REVIEW

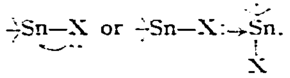
COORDINATION IN ORGANOTIN CHEMISTRY

R. C. POLLER
Chemistry Department, Queen Elizabeth College, London, W.8 (England)
(Received September 23rd, 1964)

INTRODUCTION

The chemistry of organotin compounds was reviewed[1] in 1960; this review included a table of complex organotin compounds, but these were not discussed. Since that date a large number of papers have been published on diverse aspects of organotin chemistry in which tin has been shown to possess coordination numbers higher than four. The present review attempts to show that the ready increase in coordination number of tin from four to five, or six, is a unifying concept in organotin chemistry and is a major cause of the break in properties between the organic compounds of tin and those of the lighter Group IVB elements, silicon and germanium.

Two types of complex will be considered, the simple adducts formed between an organotin compound and a donor such as pyridine, and the autocomplexes in which a radical already attached to tin becomes a donor with the same, or another, tin atom as acceptor *i.e.* either

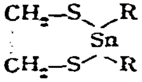


COMPLEX FORMING ABILITY OF ORGANOTIN COMPOUNDS

The tin tetrahalides form adducts with an enormous range of monodentate ligands and most of these have the composition $SnX_4 \cdot 2L$, though 1:1 adducts have also been reported[2]. The change in acceptor properties of the Group IVB elements when halogens are replaced by organic groups has been discussed by Beattie[3], and his detailed arguments will not be reproduced here. Although few quantitative studies have been made, it is clear that when, for example, the chlorine atoms in stannic chloride are successively replaced by less electronegative organic groups the acceptor strength of tin declines. Using the difference between the dipole moments in dioxane and hexane as a measure of complex-forming ability, the following series was obtained[4] $SnCl_4 > PhSnCl_3 > Bu_2SnCl_2 > Ph_2SnCl_2 > Ph_3SnCl > Bu_3SnCl$.

In general, the $RSnX_3$ compounds readily form complexes, the lowering in the acceptor strength of tin only becoming striking when weak donors are involved, such as alkyl sulphides which give adducts with $SnCl_4$ but not with $PhSnCl_3$[4,5].

The substitution of a second halogen for an organic group gives compounds which readily form adducts, and complexes such as $py_2 \cdot Et_2SnCl_2$ were included in Werner's classical studies[6] of coordination chemistry. Recently it has been shown[7] that the infra-red spectrum of $py_2 \cdot Me_2SnCl_2$ is consistent with an octahedral molecule, the methyl groups having a *trans* disposition. When the electronegativity of the two non-organic substituents attached to tin is diminished, there is a corresponding decrease in acceptor properties and it has been found[8] that compounds (I) (R = Bu or Ph) do not form stable adducts with the common donors.



(I)

The triorganotin halides show marked differences from the classes previously discussed in that 1:1 adducts are generally formed. An X-ray crystal study of $py \cdot Me_3SnCl$ has shown[9] that the molecule is a trigonal bipyramid with the pyridine and the chlorine lying on either side of the plane of the three methyl groups. This picture is consistent with the infra-red spectrum of this compound[7] and with the infra-red and NMR spectra of similar 1:1 adducts using tetramethylene sulphoxide, dimethylacetamide and dimethylformamide donors[10]. Besides the species already mentioned, halide ions can act as donors to give complex organotin anions[11] and recently a halogen-bridged dimeric structure was proposed[12] for the anion $(Me_3SnBr_2)^-$ but, in the absence of contrary evidence, a monomeric 5-coordinate structure would seem as likely.

