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SUBSTITUTION REACTIONS OF A COMPLEX OF TRIPHENYLTIN CHLORIDE AND ATTEMPTED PREPARATION OF COMPLEXES OF TRIPHENYLTIN FLUORIDE AND HYDROXIDE*

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Summary

The 1/1 complexes of hexamethylphosphoric triamide (HMPA) with triphenyltin species (Ph_3SnX, X = Cl, Br, I, N_3, CN) were prepared. Attempts were made to exchange the chloride in the complex $Ph_3SnCl(HMPA)$ with the anions F^-, OH^-, Br^-, I^-, CN^- and N_3^-. The anions F^- and OH^- produced Ph_3SnX [X = F^- and OH^- respectively], and I^- and N_3^- produced $Ph_3SnX(HMPA)$ [X = I^- and N_3^- respectively], but Br^- and CN^- did not exchange. Other attempted methods of preparation of complexes of Ph_3SnF and Ph_3SnOH were also unsuccessful.

Introduction

Substitution reactions of the type $R_3SnX + Y^- \rightarrow R_3SnY + X^-$ where X = Cl, Br or I and Y = OH, OR′, OC(O)R′, N_3, CN, NCO, NCS, NR'_2, F, Cl, Br, I etc. are well known and are generally used as preparative reactions in organotin chemistry [1]. However, although many five-coordinate complexes R_3SnXL (where L is an oxygen or nitrogen donor) have been prepared [2—7], no halide substitution reactions of any of these complexes have been reported. It was thought that this method might be suitable for preparing some hitherto unknown complexes of triorganotin fluorides, oxides and hydroxides.

Until now, no stable complexes of R_3SnF, $(R_3Sn)_2O$ or R_3SnOH with Lewis bases have been reported. This at first sight seems rather surprising since organotin halides and tin(IV) tetrahalides are "hard" acids and it would seem that the electronegative atoms, O and F, attached to tin would proffer greater stability on complexes. However, the very hardness of the tin atom in organotin fluorides and hydroxides produces strong self-coordination in these species, and it seems that this self-coordination inhibits the reaction with a Lewis base

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and the formation of discrete complexes. A chloride substitution reaction on a complex of a triorganotin chloride should be a more satisfactory route since no energy is required to break down the strongly associated self-coordination species.

We here report our attempts at chloride substitution reactions of the hexamethylphosphoric triamide (HMPA) complex of triphenyltin chloride and preparations of some complexes of this and other triphenyltin species.

Experimental

1. General

Hexamethylphosphoric triamide (from British Drug Houses) was stored over calcium chloride and distilled from calcium hydride before use. Triphenyltin chloride was made by the redistribution reaction from tetraphenyltin and tin tetrachloride [8]; all solvents (acetone, chloroform, diethyl ether and petroleum ether) were purified by standard procedures. Sodium fluoride, bromide, iodide, azide, cyanide and hydroxide were all B.D.H. reagent grade and were dried in a vacuum oven before use.

2. Preparation of Ph_3SnX species

These were prepared by shaking an excess of the sodium salt with triphenyltin chloride in ether or acetone solution. For X = F and OH the sodium salt was in aqueous solution and at least in 50% excess. The resulting precipitate was washed with water, then ethanol, then ether and sucked dry.

For X = I equimolar quantities of triphenyltin chloride and the sodium salt in acetone were used and the product was obtained after filtering off the sodium chloride precipitate. The crude material was recrystallised from chloroform/hexane.

For X = Br, N_3 and CN an excess of the sodium salt was added to an acetone solution of Ph_3SnCl and refluxed for three hours. The product was obtained on filtering the mixture and removing the solvent. Recrystallisation from chloroform/hexane produced the pure material.

The physical properties (melting points and infrared spectra) of these six compounds were in agreement with published data [9—11].

3. Preparation of hexamethylphosphoric triamide complexes of Ph_3SnX ($X = Cl$, Br, I and N_3)

Two standard procedures, which produced almost quantitative yields in all cases, were used, the first being slightly more convenient [3].

