Electrophilic Stannylation of Arenes: A New S_EAr Reaction[a]

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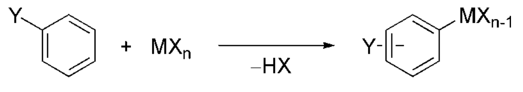
Received October 9, 2000; Revised May 24, 2001; Accepted May 25, 2001

Abstract: Electrophilic "trifluoroacetatotin(IV)" has been prepared by reaction of tin oxide with trifluoroperacetic acid/trifluoroacetic anhydride, and by reaction of tetraphenyltin with excess trifluoroacetic acid. The electrophilic tin(IV) material prepared by either route reacts reversibly with arenes to make aryl-tin compounds and trifluoroacetic acid. The compounds $(C_6H_5)_2Sn_4O_2(CF_3COO)_{10}$ and $(xylyl)_2Sn_4O_2(CF_3COO)_{10}$ have been obtained from the reactions with benzene and *p*-xylene, respectively, and their molecular structures determined by X-ray crystallography. Tin now joins Pb, Tl, and Hg in the list of main group metals whose trifluoroacetato complexes can metalate arenes by C–H activation.

Keywords: arenes; aromatic substitution; C-H activation; stannylation; tin

The direct electrophilic metalation of arenes (Equation 1) is one of the simplest means of forming aromatic derivatives of the main group elements, many of which are extremely useful in organic synthesis.[1] Following the discovery of the direct mercuration of arenes by Dimroth more than 100 years ago,[2] Hg(II),[3,4] Tl(III),[5], and Pb(IV)[6] are the best-known main group metal electrophiles that metalate arenes.[7–10] Given the exceptional importance of organotin compounds in organic synthesis,[11] it would be highly desirable to develop a method for electrophilic stannylation of arenes with inorganic compounds of Sn(IV). This way a Sn-C bond would be formed directly, without the need to use costly and hazardous active organometallic compounds and/or tin hydride reagents.[7]



(1)

Owing to the diminished nucleophilicity of CF_3COO^- as compared with CH_3COO^-, metal trifluoroacetates exhibit greater electrophilicity than their acetate counterparts.[12] Considering the precedents for facile arene metalation by $Hg(CF_3COO)_2$,[3,4] $Tl(CF_3COO)_3$ [5] and $Pb(CF_3COO)_4$,[6] we became curious about arene metalation by trifluoroacetato compounds of Sn(IV), whose $d^{10}s^0$ configuration is isoelectronic with Hg^{2+}, Tl^{3+}, and Pb^{4+}. In this communication, we report the first examples of direct intermolecular stannylation of arenes with trifluoroacetatotin(IV) complexes to produce organotin compounds. Also presented herein, as unambiguous evidence for the C-Sn bond formation, are crystal structures of σ-phenyl- and xylyl-tin compounds obtained by the *direct* stannylation of benzene and *p*-xylene.

We found that arylation-active trifluoroacetatotin compounds result from the oxidative dissolution of SnO in a mixture of trifluoroperacetic acid (generated *in situ* from CF_3COOH and 30% H_2O_2) and trifluoroacetic anhydride (Equation 2) or the dearylation of tetraphenyltin with trifluoroacetic acid[13] (Equation 3). The tin(IV) species obtained by either method behave similarly as long as tin(II) is absent.[14]

$$\mathrm{SnO} + \mathrm{CF_3COOOH} + 2\,(\mathrm{CF_3CO})_2\mathrm{O} \longrightarrow \text{"}(\mathrm{CF_3COO})_4\mathrm{Sn}\text{"} + \mathrm{CF_3COOH} \qquad (2)$$

$$\mathrm{Ph_4Sn} + 4\mathrm{CF_3COOH} \longrightarrow \text{"}(\mathrm{CF_3COO})_4\mathrm{Sn}\text{"} + 4\mathrm{PhH} \qquad (3)$$