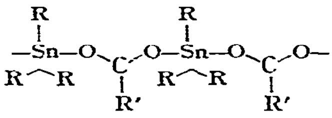
No adducts of tetraorganotin compounds have yet been reported and the dipole moments of tetraethyl- and tetraphenyl-tin in dioxane are zero[13]. While Beattie[3] has indicated that other factors besides the electronegativity of the groups attached to tin may affect its acceptor properties, it seems possible that compounds with four perfluoro-organic groups joined to tin would interact with suitable donors since it is known that the electronegativities of the CF_3 and C_6F_5 groups are comparable with that of bromine[14,15]. A coordination stage has been proposed for the abnormal, halide ion-catalysed, hydrolysis of $R_{(4-x)}Sn(C_6F_5)_x$ compounds[16].

Besides the 1:1 and 2:1 adducts, already mentioned, other donor-acceptor ratios have occasionally been described. In 1911 Pfeiffer reported[17] a stable $py_4 \cdot MeSnI_3$ adduct and, more recently, freezing point and vapour pressure measurements indicated that, besides the more usual 1:1 adducts, base$\cdot(Et_3SnCl)_2$ complexes were formed with dimethylamine, diethylamine and trimethylamine, the latter base forming only a 1:2 adduct[18].

AUTOCOMPLEXES CONTAINING 5-COORDINATE TIN

The positions of the C–O symmetric and asymmetric stretching frequencies in the infra-red spectra of the organotin carboxylates $R_3SnOOCR'$ and $R_2Sn(OOCR')_2$ indicated C_{2v} symmetry for the carboxyl group and this was, at first, taken to imply an ionic structure for these compounds[19,20]. This interpretation seemed to be strengthened when the absence of the Me–Sn symmetric stretching band[21] indicated a planar

Me_3Sn group in $Me_3SnOOCH$. It was subsequently pointed out[22] that a structure with bidentate carboxylate groups and 5-coordinate tin was also compatible with planar R_3Sn groups and C_{2v} symmetry for the carboxyl groups. More refined infra-red[23-25] and molecular weight[24,25] measurements indicate that, in general, compounds of the formula $R_3SnOOCR'$ exist as linear polymers (II) in the solid and molten states

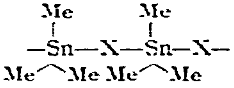


(II)

and in concentrated solutions in non-polar solvents, but are monomeric in dilute solutions. As far as association in solution is concerned, however, it should be noted that nuclear magnetic resonance measurements do not confirm these results. The NMR signals from the alkyl and acyl protons in $R_3SnOOCR'$ compounds are independent of concentration in a number of solvents[26].

Association in the trialkyltin carboxylates is inhibited when the alkyl groups are bulky or when the carboxylate oxygens are replaced by sulphur, $(iso\text{-}Pr)_3SnOOCCH_3$, $Me_3SnSOCCH_3$ and $Me_3SnSSCCH_3$ being monomeric with tin reverting to co-ordination no. 4. It is claimed that a number of compounds of the type $ClR_2SnOOCCH_3$ which are also monomeric, contain a chelating carboxyl group and 5-coordinate tin[27].

There is no evidence for the existence of R_3Sn^+ ions in the solid state and, although an ionic structure has often been proposed to explain the infusibility and insolubility of the organotin fluorides, an X-ray crystal study of Me_3SnF has shown that this is not the case[28]. The structure obtained showed association through fluorine atoms with a complex stereochemistry lying somewhere between the two extremes represented by discrete tetrahedral Me_3SnF compounds and the linear trigonal bipyramidal arrangement (III) (X = F).



$$\overset{\mathrm{Me}}{\underset{\mathrm{Me}\frown\mathrm{Me}}{-\mathrm{Sn}}}-\mathrm{X}-\overset{\mathrm{Me}}{\underset{\mathrm{Me}\frown\mathrm{Me}}{\mathrm{Sn}}}-\mathrm{X}-$$

(III)

Halogen bridging has also been invoked[29] for solid Me_3SnCl and Me_3SnBr to explain differences observed in the solid phase and solution infra-red spectra of these compounds.

