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IR and NMR Studies of Parasubstituted Phenyltin Compounds*

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*Tetrakis-*para*substituted phenyltin compounds as well as the 1:1 addition complexes formed between tris-*para*substituted phenyltin chlorides and the Lewis bases, acetone, diethyl ether, dimethyl sulfoxide and N,N-dimethylacetamide, have been investigated by infrared and nmr spectroscopy. The results provide further evidence that in aryltin compounds dπ–pπ bonding exists between the empty d orbitals of the tin atom and the pi electrons of the phenyl ring. The results also indicate that substitution on the tin atom by a chlorine atom tends to enhance dπ–pπ bonding while substitution on the aromatic ring at the* para *position has little or no effect on the tin–phenyl bond.*

Introduction

Although the bonding in alkyltin compounds has been studied extensively [1, 2] the nature of the bonding in aryltin compounds is still not well understood. For example, infrared and nmr studies on the pentacoordinated complexes of trimethyltin chloride with Lewis bases of various strengths have indicated that a distorted tetrahydral configuration is obtained when a weak base is used while a trigonal bipyramidal structure with three coplanar methyl groups results when a strong Lewis base is employed [2]. However, only recently have analogous studies of aryltin compounds been made.

There is, in phenyltin compounds, some evidence that interaction occurs between the pi electrons of the phenyl groups and the empty 5 d orbitals of the tin atom. This conclusion is based on the interpretation of infrared [3], ultraviolet [3] and proton nmr [4–6] spectra as well as dipole moment measurements [7] of phenyltin compounds.

Our interest in the possibility of dπ–pπ bonding in aryltin compounds has led us to investigate the infrared and nmr spectra of tetrakis-*para*substituted phenyl compounds of tin in solution, as well as the spectra of adducts of tris-*para*substituted phenyltin chlorides. Parasubstituted phenyl compounds were chosen because the resulting nmr spectra would approximate an AA′BB′ system and would therefore be easier to interpret.

Experimental

Solvents

Fisher Spectroanalyzed Grade benzene, chloroform, carbon tetrachloride, diethyl ether and acetone were used without further purification. Spectroquality Grade dimethyl sulfoxide and N,N-dimethylacetamide were obtained from Matheson, Coleman and Bell Co. and used without further purification. The solvents contained no impurities which could be detected by nmr spectroscopy. Except for acetone and diethyl ether, the solvents were stored over Linde 4A molecular sieve.

Reagents

Triphenyltin chloride, obtained from M and T Chemicals, Inc., was recrystallized twice from dry ligroin. M.p. 104.5 °C (Lit [8] 106 °C).

In all syntheses work, reagent grade starting materials were used without further purification.

Syntheses of Compounds

Tetrakis-*para*chlorophenyltin, tetrakis-*para*methylphenyltin and tetrakis-*para*methoxyphenyltin were prepared by a Grignard procedure according to Krause and Weinberg [9]. The melting points of the tetraaryltins synthesized are as follows: Tetrakis-*para*chlorophenyltin 195.0–196.0° (Lit. [10] 194.5–195.0°); tetrakis-*para*methylphenyltin 237.0–237.5° (Lit. [11] 238°); tetrakis-*para*methoxyphenyltin 133.0–133.4° (Lit. [12] 134.8°).

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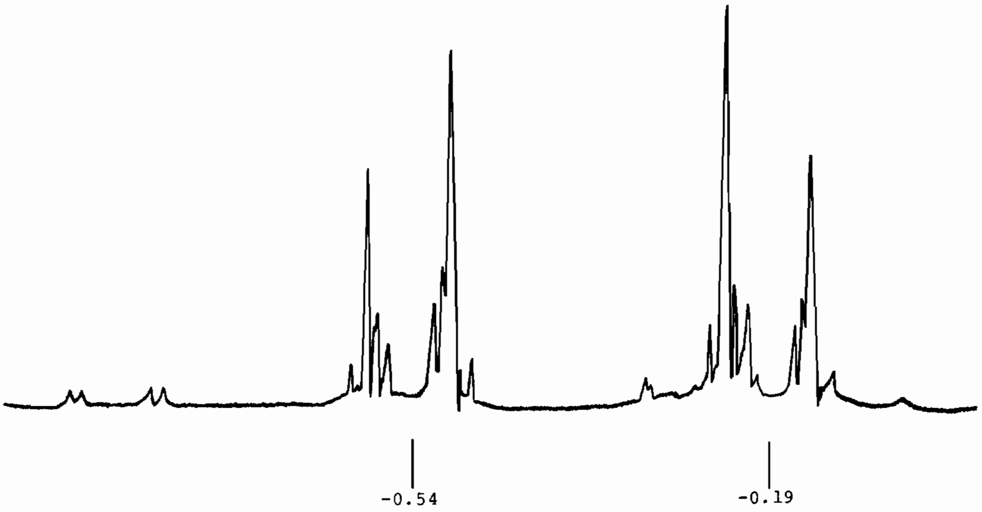