Attempts to isolate a well-characterized and analytically-pure single compound by either method were unsuccessful. We believe that the electrophilic species may consist of exchange-labile mixtures of $Sn(CF_3COO)_4$ and trifluoroacetoxypolystannoxanes.[13] At present, one of the reactive electrophiles is tentatively formulated as the hypothetical tetramer $Sn_4(\mu^3\text{-}O)_2(CF_3COO)_{12}$ parent of the isolated aryl compounds (see below). We hereafter call the materials obtained by either route "trifluoroacetatotin(IV)"

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[a] Contribution No. 8101

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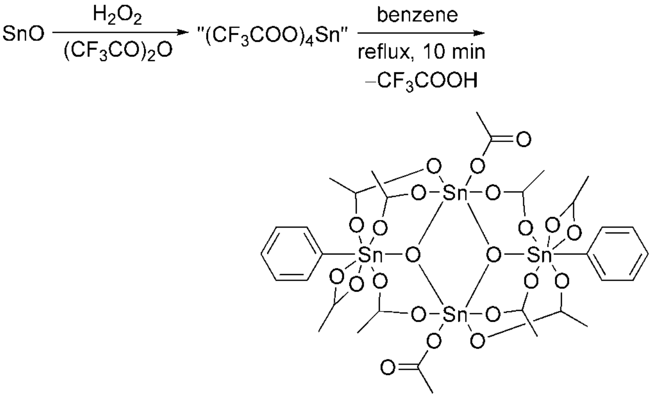
with the understanding that these materials may be more complex mixtures. The material obtained by dearylation of tetraphenyltin with trifluoroacetic acid typically contains some residual phenyltin species.

Our first observation (NMR) of arene stannylation was the reversible formation of phenyltin species when benzene and trifluoroacetic acid were added to solutions of "trifluoroacetatotin(IV)" in trifluoroacetic anhydride, according to Equation 4 where "$Sn(CF_3COO)_4$" and "$PhSn(CF_3COO)_3$" are simplified representations of more complex species.[17] One consequence of this reversibility is that the single-pass dearylation of tetraphenyltin with trifluoroacetic acid leaves some residual phenyltin compounds; the exhaustive dearylation of tetraphenyltin requires sequential removal of benzene and treatment with fresh trifluoroacetic acid.

$$\text{PhH} + \text{"}(CF_3COO)_4Sn\text{"} \rightleftharpoons \text{"}PhSn(CF_3COO)_3\text{"} + CF_3COOH \qquad (4)$$

The equilibrium of Equation 4 was shifted to the desired phenyltin product by running the reaction under reflux, so that the trifluoroacetic acid formed (b.p. 72 °C) was distilled off as the stannylation occurred. Under such conditions, the compound $[(Ph)_2Sn_4O_2(CF_3COO)_{10}]$ was the main phenyltin species isolated from the reaction of benzene with "trifluoroacetatotin(IV)" prepared from SnO (Equation 5).



(5)

The structure of this organotin cluster was established as $[Sn_4(Ph)_2(\mu^3\text{-}O)_2(\mu\text{-}CF_3COO)_6(\eta^2\text{-}CF_3COO)_2(\eta^1\text{-}CF_3COO)_2]$ by X-ray diffraction (Figure 1). The phenyl signal in the ^{1}H NMR spectrum is a complex multiplet but Sn–H coupling to the *ortho*-hydrogens can be discerned ($^3J_{H,Sn}$ = 177 Hz). The presence of one broad singlet in the ^{19}F NMR spectrum of the sample indicates that the cluster is fluxional at ambient