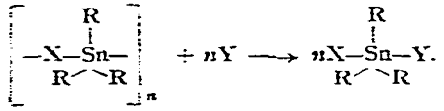
A number of examples of Me_3SnX compounds are known to which the polymeric 5-coordinate structure (III) has been assigned, these include the cases where the bridging group $X = ClO_4$[30], BF_4[31], AsF_6 and SbF_6[32]. While there seems no reason to doubt these assignments, it should be emphasised that, with the exception of Me_3SnF, they are almost entirely based upon interpretations of solid phase infra-red spectra and confirmatory evidence is desirable. The spectra of trimethyltin nitrate[33] and carbonate[30] show that these compounds are different from those already mentioned and contain non-planar trimethyltin groups.

The alkylation of stannic halides with aluminium alkyls may stop short of completion due to the precipitation of complexes such as $R_3SnX\cdot AlX_3$, addition of a powerful donor, for example a tertiary amine, avoids this difficulty[34] and the reaction then proceeds according to the equation:

$$4R_3Al + 4R'_3N + 3SnX_4 \longrightarrow 3R_4Sn + 4AlX_3\cdot NR'_3$$

Recent work[35] suggests that, in the solid state, the $R_3SnX\cdot AlX_3$ complexes may have a structure similar to (III) with bridging $AlCl_4$ groups.

N-(Trimethyltin)pyrrole is extremely readily hydrolysed, but replacement of the pyrrole group by a heterocyclic ring containing two 1,3-nitrogen atoms such as imidazole gives a stable structure (III) (X = imidazole)[36,37]. In compounds of this type the infra-red evidence is augmented by some interesting viscosity measurements[38] on solutions in non-polar solvents where association persists and causes high viscosities. The viscosity drops sharply when a more powerful donor Y is added to the system causing depolymerisation by the reaction:



$$\left[-X-\underset{R\;\;\;R}{\overset{\overset{R}{|}}{Sn}}-\right]_n + nY \longrightarrow nX-\underset{R\;\;\;R}{\overset{\overset{R}{|}}{Sn}}-Y.$$

It seems from infra-red evidence[39,40] that solid trimethyltin hydroxide is associated through oxygen bridges with a structure corresponding to (III) (X = OH) and molecular weight measurements[40] indicate a dimeric structure with a 4-membered Sn–O–Sn–O ring in solution. It should be emphasised that trimethyltin hydroxide is atypical in its chemical behaviour and it cannot be assumed that other R_3SnOH compounds have the same structure.

The ultra-violet absorption spectrum of O-triphenyltin 8-hydroxyquinolinate in 96 % ethanol showed absorptions identical with those of free 8-hydroxyquinoline and the authors[41] took this to mean that no chelation occurred in this compound. This does not preclude chelation in the solid state and another interpretation of the ultra-violet absorption measurements is that complete hydrolysis occurred in the 96 % ethanol to triphenyltin hydroxide and free 8-hydroxyquinoline.

In summary then, autocomplex formation is very common in compounds of the type R_3SnX and even when the anionic group X is derived from a strong acid, there is no evidence for the existence of free R_3Sn^+ ions in the solid state, though the infrared spectrum[33] of $(NH_3)_2\cdot Me_3SnClO_4$ suggests the ionic structure $[Me_3Sn(NH_3)_2]^+\ ClO_4^-$.

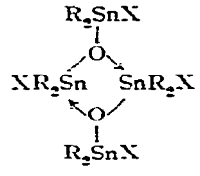
HYDROLYSIS PRODUCTS OF ORGANOTIN DIHALIDES AND RELATED COMPOUNDS

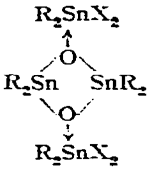
The basic hydrolysis of organotin dihalides under controlled conditions proceeds according to the following sequence:

$$R_2SnX_2 \longrightarrow \underset{A}{[R_4Sn_2X_2O]_2} \longrightarrow \underset{B}{[R_4Sn_2X(OH)O]_2} \longrightarrow R_2SnO$$

the intermediates A and B can be isolated and are reasonably stable. Compounds A and B can also be obtained synthetically by heating together, in an appropriate solvent, R_2SnX_2 and R_2SnO in the correct proportions.

