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SYNTHESIS OF 1,1′-DI-t-BUTYLSTANNOCENE AND ITS REACTION WITH TRIFLUOROBORANE. THE CRYSTAL AND MOLECULAR STRUCTURE OF η^5-$(CH_3)_3CC_5H_4Sn^+ BF_4^-$

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Summary

The reaction of $Li(CH_3)_3CC_5H_4$ with $SnCl_2$ in THF affords 1,1′-di-t-butylstannocene in 78% yield as an air-sensitive oil. ^1H and ^{13}C NMR spectra are consistent with a pentahapto-structure. Mössbauer parameters of the stannocene and its trimethylsilyl counterpart match closely those of known stannocenes and neither compound appears to undergo oligomerization. The reaction of 1,1′-di-t-butylstannocene with BF_3 in CH_2Cl_2 affords η^5-$(CH_3)_3CC_5H_4Sn^+ BF_4^-$ and other uncharacterized product(s) thought to involve tetracoordinate tin. The structure of η^5-$(CH_3)_3CC_5H_4Sn^+ BF_4^-$ was determined by single crystal X-ray diffraction (orthorhombic, *Pbcn*, (T 25°C), a 18.423(3), b 11.723(1), c 11.044(2) Å, $Z = 8$, V 2385.2 Å^3, m.p. 95–96°C, colorless, Mo-K_α, $R = 0.043$).

Introduction

Stannocenes are the subjects of increasing interest owing to their various modes of chemical reactivity [1–9] and structural behavior. The solid state structure of sublimed Cp_2Sn consists of unassociated monomeric units [10] but the compound was shown by Mössbauer spectra to undergo spontaneous oligomerization, catalyzed by dimethylformamide, in the solid state [11]:

$$n Cp_2Sn \rightarrow (Cp_2Sn)_n \qquad (1)$$

On the other hand, 1,1′-dimethylstannocene was found to be moderately stable toward polymerization [12].

The compound $(\eta^5\text{-}C_5H_5)_2Sn \cdot BF_3$, originally cited as an example of the donor functionality of stannocene [13], has been found instead to exhibit a complex structure involving the stannocenium ion and BF_4^- [14]. The instability of the simple adduct was explained on the basis of SCF Xα-sw calculations which placed the tin lone pair orbital in Cp_2Sn some 2 eV lower than the HOMO [15].

In order to examine further both the oligomerization of stannocenes and their interaction with Lewis acids, we have prepared the new derivative, 1,1′-di-t-butylstannocene, along with the known, 1,1′-bis(trimethylsilyl)stannocene [9] for Mössbauer spectroscopy. The reaction of the new derivative with trifluoroborane is described.

Experimental

All reactions were carried out under either an inert atmosphere or a vacuum according to conventional techniques [16]. The starting materials $(CH_3)_3CC_5H_5$ and $(CH_3)_3SiC_5H_5$ were prepared according to published methods [17,18]. The solvents were dried (tetrahydrofuran with $LiAlH_4$, pentane, heptane and dichloromethane with P_4O_{10}) and stored under vacuum. Elemental analyses were by Galbraith Laboratories, Knoxville, Tenn. ^1H and ^{13}C NMR spectra were obtained using a Varian FT-80 instrument operating at 80 and 20 MHz, respectively. The probe temperature was 35°C. The liquid chromatograph-mass spectrometer has been described elsewhere [19]. It was used in the positive ion mode with direct sample injection. Mössbauer spectra were obtained using an Austin Science Associates instrument with the source at room temperature and the sample cooled to liquid nitrogen temperature.