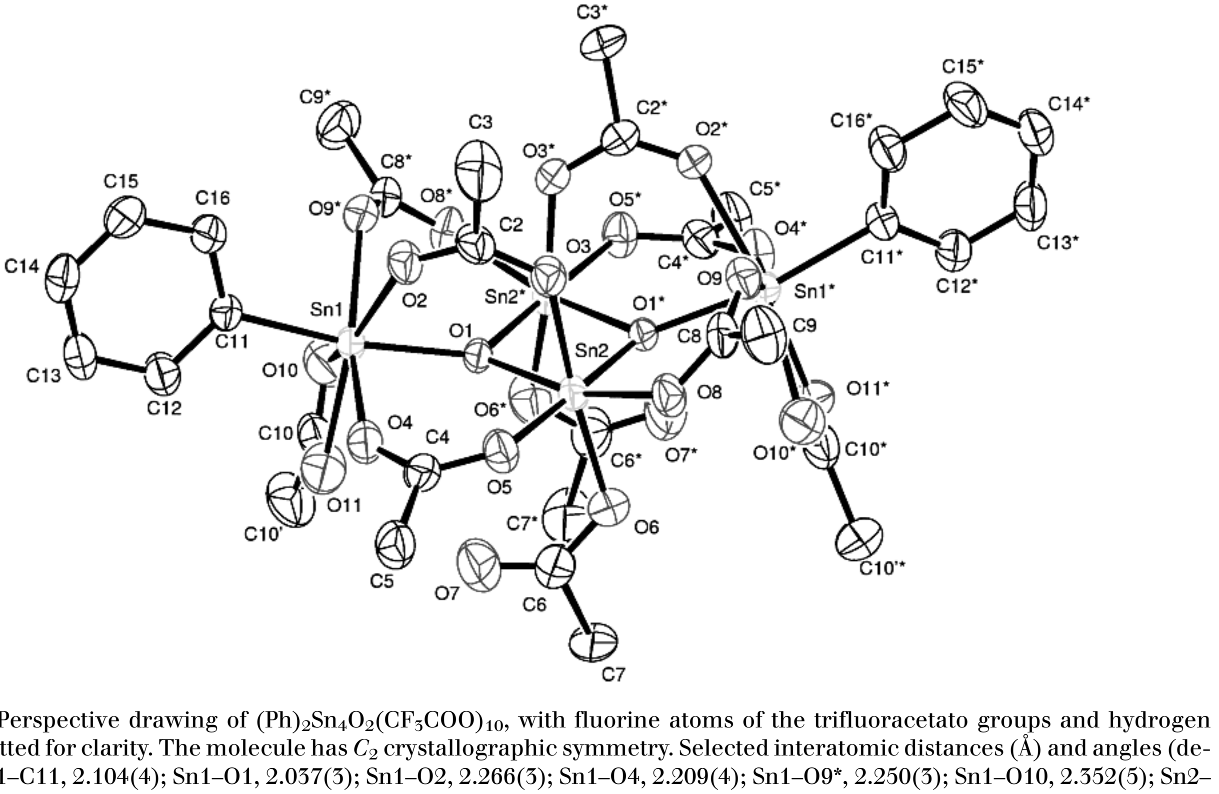


Figure 1. Perspective drawing of $(Ph)_2Sn_4O_2(CF_3COO)_{10}$, with fluorine atoms of the trifluoracetato groups and hydrogen atoms omitted for clarity. The molecule has C_2 crystallographic symmetry. Selected interatomic distances (Å) and angles (degrees): Sn1–C11, 2.104(4); Sn1–O1, 2.037(3); Sn1–O2, 2.266(3); Sn1–O4, 2.209(4); Sn1–O9*, 2.250(3); Sn1–O10, 2.352(5); Sn2–O1, 2.060(3); Sn2–O1*, 2.068(3), Sn2–O3, 2.113(3); Sn2–O5, 2.065(3); Sn2–O6, 2.005(4); Sn2–O8 2.048(3); C11–Sn1–O1, 170.00(15); C11–Sn1–O2, 89.22(16); C11–Sn1–O4, 91.64(16); C11–Sn1–O9*, 90.10(15); C11–Sn1–O10, 100.84(17); C11–Sn1–O11, 99.06(17); O2–Sn1–O4, 79.44(14); O2–Sn1–O9*, 78.90(13); O10–Sn1–O9*, 71.97(15); O10–Sn1–O11, 55.84(18); O4–Sn1–O11, 73.25(18); Sn1–O1–Sn2, 126.43(15); Sn1–O1–Sn2*, 128.35(15); Sn2–O1–Sn2*, 101.87(12), O1–Sn2–O1* 78.12(12).