Early work on the structure of these intermediates is summarised in a paper by Davies and co-workers[42], who have shown that compounds of the type *A* are dimeric and, from ^{119}Sn magnetic resonance measurements, that they contain tin atoms in two different environments; they have proposed two alternative structures, (IV) and (V). In both of these structures, two of the tin atoms show coordination number 4 and the remaining two have coordination number 5. While it is not yet possible to choose between these alternatives, the fact that two X groups can be selectively replaced by hydroxyl (to give *B*) suggests that (IV) is the more likely. There is now a very wide range of compounds known that have composition *A*; R may be alkyl or aryl and X may be halogen, carboxylate[43], camphorsulphonate[42], thiocyanate[42], aroxide[44], alkyl peroxide[45]. An X-ray crystal study[46] has confirmed the four-membered ring for the case where R = Me and X = $OSiMe_3$. It seems probable that the compound $(HOR_2Sn)_2O$, where R = *o*-phenoxyphenyl[47], has a similar structure[48].

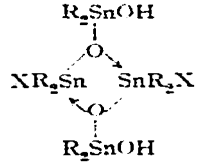

(IV)

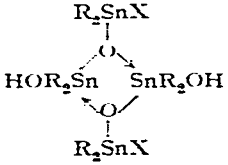

(V)

The intermediates represented by formula *B* have also been shown to be dimeric and dissolution in an alcohol converts the hydroxyl group to alkoxyl, a reaction which is reversed by exposure to atmospheric moisture[48–50]:

$$[R_4Sn_2X(OH)O]_2 \underset{H_2O}{\overset{R'OH}{\rightleftharpoons}} [R_4Sn_2X(OR')O]_2$$

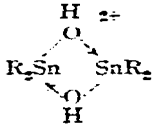
The two most likely structures for *B* are (VI) and (VII),


(VI)


(VII)

of these Okawara[50] prefers (VII) because, he maintains, the tin atoms having coordination number 5 would undergo substitution more readily. However, it has been shown[51] that the very readily hydrolysable compound $Ph_2Sn(NCO)_2$ becomes much less reactive when the coordination number is raised from 4 to 5 and the situation cannot be regarded as settled. Indeed the diffuse melting points shown by these compounds could indicate that they are mixtures of isomers with both structures (VI) and (VII) being present.

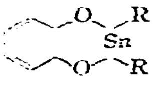
The end products from exhaustive hydrolysis of the dihalides are the infusible, insoluble polymeric oxides $(R_2SnO)_x$. The physical properties of these compounds differ markedly from those of the organopolysiloxanes $(R_2SiO)_x$ and it was suggested[52] that this could be explained in part by association of neighbouring -Sn-O-Sn-O- chains by O → Sn coordination. A more detailed structural model has now been proposed[48] in which all the tin atoms have coordination number 5 and this has been confirmed from Mössbauer spectra studies[53], which also indicate a coordinated polymeric structure. Lower organotin compounds are water soluble and the aqueous solution chemistry of some of these has been examined by Tobias and his co-workers, who have shown[54,55] that the ions R_2Sn^{2+} and R_3Sn^{+} exist as hydrates. Solutions containing these hydrated ions are acidic due to hydrolysis, and a hydrolysis product of the $R_2Sn(OH_2)_2^{2+}$ ion has the dimeric structure (VIII), showing again the importance of the 4-membered Sn-O-Sn-O ring system. In a study[56] of the stability of complexes formed between the Me_2Sn^{2+} ion and some N and O donors, the stability order picolinato > acetylacetonato > phenanthroline was found, and the Me_2Sn^{2+} ion is compared with the class (a) acceptors in the Chatt[57] classification.