Figure 1. The ^1H resonance spectrum of the phenyl region at 60 Mc sec^{-1} of tris-*para*chlorophenyltin chloride in acetone. The chemical shifts are relative to benzene in ppm.

TABLE I. Chemical Shifts and Coupling Constants for *Para*substituted Tetraaryltin Compounds in $CDCl_3$.

Substituent X	$H_B{}^a$	$H_A{}^a$	$J_{AB}{}^b$	$J(^{119}Sn–C–C–H_A)^b$	$J(^{117}Sn–C–C–H_A)^b$
CH_3O	+0.45	−0.12	8.7	46.1	44.2
CH_3	+0.12	−0.16	7.2	46.0	44.4
F^c	+0.16	−0.22	7.63	–	–
H^c	−0.16	−0.38	–	–	–
Cl	−0.11	−0.11	7.6	47.0	44.6

[a] The chemical shifts are calculated relative to benzene in ppm. The accuracy of the chemical shifts are within ±0.01 ppm. [b] The accuracy of the coupling constants is within ±0.2 cps. [c] Ref. 4.

Syntheses of tris-*para*chlorophenyltin and tris-*para*methylphenyltin chlorides have been previously described [13].

Infrared Spectra

Infrared spectra in the 200–400 cm^{-1} region were obtained by means of a Perkin-Elmer Model 225 spectrophotometer. Matched cesium iodide cells, with a path length of 0.1 mm, were used to obtain the solution spectra. In order to avoid absorption bands due to water vapor, the instrument was maintained under an atmosphere of dry nitrogen. The frequencies were measured to an accuracy of ±0.5 cm^{-1}.

NMR Spectra

The nmr spectra were obtained on Varian Model A-60 and Model HA-100 spectrometers using non-donating as well as donating solvents. The spectra were traced both ways using a sweep width of 500 cps and were found to be reproducible to ±0.5 cps. The spectra were calibrated using TMS as the internal standard.

The $J(^{119}Sn–C–C–H_A)$ coupling constants were determined from spectra that were traced both ways using a sweep width of 100 cps and were found to be reproducible to ±0.2 cps.

Results and Discussion

The type of nmr spectra expected for *para*substituted phenyltin compounds corresponds to an AA′ BB′ system. For convenience, in the following discussion, the protons on the phenyl ring *ortho* to the tin atom will be designated as H_A protons and those *meta* to the tin atom will be designated as H_B protons. The downfield multiplet observed in the proton nmr spectra is assigned to the H_A protons and the upfield multiplet is assigned to the H_B protons. These assignments as well as the method for obtaining the chemical shifts and tin coupling constants have been described in a previous paper [13].

Figure 1 shows a typical proton nmr spectrum for the compounds studied. The chemical shifts and

TABLE II. A Comparison of Coupling Constants and Chemical Shifts Between Ar_4Sn and Ar_3SnCl in $CDCl_3$.

n	$(p\text{-}ClC_6H_4)_nSnCl_{4-n}$		$(C_6H_5)_nSnCl_{4-n}$		$(p\text{-}CH_3C_6H_4)_nSnCl_{4-n}$	
	4	3	4	3	4	3
$J(^{119}Sn\text{–}C\text{–}C\text{–}H_A)^a$	47.0	61.6	–	61.7	46.0	61.5
$J_{AB}{}^a$	7.6	8.4	–	–	7.2	8.0
$H_A{}^b$	–0.11	–0.21	–0.38	–0.44	–0.16	–0.19
$H_B{}^b$	–0.11	–0.09	–0.16	–0.22	+0.12	+0.14

[a]The accuracy of the coupling constants is within ±0.2 cps. [b]The accuracy of the chemical shifts is within ±0.01 ppm.

TABLE III. Chemical Shifts and Coupling Constants for Tris-*para*chlorophenyltin Chloride.

