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BIS(2,6-BIS(TRIFLUOROMETHYL)PHENYL)TIN(II), A STABLE DIPHENYLTI--ETC(U)
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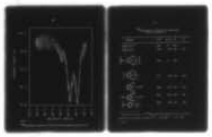

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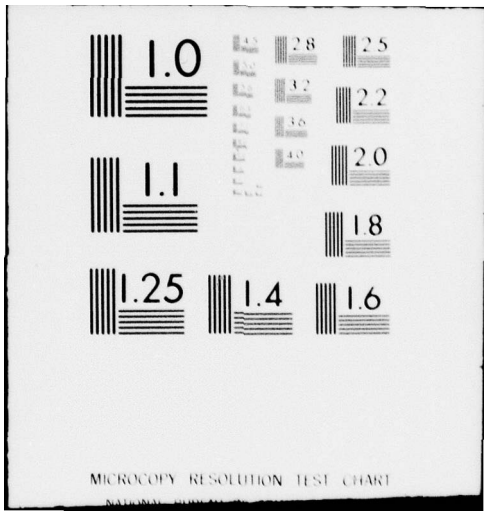
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Bis[2,6-bis(Trifluoromethyl)phenyl]tin(II), a Stable Diphenyltin(II) Compound

by

P. J. Corvan and J. J. Zuckerman

Prepared for Publication

in the

Journal of Organometallic Chemistry

University of Oklahoma
Department of Chemistry
Norman, Oklahoma 73019

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Diphenyltin(II) Derivatives
Tin-119m Mössbauer Spectroscopy
Tin(II)-Carbon Bond
Lithioarylation of Tin(II) Halides
Grignard Synthesis
Methanolysis
Tin(II)-Oxygen Bond
Tin(II)-Sulfur Bond

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The synthesis of a substituted diphenyltin(II) compound, bis[2,6-bis(trifluoromethyl)phenyl]tin(II), which is stable toward polymerization to the tin(IV) oligomers is reported for the first time. Methanolysis gives the $ArSnOCH_3$ derivatives in an exothermic reaction where Ar = 2,6-bis(perfluoromethyl)phenyl- and 2,4,6-trimethoxyphenyl, and para-toluenethiol gives bis(perfluorophenyl)-, bis[2-(dimethylamino)methyl]phenyl- and bis(2,4,6-trimethoxyphenyl)tin compounds are oligomers containing tin(IV) atoms.

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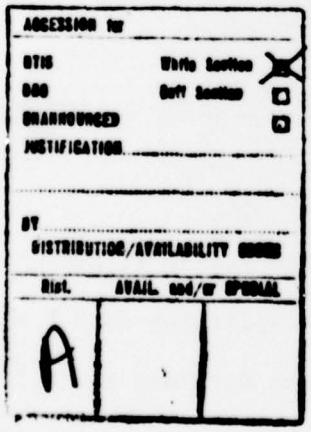
BIS[2,6-BIS(TRIFLUOROMETHYL)PHENYL]TIN(II), A STABLE DIPHENYLTIN(II) COMPOUND

P. J. Corvan and J. J. Zuckerman*
Department of Chemistry
University of Oklahoma
Norman, Oklahoma 73019

The synthesis of a substituted diphenyltin(II) compound, bis[2,6-bis(trifluoromethyl)phenyl]tin(II), which is stable toward polymerization to the tin(IV) oligomers is reported for the first time. Methanolysis gives the $ArSnOCH_3$ derivatives in an exothermic reaction where Ar = 2,6-bis(perfluoromethyl)phenyl- and 2,4,6-trimethoxyphenyl, and para-toluenethiol gives bis(para-toulenethiolato)tin(II). The solid bis(perfluorophenyl)-, bis[2-(dimethylamino)methyl]phenyl- and bis(2,4,6-trimethoxyphenyl)tin compounds are oligomers containing tin(IV) atoms.



