Journal of Organometallic Chemistry, 197 (1980) 181—197
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

SYNTHESIS AND ^{1}H NMR STUDIES OF SOME PENTACOORDINATE TIN(IV) COMPLEXES DERIVED FROM TRIPHENYLTIN HALIDES

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(Received January 21st, 1980)

Summary

Several anionic—cationic and neutral pentacoordinate tin(IV) complexes were prepared by the reaction of triorganotin(IV) halides, R_3SnX (R = Me and X = Cl; R = Ph and X = F, Cl, Br) with tetraalkylammonium halides and neutral ligands (pyridine, 4-(dimethylamino)pyridine, hexamethylphosphoramide and triphenylphosphine oxide). The complexes were examined in solution by ^{1}H NMR spectroscopy and characterized as having trigonal bipyramidal geometry around tin where the phenyl groups occupy the equatorial sites and more electronegative ligands are at axial positions. The ^{1}H NMR spectra of these complexes showed two distinct sets of aromatic multiplets arising from *ortho*-protons at low field, and *meta*- and *para*-protons at high field. A possible rationale has been offered for this observation. The upward shift of the tetraalkylammonium proton resonances in the phenyl-substituted complexes has been postulated to arise from shielding caused by the aromatic ring.

Introduction

A topic of increasing interest in recent years has been the pentacoordinate chemistry of main group elements. Particular mention could be made of the tremendous development that has taken place on the various aspects of pentacoordinate phosphorus compounds or phosphoranes as a result of detailed synthetic and stereochemical studies carried out during the last decade [1]. Systematic studies of analogous compounds based on other main group elements have begun only recently, and one of the fertile areas appears to be the chemistry of pentacoordinate tin(IV) compounds [2].

The studies of pentacoordinate tin(IV) compounds are of special significance in structural tin chemistry in view of the suggestion that pentacoordinate tin(IV) intermediates are formed during substitution reactions of triorganotin

0022—328X/80/0000—0000/$02.25,

halides [3,4] and in β-elimination processes involving 2-triphenylstannylethyl carbamates, $Ph_3SnCH_2CH_2OC(=O)NHR$, and halide ions [5]. In addition, many organotin compounds are now used in industry and agriculture [6—8], but a comprehensive knowledge of their mode of action and biological activity [9] is lacking. An intimate knowledge of the structure of these compounds is of paramount importance in order to understand the nature of bonding [10,11] in These compounds. In addition, a detailed study of several pentacoordinate tin(IV) compounds bearing assorted structural features would be highly welcome to determine whether the stereochemical principles established for predicting the geometry of a given non-metallic pentacoordinate compound [12] are applicable to the analogous organometallic species derived from main group metals. With these objectives in mind, we have prepared several pentacoordinate tin(IV) derivatives of triphenyltin halides and investigated their structures and solution properties by ^1H NMR spectroscopy.

Results and discussion

Preparative aspects

The preparation of various dihalotriphenylstannate complexes XI—XIV, XVII, XVIII ($[X_2SnPh_3]^-$ (X = F, Cl, Br) bearing various cations Me_4N^+, Et_4N^+, n-Bu_4N^+ and Ph_4As^+) from the appropriate reactants are shown in Table 1.

The trichlorodiphenylstannate anion, $[Cl_3SnPh_2]^-$, resulted from reaction of Ph_2SnCl_2 with $[Et_4N]^+Cl^-$ (1/1 mole ratio). Of the mixed halotriphenylstannate complexes (XV, XIX, XX, XXI, shown in Table 3), only the chloro(bromo) complex, $[n\text{-}Bu_4N]^+[Cl(Br)SnPh_3]^-$, could be isolated as a crystalline solid. This compound was obtained via either triphenyltin chloride or triphenyltin bromide (eq. 1). The formation of chloro(iodo)- and chloro(fluoro)-triphenylstannates in methyl cyanide according to eq. 2 and 3 was evident from the ^1H

$$Ph_3SnCl + [n\text{-}Bu_4N]^+Br^- \xrightarrow{CH_3CN} [Cl(Br)SnPh_3]^-[n\text{-}Bu_4N]^+ \xleftarrow{CH_3CN} [n\text{-}Bu_4N]^+Cl^- + Ph_3SnBr \quad (1)$$

$$Ph_3SnCl + [Et_4N]^+I^- \rightarrow [Cl(I)SnPh_3]^-[Et_4N]^+ \quad (2)$$

$$Ph_3SnF + [R_4N]^+Cl^- \rightarrow [Cl(F)SnPh_3]^-[R_4N]^+ \quad (3)$$

(R = Et, n-Bu)

NMR spectroscopic examination of the reaction mixture. However, in the heterogeneous reaction (eq. 3), only a portion (ca. 40—45%) of the triphenyltin fluoride used underwent complexation with Cl^-. The rest remained insoluble even after prolonged stirring of the reaction mixture. Attempts to isolate the complexes by crystallization were unsuccessful because of reversion to starting materials. Similarly, while evidence could be obtained by ^1H NMR examination for existence of a neutral 1/1 complex of Ph_3SnF and hexamethylphosphoramide (HMPA), no crystalline adduct could be isolated. The present results are in agreement with the previous observations of Elegbede and McLean [13] who failed to isolate the same adduct obtained in this way or via fluoride substitution on $Ph_3SnCl \cdot HMPA$. The inability to isolate any stable adduct of Ph_3SnF

with Cl^- or an oxygen donor (HMPA) in the solid state is probably due to the strong tendency of Ph_3SnF to undergo autocomplexation in the solid state [14] to give a polymeric structure involving a fluorine-bridged five-coordinate tin species (cf. the X-ray structure of Me_3SnF [15]). Spectroscopic data supporting the evidence for the presence of $[Cl(I)SnPh_3]^-$, $[Cl(F)SnPh_3]^-$ and $Ph_3SnF \cdot HMPA$ in solution lead one to suggest only a weak Lewis acid—base interaction between the triphenyltin halide and the incoming ligand; the stability of the species in solution probably arises from specific solvation effects. Much to our surprise, reaction of Ph_3SnF with $[Et_4N]^+F^- \cdot 2\,H_2O$ in methyl cyanide gave a crystalline product which was characterized as tetraethylammonium difluorotriphenylstannate ($[Et_4N]^+[F_2SnPh_3]^-$, XIII). This appears to be the first example of a stable complex of Ph_3SnF with a Lewis base. The formation of this complex (XIII) reflects the "hard" nature of the fluoride ligand (harder than Cl^- or an oxygen donor) [16] which readily attacks the tin center in the polymeric Ph_3SnF (a "hard" acid *) [13,19,20] leading to a breakdown of the polymeric structure and formation of the discrete pentacoordinate tin(IV) species, $[F_2SnPh_3]^-$. Dimethyltin fluoride, having a similar polymeric structure with six-coordinate tin(IV) [21], was also found to react with fluoride ion to yield crystalline pentacoordinate anionic tin species, $[F_3SnMe_2]^-$ [22].