(*a*). An approximately ten-fold excess of HMPA in chloroform was stirred for 10 min with a solution of the Ph_3SnX species in chloroform. Then the solvent and excess HMPA was removed under vacuum.

(*b*). Ph_3SnX was heated in at least a ten-fold excess of HMPA until it dissolved (usually 80° for 10 min). On cooling, twice the volume of petroleum ether was added and the product was allowed to crystallise out.

Generally about 0.5 g of the starting Ph_3SnX was used in the preparations but with Ph_3SnCl 10 g was used since this complex was required for later work. Further purification of the complexes was effected by recrystallisation from

TABLE 1

MELTING POINTS AND ANALYTICAL DATA ON HMPA COMPLEXES OF TRIPHENYLTIN SPECIES

Complex	M.P. °C	Analysis, found (calcd.) (%)			
		C	H	N	Hal
Ph$_3$SnCl(HMPA) [C$_{24}$H$_{33}$N$_3$OClPSn]	160—162	51.59 (51.02)	6.19 (5.85)	7.57 (7.40)	6.10 (6.29)
Ph$_3$SnBr(HMPA) [C$_{24}$H$_{33}$N$_3$OBrPSn]	146—148	47.83 (47.40)	5.83 (5.43)	7.00 (6.89)	15.18 (16.03)
Ph$_3$SnI(HMPA) [C$_{24}$H$_{33}$N$_3$OIPSn]	116	44.10 (43.96)	3.46 (3.50)	6.12 (6.39)	19.05 (19.36)
Ph$_3$SnN$_3$(HMPA) [C$_{24}$H$_{33}$N$_6$OPSn]	105—106	52.08 (52.17)	4.40 (4.17)	14.90 (15.20)	

chloroform and petroleum ether. The properties of the Ph$_3$SnX(HMPA) complexes are given in Tables 1 and 2.

Microanalyses were performed by the Microanalytical Laboratory, Department of Chemistry, University of Ibadan. Infrared spectra were recorded as Nujol mulls on a Perkin—Elmer PE 457 Grating Infrared Spectrophotometer using polystryrene as a calibrant. ^{1}HNMR spectra were recorded as chloroform solutions using TMS as internal reference on a Perkin—Elmer R12 NMR Spectrometer.

4. *Halide substitution reactions of Ph$_3$SnCl(HMPA)*

These reactions were initially attempted using equimolar quantities of Ph$_3$SnCl(HMPA) and the alkali metal salt in acetone (sometimes aqueous) solution at room temperature. If no reaction was observed, excess of the alkali metal salts and higher temperatures were used. Examples of the procedures are given below.

(a). X = F. 0.06 g (1 mmole) potassium fluoride in 2 ml of water and 0.56 g (1 mmole) of Ph$_3$SnCl(HMPA) in 10 ml of acetone were mixed together. A white precipitate was obtained immediately and this was filtered and washed

TABLE 2

NMR DATA FOR HEXAMETHYLPHOSPHORIC TRIAMIDE AND ITS TRIPHENYLTIN COMPLEXES IN CHCl$_3$ SOLUTION

Compound	τ(CH$_3$) (ppm) (±0.02)	J(P—N—CH$_3$) (Hz)	C$_6$H$_5$ multiplets (2 sets) (ppm)	
			Centre of each	Individual peaks
HMPA	7.36	9.2		
Ph$_3$SnCl(HMPA)	7.60	9.4	2.62 2.20	2.67, 2.61, 2.55 2.28, 2.22, 2.17, 2.10
Ph$_3$SnBr(HMPA)	7.70	9.5	2.64 2.16	2.70, 2.66, 2.61, 2.55 2.23, 2.20, 2.14, 2.08
Ph$_3$SnI(HMPA)	7.40	9.2	2.55 2.35	2.64, 2.59, 2.53 2.40, 2.35
Ph$_3$SnN$_3$(HMPA)	7.60	9.4	2.55 2.25	2.64, 2.59, 2.53 2.30, 2.25, 2.20