temperature, probably undergoing fast exchange of the CF_3COO ligands. Bromination of the isolated material led to the clean formation of bromobenzene which was identified and quantified by ^1H NMR. The quantity of PhBr produced translated into 91% purity of $[(Ph)_2Sn_4O_2(CF_3COO)_{10}]$ under the assumption that this was the only Ph-Sn species formed in the direct stannylation of benzene, an assumption that must be taken cautiously as other phenyltin species may be present in the isolated product.

"Trifluoroacetatotin(IV)" readily dissolved in boiling toluene, and the evaporated solution yielded a solid which contained tolyl-Sn species. The methyl signals of this material appeared in the ^1H NMR spectrum (CD_2Cl_2) as an unresolved cluster of peaks at 2.4 – 2.5 ppm and a singlet at 2.6 ppm with well-resolved tin satellites ($J_{H,Sn}$ = 6.5 Hz). Presumably several Sn complexes are involved in the stannylation and toluene is stannylated in several positions. Bromination of the solids formed by stannylation of toluene resulted (GC-MS, NMR) in the formation of 3-bromotoluene and 4-bromotoluene in ca. 2:1 ratio, with trace amounts of 2-bromotoluene.[18] This ratio is in full accord with the H/D exchange data presented below.

A *p*-xylyltin compound was prepared by dissolution of "trifluoroacetatotin(IV)" (prepared from the dearylation of tetraphenyltin with trifluoroacetic acid) in hot *p*-xylene. The residue remaining after evaporating the *p*-xylene solvent was largely a single compound. Recrystallization from hot pentane provided crystals suitable for X-ray diffraction and the crystal structure established the compound as $[(xylyl)_2Sn_4(\mu^3\text{-}O)_2(\mu\text{-}CF_3COO)_6(\eta^1\text{-}CF_3COO)_4]$ (Figure 2).

The coordination of the arylated Sn atoms in the phenyl (**A**, Figure 1, Figure 3) and xylyl (**B**, Figure 2, Figure 3) complexes offers an interesting contrast. The non-bridging CF_3COO ligand in the phenyl complex is η^2, resulting in a 7-coordinate phenyl-tin center, but the non-bridging CF_3COO ligand in the xylyl analogue is η^1, resulting in octahedral coordination about the xylyl-tin center. However this xylyl-tin octahedron is distorted owing in part to interaction with the *ortho*-methyl group of the xylyl ligand. Using the positions of the H atoms as determined by the X-ray diffraction data (H-C 0.963 Å) the H-Sn distance is 2.84 Å; that same H atom is 2.54 and 2.60 Å, respectively, from the tin-bonded trifluoroacetato O atoms nearest to it. It is intriguing that in both structures it is the "organotin" centers that enlarge their coordination spheres while the "inorganic" tin centers remain octahedral 6-coordinate. Other aspects of the two structures are unexceptional, including the Sn_4O_2 core which is often encountered in tin chemistry (see for example references[15,19]).