The neutral 1/1 adduct, $Ph_3SnCl \cdot HMPA$ (XXIII) was conveniently prepared in excellent yield by adding one equivalent of HMPA to a solution of Ph_3SnCl in CCl_4 at room temperature. This method appears to be superior to that reported earlier [13] as no difficultly-removable excess HMPA is used.

The formation of a weak 1/1 complex between Ph_3SnCl and pyridine in benzene solution has been suggested by Gradon and coworkers [19,23] in the light of thermodynamic data obtained by calorimetric titration. In the present study, although ^1H NMR spectroscopic examination of a 1/1 mixture of Ph_3SnCl and pyridine in CH_2Cl_2 at 25°C suggested the formation of $Ph_3SnCl \cdot py$ (py = pyridine) in solution no solid adduct could be isolated. Drying of the original reaction mixture in vacuo (at 25°C) gave quantitative recovery of Ph_3SnCl. This result contrasts with the behavior of Me_3SnCl which forms a crystalline adduct with pyridine, $Me_3SnCl \cdot py$ [24,25] and probably reflects the lower Lewis acidity of the phenyltin chloride relative to the methyl analog [20]. However, the isolation of the 4-(dimethylamino)pyridine (DMAP) adduct, $Ph_3SnCl \cdot DMAP$ (XXV) in the solid state supports the reported thermodynamic data for the reaction of triorganotin halides with substituted pyridines, which indicate that more basic pyridines yield more stable complexes [23].

^1H NMR Spectra

The ^1H NMR data of the pentacoordinate tin(IV) complexes derived from Ph_3SnCl, Ph_3SnF, Ph_3SnBr and Ph_2SnCl_2 are given in Table 3. For the sake of

(Continued on p. 189)

* Although tin(IV) is usually regarded as a "hard" acid, the presence of three "soft" phenyl groups in Ph_3SnF might confer considerable softness on the tin center owing to considerable drainage of π-electron density from the phenyl rings to the metal. Furthermore, the importance of *d*-electrons in metals should be considered [17,18].

TABLE 1

PREPARATIONS, MELTING POINTS AND ANALYTICAL DATA OF PENTACOORDINATE TIN(IV) COMPLEXES DERIVED FROM PHENYLTIN HALIDES AND TRIMETHYLTIN CHLORIDE

	Compound	m.p. (°C)	Preparation	Recrystallization Solvent	Analytical data (Found (calcd.) (%))			
					C	H	N	Halogen
XI	$[Me_4N]^+[Cl_2SnPh_3]^-$	287–290(d) (lit. [27] 300)	$[Me_4N]^+Cl^- + Ph_3SnCl$ [a]	CH_3CN	53.82 (53.37)	5.88 (5.50)	2.98 (2.83)	
XII	$[Et_4N]^+[Cl_2SnPh_3]^-$	135 (lit. [27] 139)	$[Et_4N]^+Cl^- + Ph_3SnCl$	CH_3CN/CCl_4 (1/10)	56.23 (56.65)	6.30 (6.40)	2.41 (2.54)	
XIII	$[Et_4N]^+[F_2SnPh_3]^-$	157–158	$[Et_4N]^+F^- \cdot 2H_2O + Ph_3SnF$	CH_3CN/Et_2O (1/1)	59.69 (60.25)	6.92 (6.76)	2.62 (2.71)	6.8 (7.34)
XIV	$[Et_4N]^+[Br_2SnPh_3]^-$	165–166	$[Et_4N]^+Br^- + Ph_3SnBr$	CH_3CN	48.88 (48.78)	5.26 (5.47)	2.16 (2.19)	
XV	$[n\text{-}Bu_4N]^+[Cl(Br)SnPh_3]^-$	123–124	$[n\text{-}Bu_4N]^+Br^- + Ph_3SnCl$ or $[n\text{-}Bu_4N]^+Cl^- + Ph_3SnBr$	CH_3CN/Et_2O (1/3)	57.86 (57.70)	7.22 (7.26)	1.92 (1.98)	
XVI	$[Et_4N]^+[Cl_3SnPh_2]^-$	131–132 (lit. [27] 136)	$[Et_4N]^+Cl^- + Ph_2SnCl_2$	$CH_3CN/CHCl_3$ (1/4)	47.12 (47.14)	6.10 (5.93)	2.51 (2.47)	21.09 (20.87)
XVII	$[Ph_4As]^+[Cl_2SnPh_3]^-$	184–185 (lit. [38] 173–175)	$[Ph_4As]^+Cl^- \cdot xH_2O + Ph_3SnCl$	CH_3CN/CCl_4 (1/4)	62.71 (62.71)	4.35 (4.60)		8.82 (8.86)
XVIII	$[n\text{-}Bu_4N]^+[Cl_2SnPh_3]^-$	115–118(d)	$[n\text{-}Bu_4N]^+Cl^- + Ph_3SnCl$	CCl_4/Skelly B (2/1)	61.78 (61.53)	8.08 (7.75)	2.08 (2.11)	10.87 (10.68)
XXIII	$Ph_3SnCl \cdot HMPA$	159–160	$O=P(NMe_2)_3 + Ph_3SnCl$	CCl_4 [b]	51.30 (51.02)	6.11 (5.85)	7.68 (7.40)	6.24 (6.29)
XXV	$Ph_3SnCl \cdot DMAP$	156–158	$(\gamma\text{-}NMe_2)C_5H_4N + Ph_3SnCl$	CH_3CN/Et_2O (1/3)	58.88 (59.10)	4.67 (4.92)	5.40 (5.51)	
XXVIII	$[Et_4N]^+[Cl_2SnMe_3]^-$	212(d)	$[Et_4N]^+Cl^- + Me_3SnCl$	CH_3CN/Et_2O (1/1)	36.48 (36.20)	7.86 (8.01)	4.13 (3.84)	
XXIX	$Me_3SnCl \cdot OPPh_3$	157–158	$O=PPh_3 + Me_3SnCl$	C_6H_6/Skelly B	52.90 (52.8)	5.21 (5.06)	7.32 (7.42)	
XXX	$[Ph_4As]^+[Cl_2SnMe_3]^-$	171–172	$[Ph_4As]^+Cl^- \cdot xH_2O + Me_3SnCl$	CH_3CN/Et_2O (1/1)	52.39 (52.45)	4.82 (4.74)	11.81 (11.47)	

[a] The reaction mixture was heated under reflux for 1/2 hour and cooled to room temperature when crystals of XI deposited.
[b] The crude product was dissolved in hot CCl_4 and the solution cooled to room temperature.