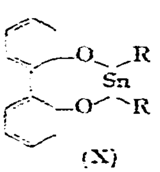
(VIII)

AUTOCOMPLEXES AND ADDUCTS CONTAINING 6-COORDINATE TIN

For compounds of the general formula R_2SnX_2 where X has donor properties, the possibility of tin achieving coordination number 6 by autocomplex formation arises. Although less work has been done in this field, it seems likely that the high-melting insoluble fluorides R_2SnF_2 are polymeric[22], though this is not the case with dimethyltin dinitrate, in which tin retains the tetrahedral configuration[58]. The dicarboxylates $R_2Sn(OOCR')_2$ are monomeric and it is suggested that the carboxyl groups in these compounds are chelating[22,27]. Organotin compounds form derivatives with diphenyltriazine[59] (= dpt) and this group is probably chelating in $Me_2Sn(dpt)_2$ and $PhSn(dpt)_2Cl$. A number of 8-hydroxyquinoline derivatives $R_2Sn(oxine)_2$ have been described[60-62,41] and there is evidence from ultra-violet absorption spectra[41] for chelation in these compounds. The high melting points and insolubility of the catechol and 2,2'-dihydroxybiphenyl derivatives (IX) and (X) indicate that they are coordinated intermolecularly by O→Sn links, this association being broken down by dissolution in a donor solvent such as pyridine[63].



(IX)



(X)

Since the organotin dihalides are frequently low-melting solids the crystalline adducts formed from these compounds and either 2,2'-bipyridine or 1,10-phenanthroline are useful for characterisation purposes[60,64,65]. With one exception, 1:1 adducts are formed and, although structural evidence is virtually non-existant, a simple 6-coordinate structure is probable for most of these compounds. The exception is bipy·$[Ph_2Sn(NCO)_2]_2$ in which tin is 5-coordinate and which is the first example of a compound containing a bridging bipyridine group[51]. Although $Ph_2Sn(NCO)_2$ is very readily hydrolysed by atmospheric moisture the bipyridine derivative is stable and this stabilisation of reactive species represents a valuable use of complex formation in organotin chemistry. Bipyridine can be removed from these adducts readily, and treatment of bipy·Bu_2SnCl_2 with either mercuric chloride or ferrous ions gives respectively the bipy·$HgCl_2$ and bipy$_3$·Fe^{2+} adducts[64]. Ultra-violet absorption spectra measurements indicate that the bipyridine adducts dissociate in a number of solvents[62,51].

SOME APPLICATIONS OF ORGANOTIN COMPLEX CHEMISTRY

The tendency of certain organotin compounds to form complexes has been exploited in analytical chemistry either in the spectrophotometric determination of compounds, which form coloured complexes, or in the removal of interfering organotin species. A colorimetric method for the determination of diethyl- and triethyl-tin compounds has been proposed, based on the formation of complexes of these compounds with dithizone[66]. The constitution of these dithizone derivatives has been discussed[67], though a chelated structure, at least for the compounds R_2Sn(dithizone)$_2$, seems as likely as the 4-coordinate structure proposed. Mixtures of several types of organotin compounds have been analysed by using complex formation for the selective removal of the different classes of organotin compounds[68,69].

The most important commercial use of organotin compounds is for the stabilisation of polyvinyl chloride against degradation by light and heat[70]. Although the majority of compounds used for this purpose contain 4-coordinate tin, patents concerning the use of complex compounds have appeared[71]. Recent work[72] on the mechanism of stabilisation of PVC by simple organotin compounds, R_2SnX_2, suggests that an initial coordination between the stabilizer and the polymer may be important.