If the stannylation reaction of Equation 4 is indeed reversible one would expect H/D exchange if

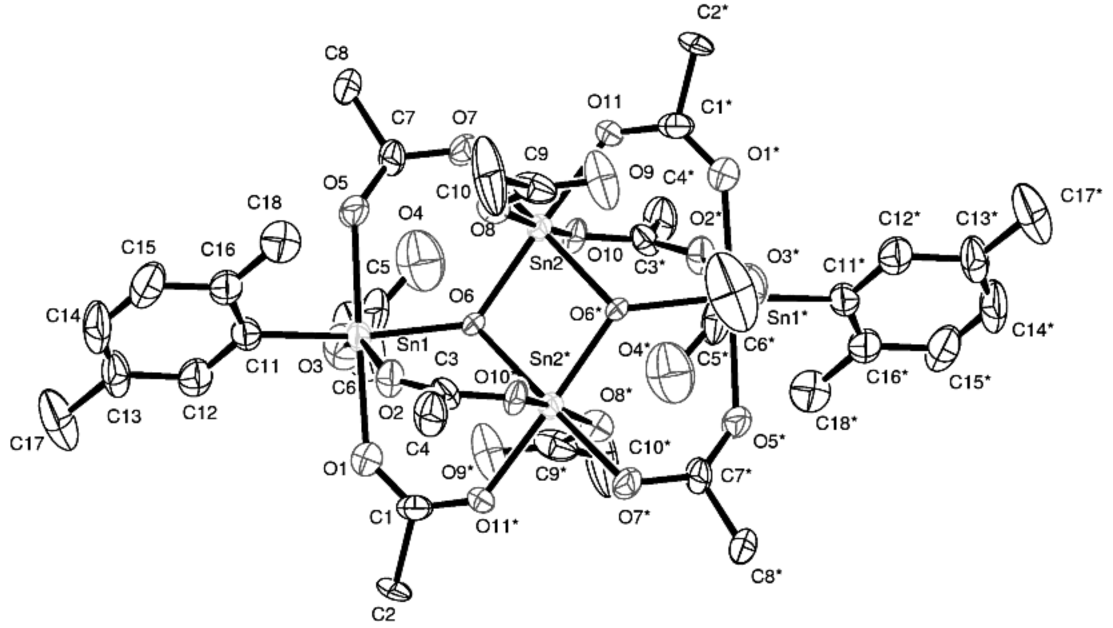


Figure 2. Perspective drawing of $(xylyl)_2Sn_4O_2(CF_3COO)_{10}$, with fluorine atoms of the trifluoracetato groups and hydrogen atoms omitted for clarity. The molecule is centrosymmetric. Selected interatomic distances (Å) and angles (degrees): Sn1–C11, 2.121(9); Sn1–O1, 2.163(7); Sn1–O2, 2.390(6); Sn1–O3, 2.017(8); Sn1–O5, 2.216(7); Sn1–O6, 2.021(5); Sn2–O6, 2.054(5); Sn2–O6*, 2.073(5); Sn2–O7, 2.054(6); Sn2–O8 2.023(6); Sn2–O10, 2.037(6); Sn2–O11 2.067(6); C11–Sn1–O6, 157.4(3); C11–Sn1–O1, 97.0(3); C11–Sn1–O2, 83.6(3); C11–Sn1–O3, 103.5(4); C11–Sn1–O5, 88.3(3); O1–Sn1–O2, 77.3(2); O1–Sn1–O3, 79.7(3); O1–Sn1–O5, 168.9(3); O2–Sn1–O3, 156.6(3); Sn1–O6–Sn2, 130.8(3); Sn1–O6–Sn2*, 125.2(3); O6–Sn2–O6*, 79.1(2); O7–Sn2–O11, 83.3(2); O8–Sn2–O10, 171.5(3).

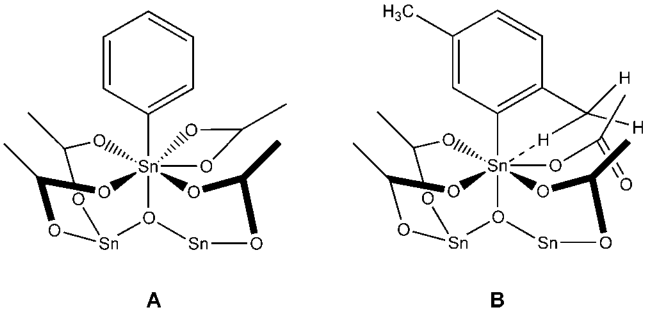


Figure 3. Structures **A** and **B**.