TABLE 2

^1H NMR DATA OF TETRAALKYLAMMONIUM HALIDES, $[Ph_4As]^+Cl^-$, HMPA, PYRIDINE, DMAP, Ph_2SnCl_2 AND Ph_3SnCl

	Compound	Solvent	Chemical shifts (δ) (±0.05)		
			Aromatic Protons	N—CH_2 or N—CH_3	N—CCH_3 or N—$CCH_2CH_2CH_3$
I	$[Me_4N]^+Cl^-$	DMSO-d_6/ H_2O		3.18(s) 3.20(s) [a]	
II	$[Et_4N]^+Cl^-$	$CDCl_3$ or CH_2Cl_2		3.50(q, 8H)	1.4(m, 12H)
III	$[n\text{-}Bu_4N]^+Cl^-$	$CDCl_3$		3.42(b, m, 8H)	0.65—2.1(b, m, 28H)
IV	$[n\text{-}Bu_4N]^+Br$	$CDCl_3$		3.40(b, m, 8H)	0.65—2.05(b, m, 28H)
V	$[Ph_4As]^+Cl^- \cdot xH_2O$ [b]	CH_2Cl_2 or CH_3CN	7.8(m)		
VI	$O=P(NMe_2)_3$	$CDCl_3$		2.68(d) ^3J(P—N—C—H) = 9 Hz	
VII	C_5H_5N	CH_2Cl_2	7.25(m, 2H, β-) 7.67(m, 1H, γ-) 8.65(m, 2H, α-)		
VIII	(γ-NMe_2) C_5H_4N	CH_2Cl_2	6.48(m, 2H, β-) 8.18(m, 2H, α-)	2.95(s, 6H)	
IX	Ph_2SnCl_2	$CDCl_3$	7.15—8.0 [c]		
X	Ph_3SnCl	$CDCl_3$	7.1—7.9 [d]		

[a] From the Sadtler Standard ^1H NMR Spectra No. 6821.
[b] H_2O signal at δ 2.7 ppm.
[c] Satellite bands appear at δ 7.1 and 8.35 ppm.
[d] Lowfield satellite band appears at δ 8.20 ppm.

TABLE 3

^{1}H NMR DATA OF PENTACOORDINATE TIN(IV) COMPLEXES

	Compound	Solvent	Chemical shifts (δ, ppm) (±0.05)			
			Aromatic protons [a]		N—CH_2 or N—CH_3	N—CCH_3 or N—$CCH_2CH_2CH_3$
			ortho	*meta* and *para*		
XI	$[Me_4N]^+[Cl_2SnPh_3]^-$ [b]	DMSO-d_6	8.05	7.35	3.1(s, 12 H)	
		HMPA	8.18	7.30	[c]	
XII	$[Et_4N]^+[Cl_2SnPh_3]^-$	$CDCl_3$	8.05	7.35	2.5(q, 8 H)	0.7(m, 12 H)
		CH_2Cl_2	8.10	7.35	2.55(q, 8 H)	0.75(m, 12 H)
		CH_3COCH_3	8.30	7.30	3.05(q, 8 H)	1.05(m, 12 H)
		CD_3OD	7.85	7.45	3.15(q, 8 H)	1.10(m, 12 H)
		CD_3CN	8.10	7.40	2.98(q, 8 H)	1.05(m, 12 H)
		DMSO-d_6	8.05	7.42	3.15(q, 8 H)	1.08(m, 12 H)
		HMPA	8.30	7.20	3.33(q, 8 H)	1.17(m, 12 H)
XII	$[Et_4N]^+[F_2SnPh_3]^-$	CH_2Cl_2	8.10	7.32	2.47(q, 8H)	0.7(m, 12 H)
		CD_3CN	8.10	7.32	2.95(q, 8 H)	1.05(m, 12 H)
XIV	$[Et_4N]^+[Br_2SnPh_3]^-$	CH_2Cl_2	8.07	7.45	2.85(q, 8 H)	0.97(m, 12 H)
XV	$[n\text{-}Bu_4N]^+[Cl(Br)SnPh_3]^-$	$CDCl_3$	8.00	7.45	3.10(b, m, 8 H)	0.6—1.7(b, m, 28 H)
XVI	$[Et_4N]^+[Cl_3SnPh_2]^-$	CH_2Cl_2	8.20	7.40	2.85(q, 8 H)	1.00(m, 12 H)
XVII	$[Ph_4As]^+[Cl_2SnPh_3]^-$	CH_2Cl_2	8.13 [d]	7.30		
		CH_3CN	8.10 [d]	7.25		
XVIII	$[n\text{-}Bu_4N]^+[Cl_2SnPh_3]^-$	$CDCl_3$	8.15	7.30	2.50(b, m, 8 H)	0.5—1.4(b, m, 28 H)
		CH_2Cl_2	8.16	7.35	2.75(b, m, 8 H)	0.5—1.7(b, m, 28 H)
		CD_3OD	7.85	7.45	3.10(b, m, 8 H)	0.6—2.0(b, m, 28 H)