REFERENCES

1 R. K. Ingham, S. D. Rosenberg and H. Gilman, *Chem. Rev.*, (1960) 459.
2 J. Laanes and T. L. Brown, *Inorg. Chem.*, 3 (1964) 148.
3 I. R. Beattie, *Quart. Rev. (London)*, 17 (1963) 382.
4 I. P. Gol'dshtein, E. N. Gur'yanova, E. D. Deleneskaya and K. A. Kocheshkov, *Dokl. Akad. Nauk SSSR*, 136 (1961) 1079.
5 I. P. Gol'dshtein, E. N. Gur'yanova and K. A. Kocheshkov, *Dokl. Akad. Nauk SSSR*, 138 (1961) 1099.
6 A. Werner, *Z. Anorg. Chem.*, 17 (1898) 82.
7 I. R. Beattie and G. P. McQuillan, *J. Chem. Soc.*, (1963) 1519.
8 (a) R. C. Poller, *Proc. Chem. Soc.*, (1963) 312;
(b) R. C. Poller and J. A. Spillman, unpublished observations.
9 R. Hulme, *J. Chem. Soc.*, (1963) 1524.
10 N. A. Matwiyoff and R. S. Drago, *Inorg. Chem.*, 3 (1964) 337.
11 P. Pfeiffer, *Ann. Chem.*, 376 (1910) 310.
12 D. Seyferth and S. O. Grim, *J. Am. Chem. Soc.*, 83 (1961) 1610.