Synthesis of $(\eta^5\text{-}(CH_3)_3CC_5H_4)_2Sn$ *(I)*

A THF solution of $SnCl_2$ was slowly added to a solution of $Li(CH_3)_3CC_5H_5$ [17] (2 equiv.) in THF at ice temperature. After stirring overnight at room temperature, the solvent was vapor transferred from the reaction mixture and the residue was held under dynamic vacuum for 12 h. The highly air-sensitive product was obtained in 80% yield as a light brown oil, b.p. 96–97°C (3×10^{-3} torr), by extraction of the residue with heptane. Anal. Found C, 59.14, H, 7.23. $C_{18}H_{26}Sn$ calcd.: C, 59.87; H, 7.25%. ^1H NMR (60 MHz) in $CDCl_3$: δ 1.24 (s, 18H, Me_3C), 5.71 (m, 4H, $H_{2,5}$ or $H_{3,4}$), 5.91 (m, 4H, $H_{2,5}$ or $H_{3,4}$) ppm. $^{13}C\{^1H\}$ NMR (20 MHz): δ31.7(CMe_3), 33.6(CMe_3), 107.3(C(3,4)), 108.3(C(2,5)), 144.6(C(1)) (ref. Me_4Si), ^{119m}Sn Mössbauer, IS = 3.64 ± 0.05 mm s^{-1} (FWHH 1.6 mm s^{-1}) (Source: $Ba^{119m}SnO_3$).

Synthesis of $(\eta^5\text{-}(CH_3)_3SiC_5H_4)_2Sn$

A solution of $(CH_3)_3SiC_5H_5$ (2.76 g, 20.0 mmol) in 30 ml of THF at ice temperature was treated with 12.9 ml (20.0 mmol) of n-BuLi (1.55 M in hexane). After warming to and stirring at room temperature for 20 h, the reaction mixture was again cooled with an ice bath and treated with a solution of 1.89 g $SnCl_2$ (10.0 mmol) in 12 ml of THF. The reaction mixture was stirred overnight after which the solvent was removed by vapor transfer and the product separated by extraction into 20 ml of heptane. Vapor transfer of the heptane left the product in 78% yield as a light tan oil. Anal. Found: C, 48.2; H, 6.77. $C_{16}H_{26}Si_2Sn$ calcd.: C, 48.87; H, 6.66%. NMR data are agreement with literature values [9]. ^{119}Sn Mössbauer: IS 3.58 ± 0.05 mm s^{-1}.

Reaction of I with trifluoroborane

In a typical reaction, 0.86 g (2.2 mmol) of I was placed in a 50 ml flask fitted with a Teflon valve adapter for the vacuum line. About 25 ml of CH_2Cl_2 and 2.17 mmol of BF_3 were condensed into the flask which was closed and magnetically stirred during slow warming to room temperature and for 12 h thereafter. In one reaction the volatile constituents of the product mixture were fractionated through a series of cold traps and no BF_3 remained unreacted at this point. The volume of the reaction mixture was then reduced to 2–3 ml by vapor transfer and about 20 ml of hexane was condensed into the flask. The contents were then warmed slowly to room temperature without agitation; after 12 h colorless crystals were filtered from the mixture and dried using a stream of nitrogen within the glove box. The product was identified as η^5-t-BuCpSn$^+$ BF_4^- (II), m.p. 95–96°C, by its elemental composition and an X-ray structure determination. Anal. Found: C, 32.89; H, 3.98. $C_9H_{13}BF_4Sn$: calcd. C, 33.08; H, 3.98%. ^1H NMR (60 MHz) in $CDCl_3$: δ 1.37 (s, 9H, Me_3C), 6.52 (s, 4H, $H_{2,3,4,5}$). $^{13}C\{^1H\}$ NMR (20 MHz) in $CDCl_3$: δ 147.5 (C(1)), 108.7(C(2,5)), 107.2(C(3,4)), 32.3(C*Me*$_3$), 31.7(*C*Me$_3$). ^{11}B NMR (96 MHz): δ -1.1 (ref. $BF_3 \cdot OEt_2$). ^{119m}Sn Mössbauer IS 3.67 ± 0.06 mm s^{-1}.