CF_3COOD or Ar-D is present. In fact, solutions of benzene-d_6 in CF_3COOH do exhibit H/D exchange when treated with catalytic amounts of "trifluoroacetatotin(IV)" (benzene:tin ca. 13:1), reaching equilibrium after about 2 days at 35 °C or within a week at room temperature. Added potassium trifluoroacetate or acetonitrile suppressed H/D exchange, consistent with the quenching of electrophilic metalation by nucleophiles. Also, added trifluoromethanesulfonic acid inhibited H/D exchange. Toluene-d_8 dissolved in CF_3COOH at room temperature undergoes rapid H/D exchange at both *meta*- and *para*-positions under catalysis by "trifluoroacetatotin(IV)" (toluene:tin ca. 67:1), with exchange at the *ortho*-position also occurring but noticeably slower, a pattern consistent with the bromination results described above. H/D exchange at the methyl group of toluene has not been observed. Had the addition of trifluoromethanesulfonic acid facilitated, instead of inhibited, H/D exchange, we would suspect that H/D exchange is simple prototropic exchange brought about by some tin-generated superacidic species. But the slower rate of exchange at the sterically-encumbered *ortho*-positions of toluene relative to exchange at *meta*- and *para*-positions, and the observed inhibition by $HOSO_2CF_3$, support the interpretation that H/D exchange occurs by reversible stannylation, probably via a Wheland intermediate[20] whose deprotonation is suppressed by added $HOSO_2CF_3$.

With these findings we add Sn(IV) to the list of metals whose complexes can metalate free arenes via C-H bond activation. While tin(II) is known to form π-arene complexes[21] and to participate in intramolecular ligand stannylation,[9] previous work with benzene solutions of trifluoroacetato complexes of tin(II) or mixed-valent Sn(II)/Sn(IV) complexes did not reveal any tendency for intermolecular stannylation.[15,16] Thus for tin – as for Hg, Tl, and Pb – it is the higher oxidation state of the metal center that electrophilically activates C-H bonds to metalate free arenes.

Experimental Section

Apart from the dissolution of SnO (see below) all reactions were performed in a nitrogen-filled drybox using dried solvents.

Preparation of Sn(IV) Electrophile, "Trifluoroacetatotin(IV)", from SnO

Aqueous H_2O_2 (30%; 0.40 mL) was slowly added (Caution: *exothermic reaction*) dropwise to a vigorously stirred mixture of SnO (0.50 g; from Alpha Products, 99.5% purity), CF_3COOH (3 mL), and trifluoroacetic anhydride (4 mL). This mixture was stirred at room temperature for 2 days, until the dark solids (SnO) all dissolved.[22] The resulting white opaque solution was evaporated under N_2 and the residue was treated first with trifluoroacetic anhydride (6 mL) and then with a solution of trifluoroperacetic acid freshly prepared by slowly adding 0.63 mL of 30% H_2O_2 to $(CF_3CO)_2O$ (10 mL; Caution: *exothermic reaction*) at 0 – 5 °C. The mixture was stirred at room temperature for 30 h, filtered through glass-wool under N_2, and reduced in volume to ca. 2–4 mL. Dry CH_2Cl_2 (30 mL), followed by hexane (5 mL) were added, and the mixture was stirred until the originally precipitated oil solidified. The solid was separated, washed with hexane, and dried under vacuum. The yield of "trifluoroacetatotin(IV)" was 0.69 g. Attempts to obtain X-ray quality crystals of this material were unsuccessful. The amount, 0.69 g, corresponds to 40% yield (calculated on SnO) of tentatively formulated $[Sn_4(\mu^3\text{-}O)_2(CF_3COO)_{12}]$ (the hypothetical parent of the aryl compounds shown in Figure 1 and Figure 2).