successively with water, ethanol and ether and dried. The product was insoluble in all solvents, and its infrared spectrum was identical to that of an authentic sample of triphenyltin fluoride. It decomposed at 350° (lit. [10] 357°). Elemental analysis confirmed that the product was Ph_3SnF. (Found: C, 58.42; H, 3.89. $C_{13}H_{15}FSn$ calcd.: C, 58.54; H, 4.07%.) In the reaction 0.35 g (0.95 mmole) Ph_3SnF was obtained (95% yield). The same result can be achieved by adding solid potassium fluoride to an acetone solution of Ph_3SnCl(HMPA). When the reaction was carried out in HMPA instead of acetone, the same result was obtained.

(b) X = OH. The same method as above was used but also the milder treatment described now. The same result was obtained with both.

Ph_3SnCl(HMPA) was prepared from 0.4 g (1 mmole) Ph_3SnCl and 4 ml HMPA as in *3(b)* above but instead of adding petroleum ether a slight excess of 10% aqueous ammonia was added and the mixture was shaken for some time. The two layers were separated and 10 ml petroleum ether was added to the HMPA layer. A white crystalline product separated out on standing. The infrared spectrum and melting point (121—122°) showed this to be triphenyltin hydroxide (lit. [10] m.p. 123—124°). This was confirmed by elemental analysis (Found: C, 58.52; H, 4.48. $C_{18}H_{16}OSn$ calcd.: C, 58.86; H, 4.36%.)

(c). X = Br. To an acetone solution of Ph_3SnCl(HMPA) (0.56 g, 1 mmole), sodium bromide (0.21 g, 1.2 mmole) was added and the mixture was refluxed for 3 h. The solvent was then removed under vacuum and the residue was extracted with 5 ml of chloroform. Precipitation with petroleum ether produced 0.5 g of a white solid whose melting point (160°), IR and NMR spectra were identical to the starting material. This was confirmed by elemental analysis (found for halogen 6.02%). The use of silver bromide also produced no reaction, as did the use of an aqueous solution of sodium bromide instead of the solid.

(d). X = CN. A solution of 0.56 g (1 mmole) Ph_3SnCl(HMPA) in acetone was refluxed with 0.04 g (1 mmole) sodium cyanide for 3 h. On filtering and adding petroleum ether, the starting material was recovered and characterised as in (*c*), when silver cyanide was used instead of sodium cyanide.

(e). X = I. A solution of 0.15 g (1 mmole) sodium iodide in acetone was added to an acetone solution of Ph_3SnCl(HMPA) (1 mmole). No precipitate appeared but on refluxing for 3 h a white solid was obtained on cooling. This was filtered off, petroleum ether was added to the filtrate and a white crystalline product was obtained. This was recrystallised from chloroform/petroleum ether to give 0.5 g of Ph_3SnI(HMPA) (76% yield), which was confirmed by IR, ^{1}HNMR and a mixed melting point (116°) with an authentic sample.

(f). X = N_3. 0.1 g (1.54 mmole) sodium azide was refluxed with 0.56 g (1 mmole) Ph_3SnCl(HMPA) in acetone for 3 h. After filtering and adding petroleum ether to the filtrate, 0.4 g of Ph_3SnN_3(HMPA) was obtained.

5. Attempted preparation of complexes of Ph_3SnOH, Ph_3SnF and Ph_3SnCN by direct reaction

Attempts were made to prepare adducts of Ph_3SnOH, with HMPA, dimethyl sulfoxide, pyridine *N*-oxide, 1,10-phenanthroline, 2,2-bipyridine, 4-picoline and pyridine as ligands.

With liquid ligands, Ph_3SnOH was added to excess of the ligand then heated until it dissolved. No reaction was observed since stoichiometric quantities of solid Ph_3SnOH were always obtained on adding petroleum ether or diethyl ether. The reactions with the solids were attempted in chloroform solution but again on treatment with the petroleum ether or diethyl ether, all the Ph_3SnOH was recovered.