After the crystals of II were filtered off, volatiles were removed from the filtrate by vapor transfer leaving an oily residue: ^1H NMR in $CDCl_3$: δ 1.26, 5.66 and 5.85 ppm; ^{13}C NMR in $CDCl_3$: δ 144.93, 108.1, 106.7, 32.9 and 31.34 ppm; ^{11}B NMR: δ -0.8(br, s) ppm. The LC-MS (positive ion mode) of the residue in THF solution exhibited the ions (in order of decreasing relative abundance (RA)): $(CH_3)_3CC_5H_4Sn^+$ (envelope), $THF \cdot BF_3(-H)^+$, $(CH_3)_3CC_5H_5(+H)^+$, $(CH_3)_3CC_5H_4 \cdot THF^+$, $(CH_3)_3CC_5H_4SnF(-H)^+$, $(CH_3)_3CC_5H_4F \cdot THF^+$, $((CH_3)_3CC_5H_4)_2Sn^+$, $(CH_3)_3CC_5H_4Sn \cdot THF^+$, $SnF_2 \cdot THF(+H)^+$, $((CH_3)_3CC_5H_4)_2SnF(-H)^+$, $((CH_3)_3CC_5H_4)_2Sn \cdot THF^+$, $((CH_3)_3CC_5H_4)_3Sn^+$, and $((CH_3)_3CC_5H_4)_3SnF^+$ along with the ions $THF(-H)^+$ and $(THF)_2(-H)^+$ characteristic of the solvent.

X-Ray experimental data

A large, clear colorless block of approximate dimensions 0.80 × 0.40 × 0.30 mm was mounted on an Enraf–Nonius CAD-4 automatic diffractometer. Since the sample was air-sensitive, it was placed in a thin-walled glass capillary. The radiation used was Mo-K_α monochromatized by a dense graphite crystal assumed for all purposes to be 50% imperfect. Final cell constants, as well as other information pertinent to data collection and refinement, are listed in Table 1. The Laue symmetry was determined to be *mmm*, and the space group was shown unambiguously to be *Pbcn*. Intensities were measured using the θ–2θ scan technique, with the scan rate depending on the net count obtained in rapid pre-scans of each reflection. Two standard reflections were monitored periodically during the course of the data collection as a check of crystal stability and electronic reliability, and these showed a 7.3% decay over the 50 h of data collection. A linear decay correction was applied as a function of exposure time to compensate for this. In reducing the data, Lorentz and polarization factors were applied, as well as an empirical absorption correction based on azimuthal ψ scans of six reflections having χ near 90 degrees [20].

The structure was solved by use of the Patterson technique, which revealed the position of the tin atom. The usual sequence of isotropic and anisotropic refinement was followed, after which the hydrogens were entered in ideally calculated positions and held fixed. The BF_4 anion was found to be heavily disordered, but no attempt was made to refine the fluorine occupancies. After all shift/esd ratios were less than 0.4, the full-matrix least squares converged at the agreement factors listed in Table 1. Twenty-five reflections exhibiting high errors were removed from the refinement,

TABLE 1

DATA COLLECTION AND PROCESSING PARAMETERS FOR II

Space group	*Pbcn*, orthorhombic
Cell constants	a 18.423(3) Å
	b 11.723(1)
	c 11.044(2)
	V 2385.2 Å^3
Molecular formula	$C_9H_{13}SnBF_4$
Molecular weight	326.7
Molecules per cell	$Z = 8$
Density (calc)	ρ 1.82 g cm^{-3}
Absorption coefficient	μ 21.7 cm^{-1}
Radiation (Mo-K_α)	λ0.71073 Å
Collection range	$4° \leqslant 20 \leqslant 40°$
Scan width	$\Delta\theta = (0.95 + 0.35 \tan\theta)°$
Maximum scan time	180 s
Scan speed range	0.50 to 5.70° min^{-1}
Total data collected	2159
Independent data, $I > 3\sigma(I)$	1298
Total variables	136
$R = \Sigma\|\|F_0\| - \|F_c\|\|/\Sigma\|F_0\|$	0.043
$R = [\Sigma w(\|F_0\| - \|F_c\|)2/\Sigma w\|F_0\|^2]^{1/2}$	0.048
Weights	$w = \sigma(F)^{-2}$