XVIII	$[n\text{-}Bu_4N]^+ [Cl_2SnPh_3]^-$	CD_3CN	8.10	7.30	2.90(b, m, 8 H)	0.6—1.8(b, m, 28 H)
		DMSO-d_6	8.05	7.35	3.10(b, m, 8 H)	0.6—1.85(b, m, 28 H)
		HMPA	8.32	7.17	3.35(b, m, 8 H)	0.65—2.0(b, m, 28 H)
XIX	$[Et_4N]^+ [Cl(F)SnPh_3]^-$ [c]	CH_3CN	8.12	7.33	3.10 [f](q, 8 H)	1.12 [f](m, 12 H)
XX	$[Et_4N]^+ [Cl(I)SnPh_3]^-$ [h]	CD_3CN	8.00	7.50	3.15(q, 8 H)	1.15(m, 12 H)
XXI	$[nBu_4N]^+[Cl(F)SnPh_3]^-$ [e]	$CDCl_3$	8.05	7.20	2.75 [f](b, m, 8 H)	0.5—1.55 [f](b, m, 28 H)
XXII	$Ph_3SnF \cdot HMPA$ [e]	HMPA	7.90	7.35	[c]	
XXIII	$Ph_3SnCl \cdot HMPA$ [g]	$CDCl_3$	7.83	7.41	2.45(d, 18 H) $^3J_{(P-N-C-H)} = 9$ Hz	
XXIV	$Ph_3SnCl \cdot py$ [h]	CH_2Cl_2	7.08—7.87(m, 18 H) [i] 8.41(m, 2 H) [j]			
XXV	$Ph_3SnCl \cdot DMAP$ [k]	CH_2Cl_2	7.75	7.40	2.88(s, 6 H)	

[a] Values are given for the approximate center of the multiplets. One of the satellite bands, due to coupling of ^{117}Sn and ^{119}Sn with the *ortho*-protons of the phenyl rings appears 0.6—0.7 ppm downfield from the main *ortho*-proton resonances. The highfield satellite band overlaps with the *meta*- and *para*-proton resonances.

[b] Insolubility of this compound precluded its ^1H NMR measurement in other common solvents.

[c] N—CH_3 proton signals could not be located owing to their overlap with those of HMPA.

[d] The aromatic multiplet arising from $[Ph_4As]^+$ is centered at δ7.7 ppm.

[e] Not isolated in the solid state. A 1/1 mixture of Ph_3SnF and the tetraalkylammonium chloride or HMPA was stirred together in methyl cyanide. The unreacted Ph_3SnF was removed by filtration and the filtrate examined by ^1H NMR spectroscopy.

[f] Since excess tetraalkylammonium chloride [e] was inherently present along with the desired complex, $[R_4N]^+ [Cl(F)SnPh_3]^-$, in solution and owing to rapid exchange of the cation bound to the complex with the free cation originating from partial dissociation of the complex and from the excess free ammonium salt, these observed chemical shifts reflect the average value.

[g] ^{31}P NMR data: singlet at +25.6 ppm.

[h] Obtained only in solution: not isolated in the solid state.

[i] Overlapped multiplets arising from the resonances of phenyl protons ($SnPh_3$) and β- and γ-protons of the pyridine ligand.

[j] α-protons of the pyridine ligand.

[k] The β-protons of 4-(dimethylamino)pyridine in the complex appear at δ6.3 ppm and the α-proton signals (of DMAP) overlap with those of the *ortho*-proton resonances of the phenyl group ($SnPh_3$).

TABLE 4

^{1}H NMR DATA (IN $CDCl_3$) OF PENTACOORDINATE TIN(IV) COMPLEXES DERIVED FROM Me_3SnCl

	Compound	Chemical shifts (δ) (±0.05)				(Coupling constants (Hz) (±1)	
		Aromatic Protons	Sn—CH_3	N—CH_2	N—CCH_3	$J(^{119}Sn-C-H)$	$J(^{117}Sn-C-H)$
XXVII	Me_3SnCl		0.65			58.5	55.5
XXVIII	$[Et_4N]^+[Cl_2SnMe_3]^-$		0.75	3.42(q)	1.40(m)	70.5	67.5
XXIX	$Me_3SnCl \cdot O=PPh_3$ [a]	7.6(m)	0.65			67.5	64.5
XXX	$[Ph_4As]^+[Cl_2SnMe_3]^-$	7.75(m)	0.75			70.5	68.2

[a] ^{31}P NMR data: Singlet at +25.3 ppm.

data comparison, the ^1H NMR absorptions of appropriate tetraalkylammonium halides $[R_4N]^+X^-$, HMPA, pyridine, DMAP, Ph_3SnCl and Ph_2SnCl_2 are recorded in Table 2. A typical spectrum of $[Et_4N]^+ [Cl_2SnPh_3]^-$ (XII) along with those of $[Et_4N]^+Cl^-$ and Ph_3SnCl in methylene chloride recorded at 60 MHz is shown in Fig. 1. The following features were exhibited by the complexes in their ^1H NMR spectra: (i) Both anionic and neutral complexes showed two distinct sets of aromatic proton signals (relative intensity ratio ~1/1.8). (ii) In the cationic—anionic complexes, the protons associated with a given cation were found to be more shielded than in the corresponding simple ammonium salt, $[R_4N]^+ X^-$. Peak positions due to these protons were also dependent on the choice of solvent and to some extent sensitive to concentration changes. (iii) The shielding effect on the α-protons of the tetraalkylammonium cation was greater than that on β- or more distant alkyl protons. In addition, protons of bulkier cations (e.g.: $[n\text{-}Bu_4N]^+$ and $[Ph_4As]^+$) experienced less shielding than those of relatively smaller ones (e.g.: $[Et_4N]^+$).

The observation of two sets of aromatic multiplets in the ^1H NMR spectra of these complexes was quite interesting in view of the fact that the analogous complexes (e.g.: $[Et_4N]^+ [Me_3SnCl_2]^-$, $[Ph_4As]^+ [Me_3SnCl_2]^-$ and $Me_3SnCl \cdot O{=}PPh_3$) derived from trimethyltin chloride showed a single sharp line flanked by tin satellite bands for the tin-methyl ($SnMe_3$) protons (See Table 4). Similar features (as noted above) were previously observed in the ^1H NMR spectra of the closely related triethylammonium (organocyanoamino)chlorotriphenylstannates, $[Et_3NH]^+ [R(CN)NSnPh_3Cl]^-$ [26] and hexamethylphosphoramide adducts of triphenyltin species [13]. On the basis of spectroscopic data (^1H NMR, IR and Mössbauer), the structures of the anions $[R(CN)NSnPh_3Cl]^-$ were suggested to be trigonal bipyramidal around tin with the phenyl groups occupying equatorial positions [26]; Unfortunately, no explanation was offered for the observation of two aromatic proton signals in these complexes and in one case [26] the two multiplets were assigned to phenyl rings in different environments. However, this does not agree with the equatorial placement