Preparation of Sn(IV) Electrophile, "Trifluoroacetatotin (IV)", from Tetraphenyltin: Dearylation[13]

A mixture of 6.8 g tetraphenyltin and 19 g trifluoroacetic acid was stirred at room temperature, and became a dark solution after about 9 h. After 2 days the solution was evaporated to a dark paste and the residue was washed with CH_2Cl_2, leaving 5.2 g insoluble material. This material, although useable for arylation studies, was not exhaustively dephenylated.

To assay this material, 0.115 g dissolved in 1 mL trifluoroacetic anhydride was analyzed by ^1H NMR and found to contain residual CH_2Cl_2 ($\delta = 5.7$, s), benzene (7.7, s), phenyltin species (8.0–8.7, m), and trifluoroacetic acid (10.9, s) (relative integral intensities of respective NMR signals: trifluoroacetic acid, 1.00; phenyltin 1.15; benzene 0.01). The solution was kept at 30–35 °C for 6 days, after which the benzene signal was much stronger and the phenyltin signals correspondingly weaker (relative integral intensities of respective NMR signals: trifluoroacetic acid, 1.00; phenyltin 0.59; benzene 0.56).

From a companion sample, identical except for the addition of 0.13 g benzene as a standard, we determined the amount of phenyltin species initially present to be roughly 15% of the total dissolved tin content. In this companion sample the amount of phenyltin species increased when kept at 30 – 35 °C over 6 days, as the presence of added benzene forced the formation of additional phenyltin species in the equilibrating mixture.

Preparation of Sn(IV) Electrophile, "Trifluoroacetatotin(IV)", from Tetraphenyltin: Exhaustive Dearylation

A sample of the "trifluoroacetatotin(IV)" prepared above, 0.31 g, dissolved in 2 mL warm trifluoroacetic acid (30 – 35 °C). Initial NMR assay revealed phenyltin species and benzene, approximate integral ratio 1:3.4. After 6 days at 35 °C, the NMR integral ratio was approximately 1:6.6, demonstrating considerable conversion of the residual phenyltin species into completely dephenylated tin species. Upon cooling this solution a precipitate was formed, and 0.13 g solids were collected. NMR analysis of these solids (trifluoroacetic acid) revealed only traces of benzene and phenyltin species.

Stannylation of Benzene

To 0.69 g of "trifluoroacetatotin(IV)" (obtained by oxidative dissolution of SnO) was added dry benzene (6 mL) and the mixture was stirred under reflux (N_2) for 10 min. Most of the solids dissolved to give a pale pinkish-tan solution which was separated warm from a small amount of viscous oil and left at room temperature. After 2 days, white crystalline material precipitated, which was washed with hexane and dried under vacuum. The yield was 0.39 g. An X-ray quality crystal found in the solid product was used for the X-ray analysis (Figure 1); ^{1}H NMR (CD_2Cl_2, 20 °C): $\delta = 7.7$ (m, 3H, *m,p*-C_6H_5), 7.9 (m, 2H, $J_{H,Sn} = 177$ Hz, *o*-C_6H_5). A weak singlet at 7.4 ppm from benzene was also observed. ^{19}F NMR (CD_2Cl_2, 20 °C): $\delta = 75.7$ (s).

To determine the amount of phenyltin species in this product, 301 mg of it were treated, in $CDCl_3$ (2 mL), with excess aqueous bromine (4 mL). After 1 h of vigorous stirring at room temperature all solids dissolved. ^{1}H NMR analysis of the organic phase with 1,2-dichloroethane as an internal standard indicated the presence of bromobenzene (48 mg), benzene (8 mg), and no other products.