presumably caused by the presence of a very small satellite crystal which was noticed during the course of the space group determination. Anomalous dispersion coefficients for the heavier elements were included. No unusually high correlations were noted between any of the variables in the last cycle of least squares refinement, and the final difference density map was featureless. All calculations were made using Molecular Structure Corporation's TEXRAY 230 modifications of the SDP-PLUS series of programs. Positional parameters, bond distances and bond angles for II are listed in Table 2, 3 and 4, respectively.

Results and discussion

1,1′-Di-t-butylstannocene (I) was obtained in 78% yield as a highly air-sensitive, light brown oil, b.p. 96–97°C (3×10^{-3} torr), by the reaction of $SnCl_2$ with $Li(CH_3)_3CC_5H_4$ [17] (2 equiv.) at ice temperature in THF followed by removal of volatiles and extraction with heptane. The ^1H NMR spectrum of I was assigned based on its similarity to the published spectrum of $(\eta^5\text{-}MeC_5H_4)_2Sn$ [12], the principal difference being that the ring protons (H(2,5) and H(3,4)) were not resolved in dimethylstannocene but are resolved in I. We note that those signals are resolved in the closely related derivative $(\eta^5\text{-}Me_3SiC_5H_4)_2Sn$ [9]. We were unable to detect spin coupling with the spin active tin isotopes in either the ^1H or ^{13}C spectra of I; such coupling was seen in spectra of the methyl derivative but only at reduced temperature. Both the ^1H and the ^{13}C spectra of I are consistent with the expected pentahapto structure.

Confirmation of the structure of I came from its mass (Cl, CH_4) and Mössbauer spectra. The former contained *m/e* values 237–241 representing the $(CH_3)_3CC_5H_4Sn^+$ isotopic envelope along with various fragment ions. However, no parent ion

(*Continued on p. 203*)

TABLE 2

POSITIONAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS FOR II [a]

Atom	x	y	z	$B(\text{Å}^2)$
Sn	0.59321(3)	0.65302(4)	0.57067(5)	4.79(1)
F(1)	0.4325(4)	0.6954(6)	0.6607(7)	13.2(2)
F(2)	0.4422(5)	0.5517(6)	0.576(1)	22.7(4)
F(3)	0.3401(3)	0.5796(8)	0.6540(7)	17.0(3)
F(4)	0.3723(5)	0.674(1)	0.5072(9)	23.8(4)
C(1)	0.6673(4)	0.7919(6)	0.4460(6)	4.4(2)
C(2)	0.6173(5)	0.7373(6)	0.3703(7)	5.6(2)
C(3)	0.5460(4)	0.7702(6)	0.4056(6)	5.0(2)
C(4)	0.5534(4)	0.8432(6)	0.5052(6)	4.3(2)
C(5)	0.6284(3)	0.8606(5)	0.5298(5)	3.2(1)
C(6)	0.6602(4)	0.9374(5)	0.6245(6)	3.9(1)
C(7)	0.6041(4)	0.9728(7)	0.7172(7)	5.8(2)
C(8)	0.6899(5)	1.0433(7)	0.5586(8)	7.4(2)
C(9)	0.7236(4)	0.8801(8)	0.6898(7)	6.2(2)
B	0.3936(4)	0.6235(9)	0.5996(9)	5.5(2)
H(1)	0.7182	0.7865	0.4400	$5^\star$
H(2)	0.6284	0.6901	0.3029	$5^\star$
H(3)	0.5024	0.7421	0.3697	$5^\star$
H(4)	0.5156	0.8780	0.5496	$5^\star$
H(7A)	0.6279	1.0266	0.7853	$7^\star$
H(7B)	0.5592	1.0156	0.6748	$7^\star$
H(7C)	0.5827	0.8957	0.7629	$7^\star$
H(8A)	0.7172	1.0970	0.6247	$7^\star$
H(8B)	0.7348	1.0107	0.4972	$7^\star$
H(8C)	0.6516	1.0842	0.5091	$7^\star$
H(9A)	0.7467	0.9376	0.7552	$7^\star$
H(9B)	0.7066	0.8027	0.7320	$7^\star$
H(9C)	0.7660	0.8598	0.6223	$7^\star$

