.53 (s, 6H, H(1)), $^2J(^{119}Sn, ^1H) = 67.3$ Hz, $^3J(^{19}F,^1H(1)) = 3.61$ Hz. ^{13}C NMR ($CDCl_3$, 300 K, ppm): 141.2, $^1J(^{119}Sn,^{13}C) = 765.4$ Hz, C(1′); −3.7, $^1J(^{119}Sn,^{13}C) = 531.5$ Hz, C(1). ESI-MS: MW = 302. *m*/*z* (%). Positive-ion MS: $[M - F]^+$, 284 (100); $[2M - F]^+$, 587 (17). Anal. Found: C, 43.7; H, 6.0; N, 4.7. Calcd for $C_{11}H_{18}NSnF$ (302.06): C, 43.75; H, 6.01; N, 4.64.

2-[(*N*,*N*-Dimethylaminomethyl)phenyl]di-*n*-butylstannylfluoride (6). As for **5**, to 2.30 g of **2** (5.7 mmol) was added 6.64 g (114 mmol) of KF. A yellowish oil was isolated. Yield: 1.60 g (73%). ^{1}H NMR ($CDCl_3$, 300 K, ppm): 7.08 (d, 1H, H(3′)), $^3J(^1H(4'),^1H(3')) = 5.57$ Hz; 7.25 (m, 2H, H(4′,5′)); 7.94 (d, 1H, H(6′)), $^3J(^1H(6'),^1H(5')) = 6.52$, $^3J(^{119}Sn, ^1H) = 55.72$ Hz; 3.52 (s, 2H, NCH_2); 2.26 (s, 6H, $N(CH_3)_2$); 1.66 (m, 4H, H(1)); 1.34 (m, 4H, H(2)); 1.20 (m, 4H, H(3)); 0.86 (t, 6H, H(4)). ^{13}C NMR ($CDCl_3$, 300 K, ppm): 141.7, $^1J(^{119}Sn,^{13}C) = 677.3$ Hz, C(1′); 15.9, $^1J(^{119}Sn,^{13}C) = 515.9$ Hz, C(1). ESI-MS: MW = 386. *m*/*z* (%). Positive-ion MS: $[M - F]^+$, 368 (100); $[2M - F]^+$, 755 (12). Anal. Found: C, 52.8; H, 7.8; N, 3.7. Calcd for $C_{17}H_{30}NSnF$ (386.06): C, 52.88; H, 7.83; N, 3.63.

2-[(*N*,*N*-Dimethylaminomethyl)phenyl]di-*tert*-butylstannylfluoride (7). As for **5**, to 0.80 g of **3** (2.0 mmol) was added 2.30 g (40 mmol) of KF. A yellowish oil was isolated. Yield: 0.53 g (69%). ^{1}H NMR ($CDCl_3$, 300 K, ppm): 7.08 (d, 1H, H(3′)), $^3J(^1H(4'),^1H(3')) = 6.13$ Hz; 7.23 (m, 2H, H(4′,5′)); 8.03 (d, 1H, H(6′)), $^3J(^1H(6'),^1H(5')) = 6.39$, $^3J(^{119}Sn,^1H) = 48.3$ Hz; 3.45 (s, 2H, NCH_2); 2.26 (s, 6H, $N(CH_3)_2$); 1.32 (s, 18H, H(2)), $^3J(^{119}Sn,^1H) = 81.1$ Hz. ^{13}C NMR ($CDCl_3$, 300 K, ppm): 142.7, $^1J(^{119}Sn,^{13}C) = 503.5$ Hz, C(1′); 38.1, $^1J(^{119}Sn,^{13}C) = 470.1$ Hz, C(1). ESI-MS: MW = 386. *m*/*z* (%). Positive-ion MS: $[M - F]^+$, 368 (100); $[2M - F]^+$, 755 (15). Anal. Found: C, 52.9; H, 7.9; N, 3.6. Calcd for $C_{17}H_{30}NSnF$ (386.06): C, 52.88; H, 7.83; N, 3.63.