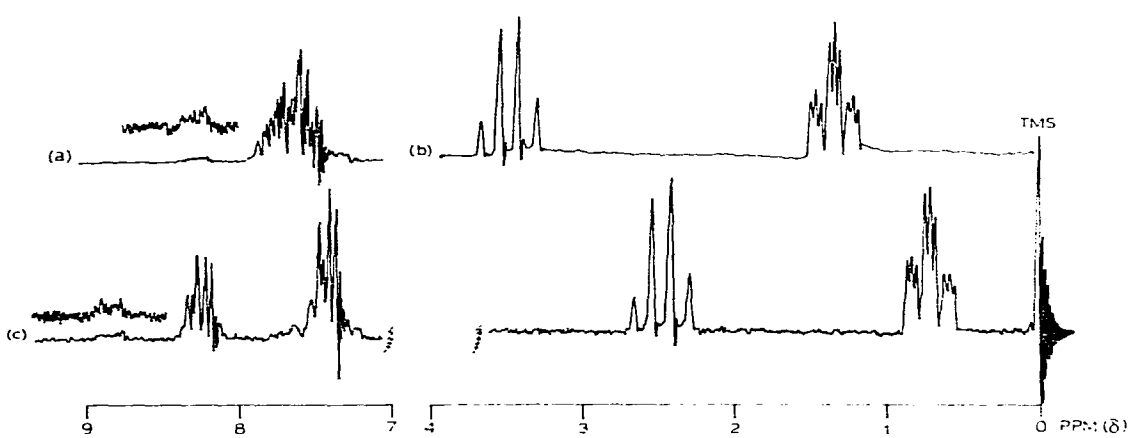
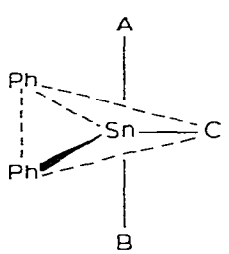


Fig. 1. ^1H NMR spectra of (a) Ph_3SnCl, (b) $[Et_4N]^+ Cl^-$ and (c) $[Et_4N]^+ [Cl_2SnPh_3]^-$ in methylene chloride at 60 MHz.

of the three phenyl rings in a trigonal bipyramidal structure. An analogous trigonal bipyramidal geometry around tin has been proposed for the anions $[Ph_2SnCl_2(Z)]^-$ (Z = Ph or Cl), in the solid state from vibrational spectroscopic data [27—29]. The recent X-ray crystal structure determination of the complexes $[Me_4N]^+$ $[Cl_2SnPh_3]^-$ (XI) [30] and $[Ph_3AsCH_2COPh]^+$ $[Cl_2SnPh_3]^-$ [31] conclusively established the slightly distorted trigonal bipyramidal structure of the anion $[Cl_2SnPh_3]^-$, in which the chlorines occupy axial sites. In view of these results and by analogy with the previously reported structures of other neutral and anionic pentacoordinate tin(IV) complexes of triorganotin halides [2], all the pentacoordinate tin species listed in Table 3 are assigned a trigonal bipyramidal geometry as shown in Fig. 2 where the phenyl groups occupy the equatorial sites and more electronegative ligands (A and B in Fig. 2) are at axial positions [32].

On the basis of this structural assignment, the three phenyl rings are chemically equivalent and assuming an A_2B_3 or A_2B_2C spin-system constituted by the aromatic protons of the phenyl ring a complex multiplet is expected. Clearly, the appearance of two sets of well-separated multiplets for the aromatic protons in the ^1H NMR spectra of these compounds (recorded at low-field strength, 60 MHz) is anomalous. Particular mention should be made of the diphenyl derivative $[Et_4N]^+$ $[Ph_2SnCl_3]^-$ (XVI) and the monophenyl derivative $[n\text{-}Bu_4N]_2^+$ $[PhSnCl_5]^{2-}$ (containing hexacoordinate tin(IV)), the ^1H NMR spectra of which also showed similar features. In both cases, the line-pattern of the aromatic multiplets was the same as found in the complexes XI—XV, XVII—XXIII derived from triphenyltin halides. The intensity ratio of the aromatic signals was again ~1/1.8. The appearance of two sets of aromatic multiplets in the ^1H NMR spectrum of $[n\text{-}Bu_4N]_2^+$ $[PhSnCl_5]^{2-}$ clearly indicated that these two sets of multiplets are not due to nonequivalent phenyls but rather to some differential effect on the *ortho*-, *meta*- and *para*-protons of a given phenyl ring in the complexes. A possible rationale of this effect is given subsequently.



Compound	A	B	C
XI, XII, XVII, XVIII	Cl	Cl	Ph
XIII	F	F	Ph
XIV	Br	Br	Ph
XV	Cl	Br	Ph
XVI	Cl	Cl	Cl
XIX, XXI	Cl	F	Ph
XX	Cl	I	Ph
XXII	F	O	Ph
XXIII	Cl	O	Ph
XXIV, XXV	Cl	N	Ph

Fig. 2. Structures of pentacoordinate tin(IV) compounds (XI-XXV). O = oxygen of HMPA; N = ring nitrogen of pyridine or 4-(dimethylamino)pyridine.

Close examination of the ^{1}H NMR spectra of Ph_3SnCl in CH_2Cl_2 solution and as a melt [33] revealed the presence of two groups of closely-spaced, partially overlapping multiplets. Although it was not possible to measure accurately the intensities of individual multiplets, the more intense high-field multiplet was assigned to the *meta*- and *para*-protons and the low-field, less intense group to the *ortho*-protons [33].

In the light of these observations, the less intense low-field multiplet in the ^{1}H NMR spectra of the pentacoordinate tin(IV) complexes (XI—XXV) is assigned to the *ortho*-proton resonances. The well-separated high-field multiplet is then assigned to the *meta*- and *para*-protons. The considerable downfield shift of the *ortho*-proton resonances in the complexes may reflect considerable transfer of π-electron density from the phenyl rings to the vacant 5*d* orbitals of tin on pentacoordination. Such enhanced deshielding of the *ortho*-protons of aryl systems in the presence of electron-withdrawing groups has been discussed [33].

The discrepancy * between the observed (ca. 1/1.8) and expected (1/1.5) intensity ratio of the two aromatic multiplets is due to overlap of the high-field tin-satellite band (arising from coupling between $^{117/119}$Sn and the *ortho*-protons) with the *meta*- and *para*-signals. It should be pointed out that in the ^{1}H NMR spectrum of an organotin compound, the positions and intensities of tin-satellite bands associated with a given proton signal should be taken into account while calculating the intensity of that resonance.