[a] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $\frac{4}{3}[a^{2\star}B_{1,1} + b^{2\star}B_{2,2} + c^{2\star}B_{3,3} + ab(\cos\gamma)^{\star}B_{1,2} + ac(\cos\beta)^{\star}B_{1,3} + bc(\cos\alpha)^{\star}B_{2,3}]$

TABLE 3

BOND DISTANCES (Å) FOR II (Numbers in parentheses are estimated standard deviations in the least significant digits.)

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
Sn	C(1)	2.532(3)	C(1)	H(1)	0.942(3)	C(7)	H(7A)	1.078(3)
Sn	C(2)	2.463(3)	C(2)	C(3)	1.424(5)	C(7)	H(7B)	1.074(3)
Sn	C(3)	2.443(3)	C(2)	H(2)	0.949(3)	C(7)	H(7C)	1.107(3)
Sn	C(4)	2.456(3)	C(3)	C(4)	1.401(4)	C(8)	H(8A)	1.088(3)
Sn	C(5)	2.559(2)	C(3)	H(3)	0.953(3)	C(8)	H(8B)	1.136(5)
F(1)	B	1.296(5)	C(4)	C(5)	1.424(4)	C(8)	H(8C)	1.012(4)
F(2)	B	1.256(5)	C(4)	H(4)	0.944(3)	C(9)	H(9A)	1.076(3)
F(3)	B	1.263(5)	C(5)	C(6)	1.499(4)	C(9)	H(9B)	1.066(4)
F(4)	B	1.242(6)	C(6)	C(7)	1.512(4)	C(9)	H(9C)	1.105(3)
C(1)	C(2)	1.399(4)	C(6)	C(8)	1.539(4)			
C(1)	C(5)	1.421(4)	C(6)	C(9)	1.529(4)			

TABLE 4

BOND ANGLES (°) FOR II (Numbers in parentheses are estimated standard deviations in the least significant digits.)

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
C(1)	Sn	C(2)	32.5(1)	C(3)	C(4)	C(5)	109.3(3)	C(6)	C(8)	H(8B)	105.7(3)
C(1)	Sn	C(3)	54.9(1)	C(3)	C(4)	H(4)	126.9(3)	C(6)	C(8)	H(8C)	113.0(3)
C(1)	Sn	C(4)	54.4(1)	C(5)	C(4)	H(4)	123.7(3)	H(8A)	C(8)	H(8B)	104.9(3)
C(1)	Sn	C(5)	32.40(8)	C(1)	C(5)	C(4)	106.5(2)	H(8A)	C(8)	H(8C)	114.1(4)
C(2)	Sn	C(3)	33.7(1)	C(1)	C(5)	C(6)	126.8(3)	H(8B)	C(8)	H(8C)	110.2(3)
C(2)	Sn	C(4)	54.9(1)	C(4)	C(5)	C(6)	126.7(2)	C(6)	C(9)	H(9A)	110.1(3)
C(2)	Sn	C(5)	54.16(9)	C(5)	C(6)	C(7)	111.7(2)	C(6)	C(9)	H(9B)	110.9(3)
C(3)	Sn	C(4)	33.2(1)	C(5)	C(6)	C(8)	107.1(2)	C(6)	C(9)	H(9B)	108.5(3)
C(3)	Sn	C(5)	54.81(9)	C(5)	C(6)	C(9)	111.3(2)	H(9A)	C(9)	H(9B)	110.8(3)
C(4)	Sn	C(5)	32.90(9)	C(7)	C(6)	C(8)	110.0(3)	H(9A)	C(9)	H(9C)	107.9(3)
C(2)	C(1)	C(5)	108.5(3)	C(7)	C(6)	C(9)	108.9(3)	H(9B)	C(9)	H(9C)	108.6(3)
C(2)	C(1)	H(1)	125.7(3)	C(8)	C(6)	C(9)	107.8(3)	F(1)	B	F(2)	98.7(4)
C(5)	C(1)	H(1)	125.8(3)	C(6)	C(7)	H(7A)	110.8(3)	F(1)	B	F(3)	116.6(5)
C(1)	C(2)	C(3)	108.7(3)	C(6)	C(7)	H(7B)	111.1(3)	F(1)	B	F(4)	107.0(5)
C(1)	C(2)	H(2)	126.3(4)	C(6)	C(7)	H(7C)	109.2(3)	F(2)	B	F(3)	112.5(5)
C(3)	C(2)	H(2)	124.9(3)	H(7A)	C(7)	H(7B)	110.1(3)	F(2)	B	F(4)	111.8(6)
C(2)	C(3)	C(4)	106.9(3)	H(7A)	C(7)	H(7C)	107.7(3)	F(3)	B	F(4)	109.8(4)
C(2)	C(3)	H(3)	124.7(3)	H(7B)	C(7)	H(7C)	107.9(3)				
C(4)	C(3)	H(3)	128.2(3)	C(7)	C(8)	H(8A)	108.3(3)				