Stannylation of *p*-Xylene

A sample of "trifluoroacetatotin(IV)" (0.10 g; obtained by dearylation of tetraphenyltin) dissolved in 1 mL hot *p*-xylene and the solution was heated to boiling, then evaporated to dryness. The residue was extracted into CH_2Cl_2 and the solution was evaporated to dryness, yielding 0.07 g solid residue. By NMR analysis the residue was $(xylyl)_2Sn_4O_2(tfa)_{10}$, purity > 95%; ^{1}H NMR (CD_2Cl_2): $\delta = 2.4$ (s, 3H, $J_{H,Sn} = 9.0$ Hz), 2.5 (s, 3H, $J_{H,Sn} = 16.5$ Hz), 7.4 (m, 2H), 7.5 (s, 1H, $J_{H,Sn} = 173.5$ Hz). Single crystals of this compound were obtained by recrystallizing a separate sample, similarly prepared, from hot pentane, and the structure was determined by X-ray diffraction (Figure 2).

Crystallographic Data

Data (excluding structure factors) for the structures have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC 164262 and CCDC-148317. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (+44) 1223–336–033, e-mail: deposit@ccdc.cam.ac.uk].

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[14] It was noticed that “trifluoroacetatotin(IV)” obtained by dearylation of tetraphenyltin (Equation 3) was sometimes poorly reactive toward arenes. The lack of reactivity might arise from contamination with tin(II) formed by redox reactions where di-, tri-, or unreacted tetraphenyltin compounds serve as reductant. It is known[15,16] that Sn(II) and Sn(IV) form stable mixed-valent trifluoroacetato clusters which do not exhibit arene stannylation. “Trifluoroacetatotin(IV)” prepared by the oxidative dissolution of SnO (Equation 2) is less prone to contamination with Sn(II). The oxidation of SnO with H_2O_2 in a mixture of trifluoroacetic acid and trifluoroacetic anhydride may involve the formation of $[Sn(CF_3COO)_2]$ which is then rapidly oxidized to Sn(IV) via mixed-valence Sn(II)/Sn(IV) species.[16]

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[17] The stannylation reaction is apparently promoted by trifluoroacetic acid, as the stannylation of benzene was noticeably slower in CF_3COOH-free solutions of “$Sn(CF_3COO)_4$” in trifluoroacetic anhydride. The persistence of phenyltin species in solutions containing trifluoroacetic acid and benzene was also noted in the synthesis of “trifluoroacetatotin(IV)” by dearylation of tetraphenyltin with trifluoroacetic acid, where repeated evaporation/dissolution was required to effectively dearylate the tin. Letting “$Sn(CF_3COO)_4$” and “$PhSn(CF_3COO)_3$” represent phenyl-free and phenyl-containing trifluoroacetatotin compounds, respectively, the equilibrium expression K_{eq} (35 °C) = ([CF_3COOH][“$PhSn(CF_3COO)_3$”])/([“$Sn(CF_3COO)_4$”]-[PhH]) = 0.9 has been found valid to within ± ca. 20%. If the tin species are represented as $Sn_4O_2(CF_3COO)_{12}$ and $(Ph)_2Sn_4O_2(CF_3COOH)_{10}$, respectively, the corresponding equilibrium expression is K_{eq} (35°C) = ([CF_3COOH][”$(Ph)_2Sn_4O_2(CF_3COOH)_{10}$”])/ ([“$Sn_4O_2(CF_3COO)_{12}$”][PhH]) = 0.4.

[18] Small amounts of benzyl bromide and trifluoroacetate were also detected (GC-MS), which likely originated from radical side-reactions upon addition of Br_2.

[19] N. W. Alcock, S. M. Roe, *J. Chem. Soc., Dalton Trans.* **1989,** 1589.

[20] See, for example, G. A. Olah, *Acc. Chem. Res.* **1971**, 4, 240.

[21] W. Frank, *Z. Anorg. Allg. Chem.* **1990**, *585*, 121.

[22] The amount of trifluoroacetic anhydride for this step was calculated to be sufficient to scavenge all water from both the hydrogen peroxide solution and the reaction of trifluoroacetic acid with SnO. A very sluggish reaction if at all is observed if larger quantities of trifluoroacetic anhydride are used.