Solvents	$H_B{}^a$	$H_A{}^a$	$H_B - H_A$	$J_{AB}{}^b$	$J(^{119}Sn\text{–}C\text{–}C\text{–}H_A)^b$	$J(^{117}Sn\text{–}C\text{–}C\text{–}H_A)^b$
CCl_4	–0.09	–0.21	+0.12	8.4	61.6	59.0
Ether	–0.11	–0.31	+0.20	8.4	61.8	58.6
Acetone	–0.19	–0.54	+0.35	8.4	63.4	60.7
DMSO	–0.27	–0.62	+0.35	8.2	66.7	63.5
DMAC	–0.26	–0.67	+0.41	8.4	66.6	63.8

[a]The chemical shifts are calculated relative to benzene in ppm. The accuracy of the chemical shifts is within ±0.01 ppm. [b]The accuracy of the coupling constants is within ±0.2 cps.

TABLE IV. Chemical Shifts and Coupling Constants for Triphenyltin Chloride.

Solvents	$H_{B,C}{}^a$	$H_A{}^a$	$H_{B,C} - H_A$	$J(^{119}Sn\text{–}C\text{–}C\text{–}H_A)^b$	$J(^{117}Sn\text{–}C\text{–}C\text{–}H_A)^b$
Neat	–0.22	–0.44	+0.22	61.7	59.0
Acetone	–0.18	–0.54	+0.36	64.0	62.5
DMSO	–0.21	–0.60	+0.39	67.5	65.0

[a]The chemical shifts are calculated relative to benzene in ppm. The accuracy of the chemical shifts is within ±0.01 ppm. [b]The accuracy of the coupling constants is within ±0.2 cps. [c]Ref. 6.

coupling constants for the tetraaryltin compounds in non-donating solvents are summarized in Table I. The coupling constants, J_{AB}, range from 7.2 to 8.7 cps, which is within the values, 7.0 to 9.2 cps, characteristic of coupling constants for adjacent hydrogen atoms on an aromatic ring.

It is also noted that the $J(^{119}Sn\text{–}C\text{–}C\text{–}H_A)$ coupling constants for the compounds studied are independent of the substituent X, indicating that the substituent on the *para* position has little or no influence on the tin–phenyl bond.

The chemical shifts can be used as a measure of dπ–pπ bonding since it has been observed that increasing negative values for chemical shifts of protons indicate decreasing pi electron densities on the aromatic ring compared to benzene [14]. In the present case, the chemical shifts of the H_A protons were found to be the best measure of dπ–pπ bonding because the chemical shifts of the H_B protons were more affected by the substituent X. Table I reveals that the chemical shifts of all the H_A protons are negative, indicating that there is some dπ–pπ interaction in tetrakis-*para*substituted phenyltin compounds.

Examination of Table II reveals that, within experimental error, for the Ar_3SnCl compounds, both the H_A and H_B protons are less shielded. Also, it is noted that both the J_{AB} and $J(^{119}Sn\text{–}C\text{–}C\text{–}H_A)$ coupling constants are larger. Therefore, while substitution of the phenyl ring has little or no effect on the tin–phenyl bond, substitution of a chlorine atom on the tin tends to enhance dπ–pπ bonding.

In Tables III through V, the data show that for the tris-*para*substituted phenyltin chlorides, the H_A protons are more deshielded as the strength of the Lewis bases increases. However, the donor molecule

TABLE V. Chemical Shifts and Coupling Constants for Tris-*para*methylphenyltin Chloride.

Solvents	H_B[a]	H_A[a]	$H_B - H_A$	J_{AB}[b]	$J(^{119}Sn–C–C–H_A)$[b]	$J(^{117}Sn–C–C–H_A)$[b]
CCl_4	+0.14	−0.19	+0.33	8.0	61.5	58.7
Ether	+0.07	−0.30	+0.37	8.0	60.5	75.9
Acetone	+0.01	−0.36	+0.37	8.0	62.2	59.6
DMSO	+0.03	−0.45	+0.48	8.0	66.4	63.4
DMAC	+0.04	−0.53	+0.57	8.0	66.0	63.2

[a]The chemical shifts are calculated relative to benzene in ppm. The accuracy of the chemical shifts is within ±0.01 ppm. [b]The accuracy of the coupling constants is within ±0.2 cps.

TABLE VI. Selected Infrared Vibrations for $(p\text{-}XC_6H_4)_3SnCl$.