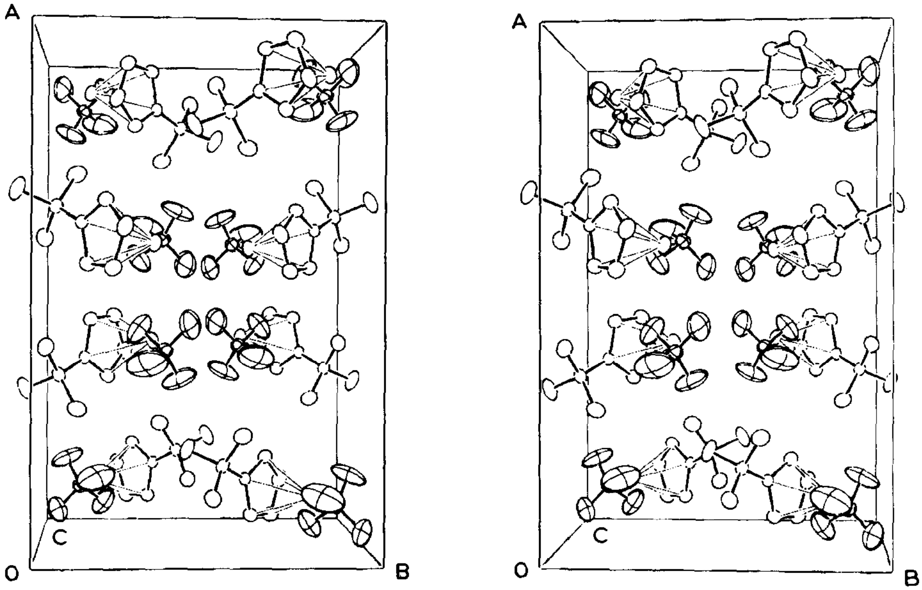

Fig. 1. Unit cell arrangement of t-BuCpSn$^+$ BF_4^- (II).

was observed. The prevalence of ions with only one ring has also been observed in the mass spectra of $(C_5H_5)_2Sn$ [13], $(MeC_5H_4)_2Sn$ [21] and $(Me_3SiC_5H_4)_2Sn$ [22]. The Mössbauer spectrum of I consists of a broad (FWHH 1.64 mm s^{-1}) single resonance at an isomer shift [23] of 3.64 ± 0.05 mm s^{-1} which is in the range expected for divalent tin compounds [24].