Infrared spectra of chloroform solutions of 1/1 mixtures of Ph_3SnOH and those donors which have a characteristic vibration, which shows a large shift on coordination (HMPA, dimethyl sulfoxide and pyridine *N*-oxide), indicated that no significant coordination takes place under these conditions. However, when the chloroform was removed from the Ph_3SnOH/HMPA mixture the shoulder at 1170 cm^{-1} which appears in HMPA was considerably stronger. This may be an indication of a Lewis acid—base interaction but since the HMPA can be readily pumped off it must be very weak.

With Ph_3SnF and HMPA again no stable complex could be isolated. However Ph_3SnF did dissolve in hot HMPA and the IR spectrum of the oil obtained after pumping off most of the HMPA had, in addition to those of Ph_3SnF and HMPA, two new peaks at 1218 and 665 (vs) cm^{-1}.

The reaction of Ph_3SnCN with HMPA using the above methods (neat or in chloroform) produced a white solid on the addition of petroleum ether. An infra-red spectrum (Nujol mull) of this solid indicated the presence of a coordinated HMPA (strong band at 1145 cm^{-1}). However any attempted purification of this complex by washing with a solvent or pumping removed the HMPA. Pure Ph_3SnCN could always be recovered.

Discussion

No thermodynamic data are available for the reactions of Sn—X bonds in Ph_3Sn—X species, but the available [12] bond energies for the Me_3Sn—X species can give some indication of the feasibility of halide exchange reactions. For exchanges of Cl^- in Me_3SnCl with OH^-, Br^- and I^-, the heats of reaction are all favourable (—29, —3 and —2 kcal/mole respectively). The exchanges with N_3^-, CN^- and F^- are also all likely to be thermodynamically favorable. This holds for Ph_3SnCl since it was discovered that all six of these anions exchange with the chloride.

The mechanism of substitution reactions of triorganotin halides though not extensively studied appears to involve a five-coordinate intermediate [13, 14]. Chan and Wong [14] postulated that the formation of this intermediate is the rate-determining step, because the ethanolysis of triisopropyltin halides has the rate order $F > Cl > Br$. If fission of the tin—halogen bond is rate determining the opposite order would be expected since the order of bond strengths is $Sn—F > Sn—Cl > Sn—Br$ in the triorganotin halides. If this five-coordinate intermediate mechanism were to hold for substitution reactions of $Ph_3SnCl(HMPA)$, there needs to be an initial rapid displacement or dissociation of the HMPA. This certainly appears to be the case with F^- and OH^- since the products Ph_3SnF and Ph_3SnOH have no HMPA co-ordinated. If the mechanism were to involve an initial fission of the Sn—Cl bond followed by an attack on the four-coordinate intermediate by F^- or OH^- one would expect to obtain a $Ph_3SnF(HMPA)$ or $Ph_3SnOH(HMPA)$ complex.

The HMPA dissociation or displacement mechanism is only expected to hold for "hard" nucleophiles, F^- or OH^-, since Ph_3SnX species would have a preference for the oxygen donor, HMPA, over the "softer" nucleophiles, Br^-, I^-, CN^- and N_3^-. This seems to be confirmed in that Br^- and CN^- do not exchange with $Ph_3SnCl(HMPA)$ despite the fact that they do exchange with Ph_3SnCl. In addition it should be noted that the Sn—Cl bond, which would break in a dissociation mechanism, will be weaker in the complex (the Sn—Cl bond in $Me_3SnClPy$ [15] is longer than that in Me_3SnCl [16]).

However two other "soft" nucleophiles, I^- and N_3^-, do displace Cl^- from $Ph_3SnCl(HMPA)$. If Br^- cannot displace HMPA from the complex it is unlikely that either of these can. Therefore it seems that the exchange takes place via a dissociation of the Sn—Cl bond.