2-[(*N*,*N*-Dimethylaminomethyl)phenyl]diphenylstannylfluoride (8). As for **5**, to 1.30 g of **4** (3.0 mmol) was added 3.42 g (60 mmol) of KF. White crystals were isolated. Mp: 159−161 °C. Yield: 0.89 g (70%). ^{1}H NMR ($CDCl_3$, 300 K, ppm): 7.15 (d, 1H, H(3′)), $^3J(^1H(4'),^1H(3')) = 7.29$ Hz; 7.36 (m, 2H, H(4′,5′)); 8.26 (d, 1H, H(6′)), $^3J(^1H(6'),^1H(5')) = 6.94$, $^3J(^{119}Sn,^1H) = 63.9$ Hz; 3.57 (s, 2H, NCH_2); 1.91 (s, 6H, $N(CH_3)_2$); 7.68 (d, 4H, H(2)), $^3J(^{119}Sn,^1H) = 62.6$ Hz, $^3J(^1H(2),^1H(3)) = 7.41$ Hz; 7.36 (m, 6H, H(3,4)). ^{13}C NMR ($CDCl_3$, 300 K, ppm): 138.1, $^1J(^{119}Sn,^{13}C) = 840.6$ Hz, C(1′); 140.2, $^1J(^{119}Sn,^{13}C) = 792.0$ Hz, C(1). ESI-MS: MW = 386. *m*/*z* (%). Positive-ion MS: $[M - F]^+$, 408 (100); $[2M - F]^+$, 835 (19). Anal. Found: C, 59.1; H, 5.1; N, 3.5. Calcd for $C_{21}H_{22}NSnF$ (426.12): C, 59.19; H, 5.20; N, 3.44.

Bis(η^5-cyclopentadienyl)titanium(IV) Difluoride (9). Cp_2TiCl_2 (0.200 g, 0.93 mmol) was added to a solution of **6** (0.746 g, 1.85 mmol) or **8** (0.821 g, 1.85 mmol) in 25 mL of dichloromethane. The mixture was stirred for 3 h at 35 °C. During this period the color changed from orange to yellow. In both cases, the solvent was evaporated in vacuo. In the case of the reaction of **6** with Cp_2TiCl_2, the crude product was washed twice with cold pentane. Pentane was evaporated to give **2** as the sole product. The solid residue was dried in vacuo to give pure **9** in quantitative yield. ^{1}H NMR ($CDCl_3$, 300 K, ppm): 6.45 (s, 10H, Cp). IR (Nujol mulls, cm^{-1}): 3111w, 1444 w, 1017w, 824m, 565s, 541m. The second reaction afforded a mixture of **4** and **9**, which is practically inseparable.

Crystallography. Selected crystallographic data for compounds **5** and **8**: Crystal system monoclinic, space group $P2_1/n$, $a = 9.5540(2)$ Å; $b = 12.6330(3)$ Å; $c = 11.1640(2)$ Å; $\beta = 111.3990(13)°$ (for **5**); 8.12000(10); 12.3250(2); 19.4110(3) Å; $\beta = 102.8680(7)°$ (for **8**). Selected structural parameters (distances (Å) and angles (deg)) are given in the Figure 1 caption. Crystals suitable for X-ray structure determination were obtained by vapor diffusion of hexane into ca. 3% dichloromethane solution for compounds **5** and **8**, respectively. Data for both colorless crystals were collected at 150(2) K on a Nonius KappaCCD diffractometer using Mo Kα radiation ($\lambda = 0.71073$ Å) and a graphite monochromator. The structures were solved by direct methods (SIR92). All reflections were used in the structure refinement based on F^2 by full-matrix least-squares technique (SHELXL97). All hydrogen atoms were recalculated into idealized positions (riding model) and assigned temperature factors $H_{iso}(H) = 1.2U_{eq}$(pivot atom) or of $1.5U_{eq}$ for the methyl moiety. Absorption corrections were

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carried out, using a multiscan procedure (SORTAV). From the last cycle of refinement of both structures, $(\Delta/\delta)_{\max} = 0.001$.

A full list of crystallographic data and parameters including fractional coordinates is deposited at the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge, CB2 1EZ, UK [fax: int. code +44(1223)336-033; e-mail: deposit@ccdc.cam.ac.uk]. CCDC deposition numbers: 215630 (**5**) and 215631 (**8**).

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Supporting Information Available: CIF files for compounds **5** and **8** and NMR spectral details are available free of charge via the Internet at http://pubs.acs.org.

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