The ^{1}H NMR spectra of the neutral adducts XXII—XXV showed the characteristic separation of *ortho*-proton signals from the *meta*- and *para*-proton resonances; but in the pyridine adducts XXIV and XXV the phenyl region becomes more complicated as a result of overlap of *meta*- and *para*-proton signals and the *ortho*-proton signals of 4-(dimethylamino)pyridine (DMAP) with the phenyl proton resonances. A striking feature noted in the spectra of these adducts is the appearance of the proton resonances associated with the ligands at a slightly higher field compared to those found in the free ligands. This upward shielding of the ligand protons in the complexes reflects a net electron-donation from the Ph_3SnCl unit via tin to the ligand upon complexation. A similar suggestion invoking a net electron-donation from a triorganotin (R_3Sn) group to the pyridine ring has been made by Anderson et al. [34] to explain the greater basicity of 2- and 4-triorganotin substituted pyridines compared to pyridine.

The unusually high chemical shift of the tetraalkylammonium protons observed in the ^{1}H NMR spectra of the complexes XI—XVI, XVIII appears to result from shielding caused by the aromatic ring-current effect of the phenyl

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* Of the three NMR active nuclei of tin (^{115}Sn, ^{117}Sn and ^{119}Sn) having nuclear spin quantum number, $I = 1/2$, the abundance of the ^{115}Sn (0.34%) isotope is very low. Hence, a significant contribution toward coupling with the *ortho*-protons will arise only from the remaining two nuclei, ^{117}Sn (7.54% abundance) and ^{119}Sn (8.62% abundance). The satellite bands which appear symmetrically at a distance of ca. 30 Hz ($J(^{117/119}Sn—C—C—H_{ortho})$ ~ 60 Hz [33]) on both sides of the main *ortho*-proton resonance (arising from species containing NMR inactive tin nuclei) would account for 16.16% of the total intensity of the *ortho*-protons. Since one half of this signal having intensity 8.08% of the *ortho*-proton resonances overlaps with the *meta*- and *para*-proton signals the ratio of the observed intensity of the *ortho*-proton resonance to that of the *meta*- and *para*-proton resonances would be $(2 - 2 \times 8.08/100)/(3 + 2 \times 8.08/100)$ or 1/1.72.

ring [35] (See Fig. 3). This is further supported by the fact that the alkyl derivative $[Et_4N]^+ [Me_3SnCl_2]^-$ (XXVIII), did not show any shielding of the protons of $[Et_4N]^+$ (See Table 4). The X-ray crystal structure analysis of $[Me_4N]^+ [Cl_2SnPh_3]^-$ [30] shows that the cation is held between the two phenyl rings and is very close to one of the rings. The distances of the two carbon atoms of $[NMe_4]^+$ from the centers of the two nearest phenyl rings are 3.752 and 4.574 Å. The central tin atom in the anion is situated 5.734 Å from the nitrogen. The shorter distance (4.420 Å) from nitrogen to the center of one of the phenyl rings compared to its distance from the tin atom (5.734 Å) and from the center of the second phenyl ring (5.739 Å) suggests a local dipole-induced dipole interaction between the electron-deficient nitrogen of the tetramethylammonium cation and the high π-electron density of the nearest phenyl ring. A similar explanation suggesting the formation of a specific molecular complex between benzene and the electron-deficient region of the solute molecule in benzene solution has been offered to rationalize the benzene-induced solvent shift of proton resonances in a wide range of organic compounds [36,37]. By contrast, in the complex, $[Ph_3AsCH_2COPh]^+ [Cl_2SnPh_3]^-$, containing a bulkier cation, the Sn—As distance is 9.679 Å; the distances from arsenic to the centers of the two phenyl rings attached to tin being 6.482 and 10.767 Å. These data reflect a greater separation of the cation from the anion and hence one would anticipate lesser shielding of the protons associated with the cation by the aromatic rings of the anion. This is very nicely demonstrated by the ^1H NMR spectrum of the very similar complex $[Ph_4As]^+ [Cl_2SnPh_3]^-$, where only a slight shielding (0.1 ppm) of the protons of the cations was observed.

Analogous placement of the other tetraalkylammonium cations is expected although these were not examined by X-ray crystallography. In the case of the diphenyl complex $[Et_4N]^+ [Cl_3SnPh_2]^-$ (XVII), in the solid state the cation can lie either between the two phenyl rings (Fig. 4a) or between a phenyl ring and the equatorial chlorine (Fig. 4b). However, in solution rapid exchange of the cation with different phenyl sites would be anticipated and the observed shielding of the tetraalkylammonium protons would reflect the statistical aver-

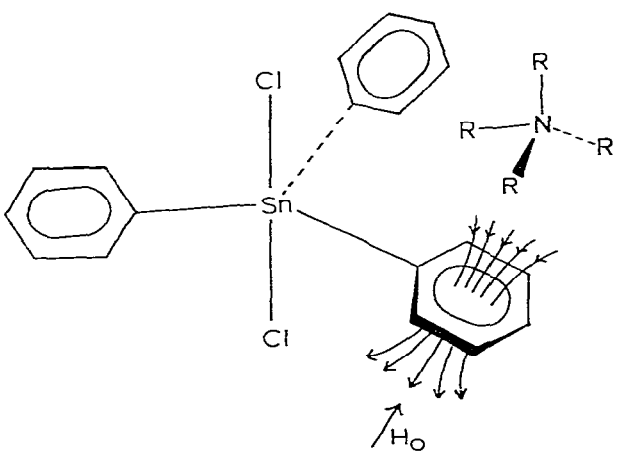

Fig. 3. Structure of $[R_4N]^+ [Cl_2SnPh_3]^-$ and shielding of $[R_4N]^+$ protons by the phenyl ring.