BIS[2,6-BIS(TRIFLUOROMETHYL)PHENYL]TIN(II), A STABLE DIPHENYLTIN(II) COMPOUND

P. J. Corvan and J. J. Zuckerman
Department of Chemistry
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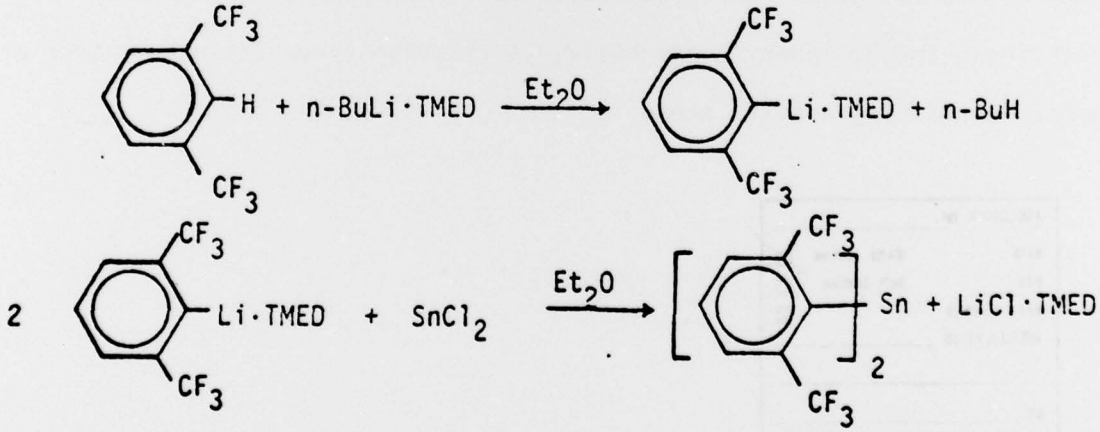
Norman, Oklahoma 73019

Sir/Madam:

We have synthesized the first example of an organotin(II) compound with a phenyltin(II) σ-bond. An ether solution of 2,6-bis(trifluoromethyl)phenyllithium prepared from the aryllithiation of 1,3-bis(trifluoromethyl)benzene by the use of the tetramethylethylenediamine n-butyllithium complex (n-BuLi·TMED)[1] was added to tin(II) chloride to precipitate a light brown solid:



The tin-119m Mössbauer spectrum of the product, shown in Figure 1, exhibits a doublet with Isomer Shift (I.S.) = 3.37 and Quadrupole Splitting (Q.S.) = 1.93 mm/s. The high I.S. value confirms that the tin atom is in the divalent state,[2,3] and as such that the compound is the first genuine example of a stable diphenyltin(II) species.

Diphenyltin was first prepared in 1920 by a Grignard route:[4]

$$C_6H_5MgBr + SnCl_2 \xrightarrow{Et_2O} \frac{1}{n}\left[(C_6H_5)_2Sn\right]_n + 2MgBrCl \qquad (3)$$

The molecular weight of the bright yellow solid increased from the monomer on aging. The same product resulted when a liquid ammonia/ether solution of diphenyltin dihydride was allowed to warm to room temperature:[5]

$$(C_6H_5)_2SnH_2 \xrightarrow[Et_2O]{NH_3(liq)} \frac{1}{n}\left[(C_6H_5)_2Sn\right]_n + H_2 \qquad (4)$$

Four modifications of diphenyltin were elucidated in the 1960's, including a product from phenyllithium:[6,7]

$$2C_6H_5Li + SnCl_2 \rightarrow [(C_6H_5)_2Sn]_n + 2LiCl \qquad (5)$$

which was purified by repeated crystallization from benzene by the addition of methanol (cf. below). The molecular weight of the yellow solid in methylene chloride corresponds to a hexamer. A colorless modification was also isolated from the hydride decomposition products in methanol. These forms can be converted to another colorless form by recrystallization from dimethylformamide. This modification melts at 250°C, and is hexameric in solution and in the solid state by an X-ray diffraction study which shows the tetrahedral diphenyltin moieties arranged in a six-membered ring in the chair-conformation.[8,9] These forms have identical infrared spectra.[3,4] Oligomers with tetra- and pentameric forms have also been isolated.[10] The diphenyltin materials exhibit singlet Mössbauer