	ν Sn–Cl	ν $Sn–C_6H_5$ (Asym)	ν $Sn–C_6H_5$ (Sym)
	$(C_6H_5)_3SnCl$		
Solvents			
Benzene	340 (s) cm^{-1}	217 (vs) cm^{-1}	240 (m) cm^{-1}
Acetone (0.0289*M*)	340 (s)	271 (vs)	240 (m)
Acetone (0.201*M*)	340 (s)	271 (vs)	240 (m)
DMSO (0.209*M*)	324 (s)	273 (vs)	–
DMSO (1.05*M*)	324 (s)	276 (vs)	–
	$(p\text{-}ClC_6H_4)_3SnCl$		
Benzene	346 (vs)	226 (vs)	<200
DMSO	342 (s)	231 (vs)	–
	$(p\text{-}CH_3C_6H_4)_3SnCl$		
Benzene	339 (vs)	248 (vs)	<200
DMSO	336 (vs)	248 (vs)	–

acts mainly as an electron donor, therefore, it would be expected that as the base strength increases, the H_A and H_B protons would be shielded rather than deshielded. The observed deshielding can be rationalized if it is assumed that dπ–pπ bonding exists between the phenyl ring and the tin atom. Then the removal of pi electron density from the phenyl ring toward the tin atom would tend to deshield the protons on the ring, especially the H_A protons.

Delocalization of the pi electrons would be maximized in a molecule having a trigonal bipyramidal structure with three coplanar phenyl groups. The data indicate that as the basicity of the solvent increases from that of ether to that of DMSO, the extent of dπ–pπ bonding also increases. Therefore, it may be assumed that the configuration of the addition compounds must be dependent on the strength of the Lewis base. Analogous to the $(CH_3)_3SnCl$ adducts [2] a weak donor gives a distorted tetrahedral structure while a strong base leads to a trigonal bipyramidal structure with three coplanar phenyl rings. This model of coordination would allow for maximum delocalization of the pi electrons.

The proposed configuration for the adducts has been substantiated by infrared studies. The infrared vibrations that are of interest are listed in Table VI. The band at 340 cm^{-1} is assigned to the tin–chlorine stretching mode while the bands at 240 and 270 cm^{-1} are assigned as the tin–phenyl symmetric and tin–phenyl asymmetric modes respectively. These assignments are in agreement with those of previous workers [15–17].

The data listed for the adducts of $(C_6H_5)_3SnCl$ in Table VI reveal that the tin–phenyl asymmetric vibrations are shifted to higher wavenumbers as the basicity of the Lewis base increases, while the tin–phenyl symmetric mode is absent when dimethyl sulfoxide is employed as the solvent. On the other hand, both the symmetric and asymmetric modes are observed when acetone is used as the solvent.

These results suggest that a trigonal bipyramidal structure with three coplanar phenyl rings is obtained when a strong Lewis base is used while a distorted tetrahedral configuration results when a weak Lewis base is employed as the solvent.

In terms of valence bond theory, adduct formation may be viewed as follows: the tin atom is very nearly sp^2 hybridized with three phenyl groups in the trigonal plane, while the axial bonds contain orbitals composed of p_z and d_{z^2} orbitals. If this model of bonding is correct, the frequency of the tin–chlorine stretching vibration would be expected to decrease upon adduct formation. Examination of Table VI reveals that the band attributed to the tin–chlorine stretching does decrease upon adduct formation. Thus, the infrared data further supports the proposed model of coordination of Lewis bases with triaryltin chlorides.

Relative Acid Strengths

Tables III through V reveal that the differences of the chemical shifts, $H_B - H_A$, increase as the strength of the Lewis base increases. However, it is noted that in the case of $(p\text{-}CH_3C_6H_4)_3SnCl$ the difference is not significant until dimethyl sulfoxide or N,N-dimethylacetamide are used as solvents. In the cases of $(C_6H_5)_3SnCl$ and $(p\text{-}ClC_6H_4)_3SnCl$, this difference is observable even when a weak donor such as acetone is used. The difference in the chemical shifts of the H_A and H_B protons indicates changes in the electron density at these positions. Thus, for a given base the magnitude of the difference between $H_B - H_A$ in the base as compared to the $H_B - H_A$ value in carbon tetrachloride, a non-basic solvent, can be used as a measure of the acid strength of the tin compound. A large difference indicates a large change in electron density which in turn reflects the coordinating ability of the triaryltin compounds. Using the difference in chemical shift, $H_B - H_A$, as a measure of acid strength, the order of acidity for the compounds studied would be as follows:

$$(p\text{-}ClC_6H_4)_3SnCl > (C_6H_5)_3SnCl > (p\text{-}CH_3C_6H_4)_3SnCl$$

A similar order of acid strength was observed for the coordination of 1,2-diamino-4-nitrobenzene with aryltin trichlorides [18].

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