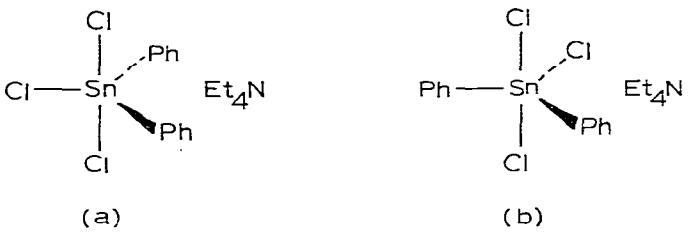

Fig. 4. Possible structures of $[Et_4N]^+ [Cl_3SnPh_2]^-$.

age of these events. This is consistent with the observation of a greater shielding effect (δ 0.95 ppm) in $[Et_4N]^+ [Cl_2SnPh_3]^-$ (XII) in CH_2Cl_2 compared to that (δ 0.65 ppm) found in $[Et_4N]^+ [Cl_3SnPh_2]^-$ (XVI) where the cation experiences less shielding by virtue of substitution of an equatorial chlorine ligand for one of the phenyl rings (See Fig. 4).

In solution, the complexes are expected to undergo partial dissociation as given by eq. 4 and assuming a very rapid exchange on an NMR time scale of the

$$[R_4N]^+[Cl_2SnPh_3]^- \rightleftharpoons [R_4N]^+ + [Cl_2SnPh_3]^- \quad (4)$$

free cation with the undissociated complex, the observed chemical shift (δ_{obs}) would be given by $\delta_{obs} = \nu_+(N_+) + \nu(N)$, where ν_+ and ν are the chemical shifts of $[R_4N]^+$ in the free ion and in the undissociated complex respectively. N_+ and N represent the mole fractions of free and undissociated cations respectively.

The higher chemical shift (δ 2.5 ppm) of tetraalkylammonium protons in less polar solvents (e.g., $CDCl_3$ and CH_2Cl_2) implies very little dissociation of the complexes $[R_4N]^+ [Cl_2SnPh_3]^-$ and suggests their existence almost exclusively as tight ion-pairs which are structurally very close to that of the crystalline solid. Measurement of ^1H NMR spectra of $[R_4N]^+ [Cl_2SnPh_3]^-$ (R = Et, n-Bu) in a series of solvents with increasing dielectric constant shows a gradual downfield shift of the *N*-methylene and other proton resonances of the alkyl chain of the cation reflecting a greater degree of dissociation of the complexes in more polar solvents. A similar downfield movement and broadening of the proton signals can be brought about by increasing the concentration of free cation by deliberate addition of the tetraalkylammonium halides. For example, the *N*-methylene and methyl signals of $[Et_4N]^+$ in $[Et_4N]^+ [Cl_2SnPh_3]^-$, which appeared at δ 2.55 and 0.75 ppm, respectively, in a 10% solution in CH_2Cl_2 moved gradually downfield with increasing amounts of added $[Et_4N]^+ Cl^-$. These results are in agreement with the trends that can be predicted from eq. 4.

The greater downfield shift observed for the tetraalkylammonium protons in methanol (dielectric constant = 31.2) and acetone (dielectric constant = 20.7) is anomalous and probably arises from a specific solute-solvent interaction irrespective of the dielectric constant. It may be that in methanol, a hydrogen bonding solvent, the axial chlorines in $[Cl_2SnPh_3]^-$ are more basic (longer Sn—Cl bond) and undergo stronger hydrogen bonding with CH_3OH thereby effecting further Sn—Cl bond lengthening. Hydrogen bonding of the type $Sn—Cl\cdots HCCl_3$ for the anion $[Cl_2SnPh_3]^-$ in chloroform solution is evident by isolation of a stable solvate, $\{[Et_4N]^+ [Cl_2SnPh_3]^-\}_2 \cdot CHCl_3$, when the com-

plex was recrystallized from chloroform (See Experimental).

The lesser shielding of the protons associated with the cationic species with increased bulk of the cations for the complexes, $M^+ [Cl_2SnPh_3]^-$ (M = Et_4N, n-Bu_4N and Ph_4As) suggests that for steric reasons the internuclear distances between the central atoms of the cation and the anion increases and the bulkier cation is situated further away from the plane of the phenyl ring. The interionic distances in $[Me_4N]^+ [Cl_2SnPh_3]^-$ and $[Ph_3AsCH_2COPh]^+ [Cl_2SnPh_3]^-$ are 5.734 and 9.679 Å, respectively. As anticipated, the protons in the very large tetraphenylarsonium cation $[Ph_4As]^+$ suffer very little shielding (0.1 ppm).

It is worth emphasizing that the separation of the *ortho*-proton resonance from the *meta*- and *para*-signals observed in this work can be employed as a diagnostic tool to indicate the pentacoordination of triphenyltin halides, Ph_3SnX (X = F, Cl, Br), with an incoming ligand. It also appears that in the complexes derived from Ph_3SnCl, the extent of separation of the two sets of aromatic resonances, to a first approximation, is directly proportional to the basicity of the newly added ligand.

Experimental

^1H NMR spectra were recorded on Perkin—Elmer R12A and Varian Model A-60 NMR spectrometers at 60 MHz using 10% (w/v) solutions of the samples in appropriate solvents. Chemical shifts are reported in ppm relative to tetramethylsilane as internal standard. ^{31}P NMR spectra were recorded on an NT-150 FT spectrometer. Chemical shifts are expressed in ppm relative to the external standard, 85% H_3PO_4. Upfield shifts are negative.

Materials

Triphenyltin chloride and diphenyltin dichloride (Alfa, Ventron) were purified by recrystallization from hexane to constant m.p.'s 106 and 40°C, respectively. Tetraalkylammonium halides (Eastman Kodak) were dried over P_2O_5 in vacuo before use. 4-(Dimethylamino)pyridine was recrystallized from carbon tetrachloride, m.p. 110—111°C. Hexamethylphosphoramide (BDH) was stored over calcium chloride and distilled under reduced pressure from calcium hydride. Methyl cyanide was distilled over P_2O_5.

Triphenyltin fluoride was prepared by dissolving triphenyltin chloride in ether and adding an aqueous solution of potassium fluoride. The heterogeneous reaction mixture was stirred vigorously for 1 h and the precipitate of Ph_3SnF was filtered and washed successively with water, acetone and ether. The white powder was dried overnight at 100°C under oil pump vacuum. Triphenyltin bromide was prepared following the published procedure [13], m.p. 121—122°C. Phenyltin trichloride and trimethyltin chloride (Alfa, Ventron) were used without further purification.