spectra typical of $[Ar_2Sn(IV)]_n$ species with I.S. variously reported in the range 1.30-1.55 mm/s,[2] and are readily reacted with oxygen, sulfur and halogens to give Ar_2SnE (E = O, S, X_2, respectively),[11] and undergo insertion into the S-S bond in dibenzyldisulfide.[8] Evidence that some forms of "diphenyltin" contain branched phenyltin chains comes from the treatment with iodine in benzene which yields appreciable quantities of triphenyltin and phenyltin iodides in addition to the expected diphenyltin diiodide.[12] This hypothesis is supported by the related equilibria with triorganotin lithium and the organolithium reagents.[13,14] The yellow color of the "diphenyltin" modifications has been attributed to branching of the tin chains.[13] Other known hexameric diphenyltin derivatives include the para-tolyl-, para-ethoxyphenyl-, para-biphenyl-, and 2-naphthyl. The properties of the 1-naphthyl species are anomalous,[12] and the 9-phenanthryl derivative, prepared by a Grignard route, is a yellow-orange solid whose molecular weight in ethylene bromide ranges from 1.5-2.7 units, depending upon the age of the sample.[15] Russian workers claim that the compound is monomeric in benzene,[16] but the Isomer Shift of their singlet Mössbauer spectrum (I.S. = 1.8 mm/s) is indicative of an oligomeric structure.[2,3]

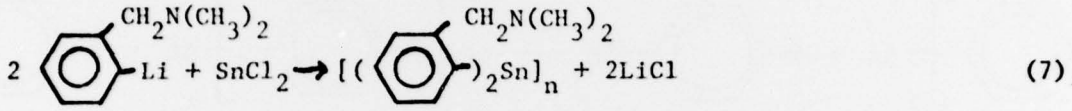
The arylation of tin(II) chloride by the pentafluorophenyl Grignard reagent:

$$2C_6F_5MgBr + SnCl_2 \xrightarrow{Et_2O} \frac{1}{n}\left[(C_6F_5)_2Sn\right]_n + 2MgBrCl \qquad (6)$$

gives a yellow solid which quickly polymerizes on drying in vacuo to a dark brown paste. Mössbauer analysis of this paste (I.S. = 1.69; Q.S. = 1.39 mm/s) confirms that this product is a tin(IV) oligomer. It is possible that the initial precipitate is an etherate, which polymerizes when the ether is removed.

The attempted synthesis of the same compound by the decarbonylation of bis(pentafluorophenylbenzoate)tin(II) failed.[17]

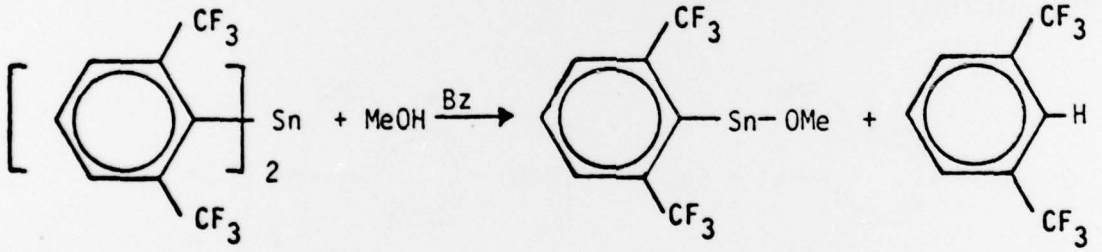
Likewise, the action of 2-[(dimethylamino)methyl]phenyllithium[18] produces a heavy brown precipitate:



(7)

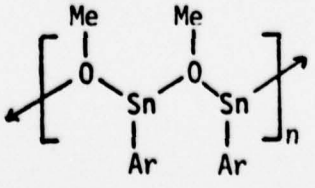
whose Mössbauer spectrum contains a very broad singlet absorption in the tin(IV) region, results in accord with recent findings.[19]

Stabilization of reactive metal complexes by the ortho-effect is well-known,[20] but our monomeric diphenyltin derivative undergoes methanolysis in an exothermic reaction:



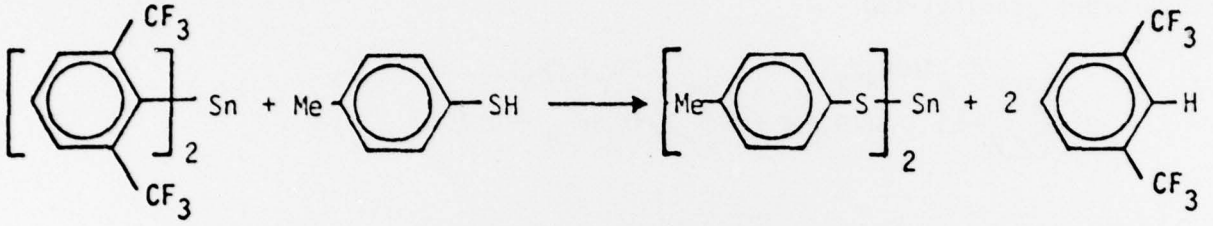
(8)

This reaction contrasts with the inert nature of the diphenyltin oligomer which is recrystallized from a methanol/benzene solvent system.[6] The doublet Mössbauer spectrum of the product (mp = 216-8°) (I.S. = 2.88; Q.S. = 2.31 mm/s) confirms the presence of tin as tin(II),[2,3] and is very similar to that of dimethoxytin(II).[21-23] The infrared spectrum shows absorptions arising from ν(C-O) at 1020 cm^{-1} and ν(Sn-O) modes at 740 cm^{-1}; the latter occuring in the spectra of tin(II) di-n-butoxide[24] and diorganotin oxides,[25] and is characteristic of a three-coordinated, associated structure with bridging methoxide and terminal aryl groups:



However, an alternative ladder structure such as that found in $\underline{h}^5$-cyclopentadienyltin(II) chloride[26] cannot be ruled out.

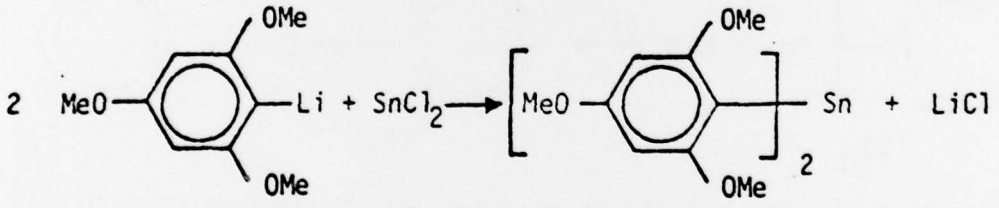
Both aryl groups are cleaved by the more acidic <u>para</u>-toluenethiol:



(9)

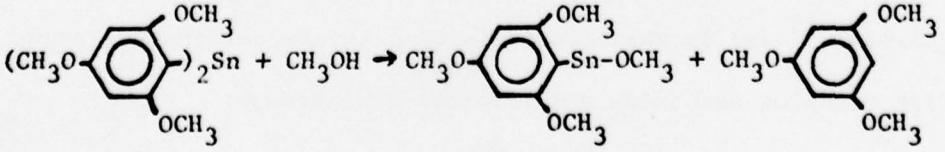
The doublet Mössbauer spectrum of the bis(<u>para</u>-toluenethiolato)tin(II) product (mp = 143-5°) (I.S. = 3.48; Q.S. = 1.79 mm/s) resembles that of tin(II) dithiophenoxide (I.S. = 3.51; Q.S. = 1.60 mm/s).[27]

The product of aryllithiation of 2,4,6-trimethoxybenzene[28] also alkylates tin(II) chloride:



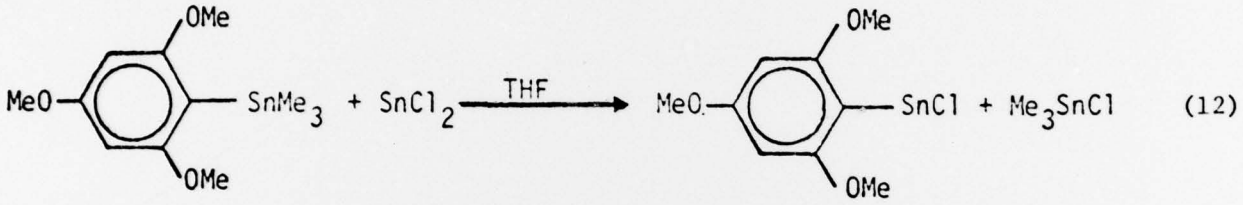
(10)

but on attempted recrystallization the white precipitate from hexane turned into a dark colored paste whose broad singlet Mössbauer spectrum was in the tin(IV) region. However, the crude product reacts exothermically with methanol to give a white solid (mp = 241-3°):



(11)

whose doublet Mössbauer and infrared spectra are very similar to that of the 2,6-bis(trifluoromethyl)phenyltin(II) methoxide. An attempt to prepare the chloride derivative by an exchange reaction of 2,4,6-trimethoxyphenyltrimethyltin(IV)[29] with tin(II) chloride gives the expected trimethyltin chloride:



(12)

but the brown waxy precipitate indicated that the product had oligomerized. Similar attempts by other workers also failed.[19]

The stability of the σ-bonded, phenyltin(II) compounds reported here derives from the 2,6-substituents blocking the tin atom from both nucleophilic attack at its vacant 5p-orbital and the use of its lone pair of electrons to attack a neighboring molecule. Bis[2,6-bis(trifluoromethyl)phenyl]tin(II) behaves as a divalent tin compound both in the solid state and in solution. On the other hand, bis(2,4,6-trimethoxyphenyl)tin, and perhaps bis(perfluorophenyl)tin, readily give a divalent methoxide derivative in solution, but exhibit a Mössbauer spectrum characteristic of a tin(IV) compound in the solid state. A parallel may be drawn with bis(9-phenanthryl)tin which is a monomer in benzene,[15] but apparently a tin(IV) polymer in the solid from Mössbauer evidence.[16] It is interesting to note that bis(pentafluorophenyl)- and bis(2,4,6-trimethoxyphenyl)tin, which have functional groups of roughly equivalent steric requirements but place opposite partial charges on the C-1 carbon atom, both form oligomeric structures.

Taft's steric substituent constants are in the order $-CF_3 >> -F > -OCH_3$, which is the same as the observed stability of the divalent species found in this study.

Acknowledgement. Our work is supported by the National Science Foundation and by the Office of Naval Research.