The isomer shift of the silicon analog of I, $(\eta^5\text{-}Me_3SiC_5H_4)_2Sn$, prepared earlier by a different method [9], was found to be 3.58 ± 0.05 mm s^{-1}, within experimental uncertainty the same as that of I. No quadrupole splitting was observed in the spectrum of either stannocene, however both resonances were broad (FWHH 1.5–1.6 mm s^{-1}). The Mössbauer parameters of these derivatives resemble those of the other known stannocenes suggesting a close electronic and structural similarity among them. There was no indication from Mössbauer or ^1H NMR spectra that either I or its silicon counterpart undergoes oligomerization upon standing for prolonged periods. This difference may result from the greater steric requirements of the ligands used here as compared to stannocene itself.

In order to assess the behavior of I as an n-donor, reactions were carried out between it and trifluoroborane in a 1/1 stoichiometry using dichloromethane as the solvent. All of the BF_3 was consumed forming an homogeneous solution which, upon concentration and addition of hexane, yielded colorless crystals of II, identified as $\eta^5\text{-}(CH_3)_3CC_5H_4Sn^+$ BF_4^- by its elemental composition, spectra and X-ray crystal structure (Fig. 1). The carbon–tin distances in the cation range from 2.443 to 2.559 Å (average 2.491 Å) which compares closely with the value for $[\eta^5\text{-}Me_5C_5Sn]^+$ $[BF_4]^-$ [25].

The solid state structure of the product from the reaction of Cp_2Sn with BF_3 in THF contains [14] BF_4^-, Cp_2Sn, $[CpSn]^+$ and THF units in a complex arrangement. Coordinate bonding exists between the stannocenium ion and THF and there is a short Sn–F distance (2.86Å) indicative of a weak interaction between the BF_4^- and

Cp_2Sn moieties. In the structure of II there are three tin-fluorine distances which are less than the sum of the Van der Waals radii but even the shortest, 3.10 Å (avg) is substantially (> 0.24 Å) longer than that in the aforementioned structure. There are no remarkable differences in bond distances within the $[CpSn]^+$ moieties in the two structures, however the overall geometrical arrangments are quite different exhibiting monomeric η^5-$(CH_3)_3CC_5H_4Sn^+$ BF_4^- units in our structure and a weak polymer involving bridging cyclopentadienyl interactions in the (η^5-C_5H_2)Sn-BF_3(THF) product [14].

Vapor transfer of solvent from the filtrate after removal of II left an oily residue from which we were not able to isolate additional products. However, some insight into the nature of the residue came from its NMR spectra. Both ^1H and ^{13}C spectra indicated the presence of the $Me_3CC_5H_4$ moiety with chemical shifts resembling those of I and quite different from II. The ^{11}B spectrum exhibited a broad singlet at a shift usually associated with either adducted BF_3 or BF_4^-. Additional information came from liquid chromatograph-mass spectra (thermospray technique) [19] of the residue dissolved in THF. The ions observed suggested that tetracoordinate tin is present in the residue. In particular, the observation of ions such as $(Me_3CC_5H_4)_3Sn^+$ and $(Me_3CC_5H_4)_3SnF^+$ may indicate that a process similar to that shown in eq. 2 occurs in the reaction of I with trifluoroborane. Such a reaction would be consistent

$$2\ \eta^5\text{-t-BuCp}_2\text{Sn} + 2\ \text{BF}_3 \rightarrow \eta^5\text{-t-BuCpSn}^+\text{BF}_4^- + (\text{t-BuCp}_3\text{SnBF}_2) \qquad (2)$$

with a 1/1 stoichiometry and the ions seen by LC-MS are appropriate for the decomposition of difluoroboryltris(t-butylcyclopentadienyl)stannane which we propose as the transient residual product.

Although the simple adduct η^5-t-$BuCp_2Sn \cdot BF_3$ was not identified in the reaction mixture, it is a possible precursor to the observed products perhaps forming at low temperature and undergoing further reaction upon warming.

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