General procedure for complex preparation

Phenyltin halides (Ph_3SnCl, Ph_3SnBr, Ph_3SnF and Ph_2SnCl_2) and the appropriate tetraalkylammonium halide or the neutral ligands (hexamethylphosphoramide and 4-(dimethylamino)pyridine) in a 1/1 mole ratio were magnetically

stirred in methyl cyanide at room temperature for 1 h in a dry nitrogen atmosphere. Evaporation of solvent from the reaction mixture gave a crystalline product which was recrystallized from a suitable solvent or a mixture of solvents at 0°C. The yields of pure products were 90—96%.

Some typical procedures are given below.

Preparation of $[Et_4N]^+ [Cl_2SnPh_3]^-$

To a solution of triphenyltin chloride (2.0 g, 52 mmol) in methyl cyanide was added tetraethylammonium chloride (0.86 g, 52 mmol). The resulting clear reaction mixture was stirred at room temperature (25°C) for 1 h. Evaporation of solvent from the reaction mixture in vacuo gave initially a viscous mass which subsequently crystallized upon further drying under oil pump vacuum. The crystalline solid was washed twice with Skelly F (b.p. 35—45°C) (30 ml) and recrystallized from a mixture of carbon tetrachloride and methyl cyanide (10/1) to give crystals of tetraethylammonium dichlorotriphenylstannate (XII) (yield 2.75 g, 95%). Recrystallization of the crude product from chloroform afforded a chloroform solvate of the complex having composition $\{[Et_4N]^+ [Cl_2SnPh_3]^-\}_2 . CHCl_3$, m.p. 135°C. Anal. Found: C, 51.85; H, 6.15; N, 2.27; Cl, 20.80. $C_{53}H_{71}N_2Cl_7Sn_2$ calcd.: C, 51.13; H, 5.81; N, 2.29; Cl, 20.32%.

Preparation of $[Et_4N]^+ [F_2SnPh_3]^-$

To a suspension of triphenyltin fluoride (1.0 g, 27 mmol) in methyl cyanide (15 ml) at room temperature was added a solution of tetraethylammonium fluoride dihydrate (0.5 g, 27 mmol) over a period of 10 minutes. On further stirring, a clear solution formed. Evaporation of solvent from the reaction mixture gave a crystalline residue which was dissolved in a mixture of methyl cyanide and ether (1/1) at room temperature. The solution was filtered and the filtrate cooled at 0°C overnight to give crystals of tetraethylammonium difluorotriphenylstannate (XIII) (yield 1.3 g, 92%).

Preparation of $Ph_3SnCl \cdot DMAP$ (XXV)

To a magnetically stirred solution of triphenyltin chloride (1.93 g, 50 mmol) in carbon tetrachloride (20 ml) was added dropwise a solution of 4-(dimethylamino)pyridine (0.61 g, 50 mmol) in carbon tetrachloride (10 ml) over a period of 1/2 h. During the course of addition, most of the desired product crystallized. The reaction mixture was stirred at room temperature for 2 h. The insoluble precipitate (2.0 g) was separated by filtration. Evaporation of solvent from the filtrate in vacuo gave an additional 0.52 g of the adduct. The residues were combined, washed twice with hexane (20 ml) and recrystallized from a mixture of methyl cyanide and ether (1/3) at 0°C to give crystals of $Ph_3SnCl \cdot$ DMAP (yield 2.38 g, 93.6%).

N.B. The hexamethylphosphoramide adduct, $Ph_3SnCl \cdot$ HMPA (XXIII), was prepared and purified following the same procedure as that described for $Ph_3SnCl \cdot$ DMAP (XXV).

Attempted Preparation of $[Et_4N]^+ [Cl(I)SnPh_3]^-$

To a solution of triphenyltin chloride (1.93 g, 50 mmol) in methyl cyanide (20 ml) was added a solution of tetraethylammonium iodide (1.28 g, 50 mmol)

in methyl cyanide (10 ml) under vigorous stirring at room temperature over a period of 10 minutes. The resulting reaction mixture was stirred at room temperature for 1/2 h during which time the solution turned slightly yellow. The slightly colored reaction mixture was filtered and the filtrate was cooled at 0°C overnight in a refrigerator when some colorless crystals (0.5 g) deposited. This compound was characterized by its m.p. and ^{1}H NMR spectroscopy to be tetraethylammonium iodide. On concentrating the mother liquor of the original reaction mixture and subsequently cooling to 0°C in a refrigerator a second crop of crystals of $[Et_4N]^+ I^-$ (0.3 g) was isolated. Evaporation of solvent from the mother liquor gave a brown residue which was treated with hot hexane and the solution was filtered hot. The brownish residue (0.35 g) left behind was found to be mostly unchanged $[Et_4N]^+ I^-$ containing traces of iodine. Evaporation of solvent from the hexane extract gave unchanged triphenyltin chloride (1.8 g).

Preparation of $[n\text{-}Bu_4N]_2^+ [Cl_5SnPh]^{2-}$

A mixture of phenyltin trichloride (0.7 g, 23 mmol) and tetra-n-butylammonium chloride (1.29 g, 46 mmol) was dissolved in methyl cyanide (10 ml) in a dry nitrogen atmosphere. The resulting solution was stirred for 1 h. Evaporation of solvent from the reaction mixture gave a crystalline solid which was recrystallized from a mixture of hexane and methylene chloride (1/1) at 0°C to yield crystals of $[n\text{-}Bu_4N]_2^+ [Cl_5SnPh]^{2-}$, m.p. 161—162°C (yield 1.90 g, 96%). Anal. Found.: C, 53.2; H, 9.21; Cl, 20.96. $C_{38}H_{77}N_2Cl_5Sn$ calcd.: C, 53.30; H, 8.98; Cl, 20.67%. ^{1}H NMR spectrum ($CDCl_3$); δ 0.65—1.95 (m, b, 56H, N—C—CH_2—CH_2—CH_3 protons), 3.25 (m, b, 16H, N—CH_2 protons), 7.37 (m, 3H, *meta*- and *para*-protons of the phenyl ring) and 8.25 (m, 2H, *ortho*-protons of the phenyl ring) ppm.

N.B. Complexes, $2[Me_4N]^+ [Cl_5SnPh]^{2-}$ [39] and $2[Et_4N]^+ [Cl_5SnPh]^{2-}$ [40] are reported but their ^{1}H NMR spectroscopic data are not available.

Acknowledgements

This work was supported by grants from the National Institutes of Health, GM-09706 (LAC) and GM-21466 (RRH), and grateful appreciation is expressed. We thank Dr. L.W. Dennis, Colorado State University, Fort Collins, Colorado, for the ^{31}P NMR spectra.

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