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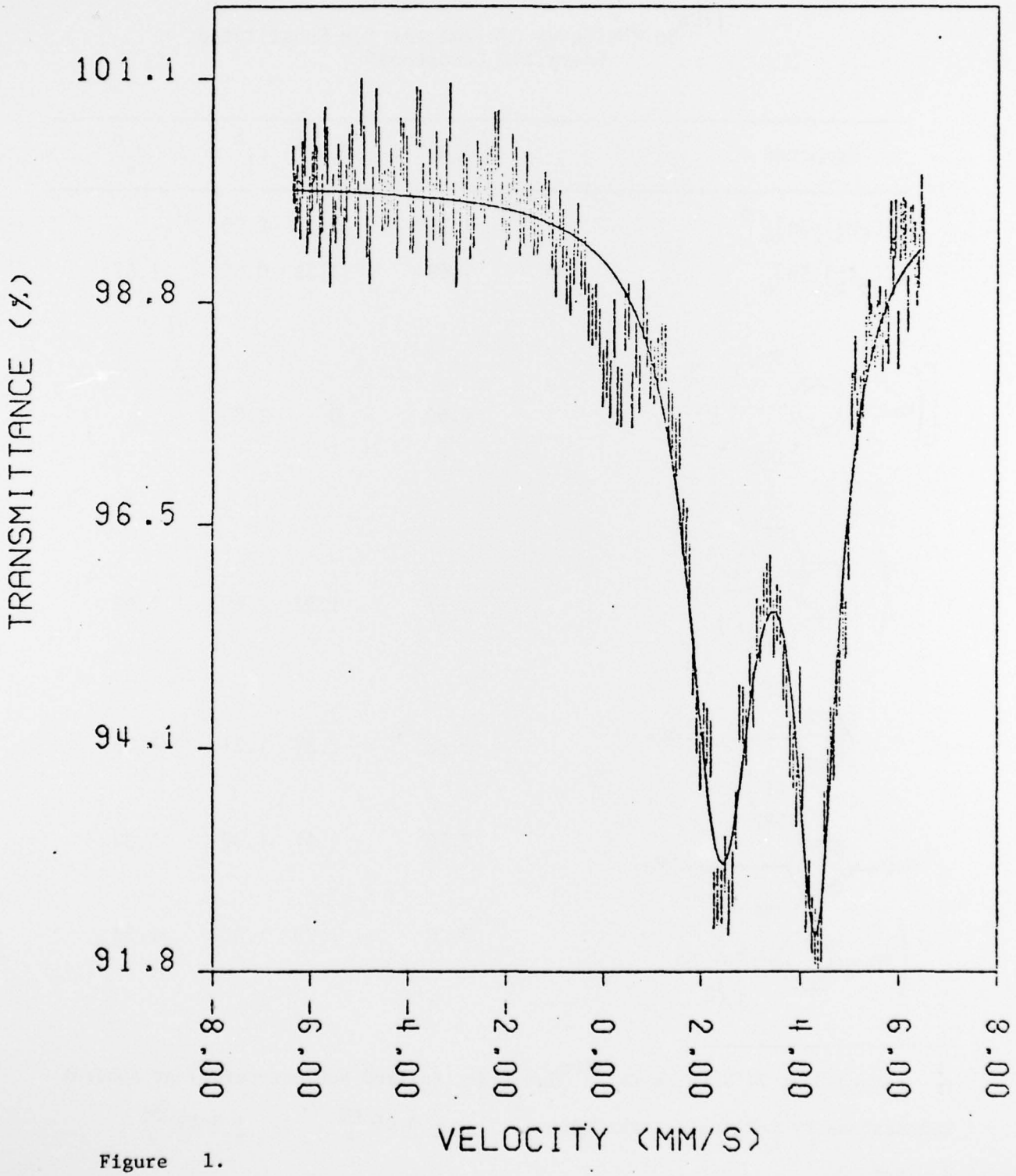
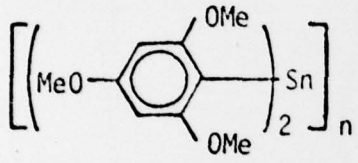
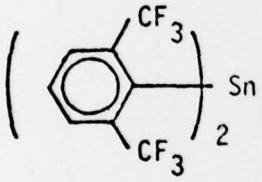
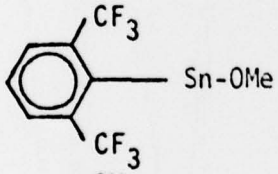
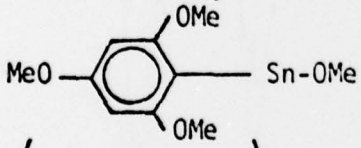
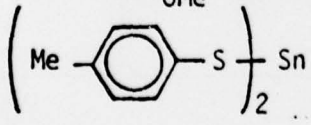


Figure 1.

^{119m}Sn Mössbauer Spectrum of Bis[2,6-bis(trifluoromethyl)phenyl]tin(II)

Table I

^{119m}Sn Mössbauer Parameters for Substituted Diaryltin Compounds[a]

Compound	I.S.[b]	Q.S.[c]	Γ_1[b]	Γ_2[b]
$[(C_6H_5)_2Sn]_6$ [d]	1.56	0	2.05	
$[(C_6F_5)_2Sn]_n$	1.69	1.39	0.85	1.57
	1.60	0	2.80	
	3.37	1.93	1.49	1.09
	2.88	2.31	1.31	1.08
	2.76	2.41	1.39	1.09
	3.48	1.79	1.45	1.38

a. Recorded at 77°K vs. a Ca $^{119m}SnO_3$ (New England Nuclear Corp.) at ambient temperature by published techniques.[30] b. $\pm$ 0.06 $\frac{mm}{s}$. c. $\pm$ 0.12 $\frac{mm}{s}$.

d. Ref. 2