In the exchange reactions with Ph_3SnCl, the driving force except in the case of F^- and OH^-, is the formation of the exergenic sodium chloride. For F^- and OH^-, the formation of Ph_3SnF and Ph_3SnOH, which are much more exergenic than Ph_3SnCl, provides the driving force. With the complexes, the formation of Sn—Br and Sn—CN bonds is probably sufficiently unfavourable compared to the fission of the Sn—Cl bond to outweigh the energetically favourable formation of sodium chloride. In these reactions predictions on the base of the "hard—soft" concept [17] would not be valid, since the hard bases, F^- and OH^-, and the soft bases, I^- and N_3^-, react whereas intermediate, Br^-, and very soft, CN^-, do not. Also the strongly autocomplexed Ph_3SnF and Ph_3SnOH are formed readily whereas the weakly autocomplexing groups either do not exchange (CN^-) or react to form the complex (N_3^-).

No studies have been done to determine equilibrium constants of reactions of the type:

$$R_3SnX + Y^- \rightleftarrows R_3SnY + X^-$$

or

$$R_3Sn(OH_2)_2^+ + X^- \rightleftarrows R_3SnX + 2\ H_2O$$

So we have no quantitative information on the hardness or softness of the R_3Sn^+ moeity (compared to, for example, CH_3Hg^+ [18]).

From the ease of formation of Ph_3SnF and Ph_3SnOH in exchange reactions, the immediate conclusion would be that Ph_3SnX (X = halide, OH) is hard. Therefore the driving force to the formation of Ph_3SnF and Ph_3SnOH is the interaction of the hard acid site, Sn, of one molecule with the hard base site, F or OH, of another molecule of Ph_3SnF or Ph_3SnOH. Therefore this result is not necessarily an indication that the Ph_3Sn^+ moiety is a hard acid. In fact, the closest system [18] for which data is available:

$$CH_3Hg(H_2O)^+ + X^- \rightleftarrows CH_3HgX + H_2O$$

where the metal in CH_3Hg^+ is isoelectronic with that in $(CH_3)_3Pb^+$, has the "soft" order of stability constants $F^- < Cl^- < Br^- < I^- < CN^-$. Further studies are required but the Ph_3Sn^+ system should also exhibit this order and the $Ph_3Sn(HMPA)^+$ system may also have considering the I^- exchange reaction.

The spectroscopic studies (both IR and NMR) carried out here do not give any consistent picture of the bonding in the complexes prepared. In the IR spectra, the PO stretching vibration of HMPA (1200 cm^{-1}) shifts to 1150—1140 cm^{-1} in the complexes Ph_3SnX (X = Cl, 1147; Br, 1142; I, 1144; CN, 1145, N_3, 1130 cm^{-1}). The magnitude of the shift has been used as an indication of donor bond strength, but it is not too reliable and does not seem to apply here. However, for $Ph_3Sn(HMPA)_2^+$ BPh_4^- a strong doublet is observed at 1110 cm^{-1} so it appears that the charged species forms a stronger donor bond.

For Ph_3SnCN and HMPA the peak at 1145 cm^{-1} indicates coordination of HMPA to the metal but the complex is not very stable. With Ph_3SnF and Ph_3SnOH, some changes take place in the IR spectra of the mixtures with HMPA, but this is not strong coordination of the oxygen of HMPA to the tin. The 1170 cm^{-1} band in the Ph_3SnOH/HMPA mixture may indicate a weak O...Sn interaction. In the Ph_3SnF/HMPA mixture the 1218 cm^{-1} peak can be assigned as ν(PO) but the new 665 cm^{-1} peak is in the ν(P—N) region. This would require an asymmetric PN_3 grouping which would be possible if there an interaction of one of the N atoms with Ph_3SnF. This tentative explanation could also explain the increase in ν(PO). Coordination through nitrogen would cause a drift of electron density from oxygen lone pair to phosphorus to nitrogen thus increasing the P—O bond strength.

In the ^{1}H NMR spectra the small but significant differences in chemical shifts of both sets of signals could be used to characterise the complexes even in mixtures. However it is not appropriate to make deductions on the bonding trends from the positions of the ^{1}H signals.

It seems clear from our attempts to make complexes of Ph_3SnF and Ph_3SnOH that the exergenic autocomplexation prevents the formation of stable solid complexes although there may be some complexation in solution.

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