13 W. Strohmeier and K. Miltenberger, *Z. Physik. Chem. (Frankfurt)*, 17 (1958) 274.
14 J. M. Holmes, R. D. Peacock and J. C. Tatlow, *Proc. Chem. Soc.*, (1963) 108.
15 J. J. Lagowski, *Quart. Rev. (London)*, 13 (1959) 233.
16 R. D. Chambers and T. Chivers, *Proc. Chem. Soc.*, (1963) 208.
17 P. Pfeiffer, B. Friedmann, R. Lehnhardt, H. Luftensteiner, R. Prade and K. Schnurman, *Z. Anorg. Chem.*, 71 (1911) 97.
18 K. K. Joshi and P. A. H. Wyatt, *J. Chem. Soc.*, (1959) 2825.
19 J. P. Freeman, *J. Am. Chem. Soc.*, 80 (1958) 5954.
20 R. Okawara and E. G. Rochow, *J. Am. Chem. Soc.*, 82 (1960) 3285.
21 R. Okawara, D. E. Webster and E. G. Rochow, *J. Am. Chem. Soc.*, 82 (1960) 3287.
22 I. R. Beattie and T. Gilson, *J. Chem. Soc.*, (1961) 2585.
23 M. J. Janssen, J. G. A. Luijten and G. J. M. van der Kerk, *Rec. Trav. Chim.*, 82 (1963) 90.
24 R. Okawara and M. Ohara, *Bull. Chem. Soc. Japan*, 36(5) (1963) 624.
25 R. Okawara and M. Ohara, *J. Organometal. Chem.*, 1 (1964) 360.
26 A. G. Davies and M. Hancock, private communication.
27 M. Wada, M. Shindo and R. Okawara, *J. Organometal. Chem.*, 1 (1963) 95.
28 H. C. Clark, R. J. O'Brien and J. Trotter, *Proc. Chem. Soc.*, (1963) 85; *J. Chem. Soc.*, (1964) 2332.
29 H. Kriegsmann and S. Pischtschan, *Z. Anorg. Allgem. Chem.*, 308 (1961) 212.
30 R. Okawara, B. J. Hathaway and D. E. Webster, *Proc. Chem. Soc.*, (1963) 13.
31 B. J. Hathaway and D. E. Webster, *Proc. Chem. Soc.*, (1963) 14.
32 (a) H. C. Clark and R. J. O'Brien, *Proc. Chem. Soc.*, (1963) 113;
(b) H. C. Clark and R. J. O'Brien, *Inorg. Chem.*, 2 (1963) 1020.
33 H. C. Clark and R. J. O'Brien, *Inorg. Chem.*, 2 (1963) 740.
34 W. P. Neumann, *Angew. Chem. Intern. Ed. Engl.*, 2 (1963) 165.
35 W. P. Neumann, R. Schick and R. Köster, *Angew. Chem. Intern. Ed. Engl.*, 3 (1964) 385.
36 J. G. A. Luijten, M. J. Janssen and G. J. M. van der Kerk, *Chimia*, 16 (1962) 10.
37 J. G. A. Luijten, M. J. Janssen and G. J. M. van der Kerk, *Rec. Trav. Chim.*, 81 (1963) 202.
38 J. G. A. Luijten, M. J. Janssen and G. J. M. van der Kerk, *J. Organometal. Chem.*, 1 (1964) 286.
39 H. Kriegsmann, H. Hofmann and S. Pischtschan, *Z. Anorg. Allgem. Chem.*, 315 (1962) 283.
40 R. Okawara and K. Yasuda, *J. Organometal. Chem.*, 1 (1964) 356.
41 L. Roncucci, G. Faraglia and R. Barbieri, *J. Organometal. Chem.*, 1 (1964) 427.
42 D. L. Alleston, A. G. Davies, M. Hancock and R. F. M. White, *J. Chem. Soc.*, (1963) 5469.
43 K. A. Kocheshkov, E. M. Panov and N. N. Zemlyanskii, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, (1961) 2255.
44 (a) W. J. Considine and J. J. Ventura, *J. Org. Chem.*, 28 (1963) 221;
(b) W. J. Considine, J. J. Ventura, A. J. Gibbons, Jr. and A. Ross, *Can. J. Chem.*, 41 (1963) 1239.
45 A. G. Davies and I. F. Graham, *Chem. Ind. (London)*, (1963) 1622.
46 R. Okawara, *Proc. Chem. Soc.*, (1961) 383.
47 R. C. Poller, *J. Chem. Soc.*, (1963) 706.
48 D. L. Alleston, A. G. Davies and M. Hancock, *J. Chem. Soc.*, in the press.
49 D. L. Alleston, A. G. Davies and B. N. Figgis, *Proc. Chem. Soc.*, (1961) 457.
50 R. Okawara and M. Wada, *J. Organometal. Chem.*, 1 (1963) 81.
51 A. S. Mufti and R. C. Poller, *J. Organometal. Chem.*, 3 (1965) 99.
52 R. C. Poller, *J. Inorg. Nucl. Chem.*, 24 (1962) 593.
53 V. I. Gol'danskii, E. F. Makarov, R. A. Stukan, V. A. Trukhtanov and V. V. Khrapov, *Dokl. Akad. Nauk SSSR*, 151 (1963) 357.
54 R. S. Tobias, I. Ogrins and B. A. Nevett, *Inorg. Chem.*, 1 (1962) 638.
55 B. A. Nevett and R. S. Tobias, *Chem. Ind. (London)*, (1963) 40.
56 M. Yasuda and R. S. Tobias, *Inorg. Chem.*, 2 (1963) 207.
57 S. Ahrland, J. Chatt and N. R. Davies, *Quart. Rev. (London)*, 12 (1958) 265.
58 C. C. Addison, W. B. Simpson and A. Walker, *J. Chem. Soc.*, (1964) 2360.
59 F. E. Brinckman and H. S. Haiss, *Chem. Ind. (London)*, (1963) 1124.
60 D. Blake, G. E. Coates and J. M. Tate, *J. Chem. Soc.*, (1961) 756.
61 W. Gerrard, E. F. Mooney and R. G. Rees, *J. Chem. Soc.*, (1964) 740.
62 T. Tanaka, M. Komura, Y. Kawasaki and R. Okawara, *J. Organometal. Chem.*, 1 (1964) 484.
63 H. J. Emeléus and J. J. Zuckerman, *J. Organometal. Chem.*, 1 (1964) 328.
64 D. L. Alleston and A. G. Davies, *Chem. Ind. (London)*, (1961) 551.
65 D. L. Alleston and A. G. Davies, *J. Chem. Soc.*, (1962) 2050.
66 W. N. Aldridge and J. E. Cremer, *Analyst*, 82 (1957) 37.
67 H. Irving and J. J. Cox, *J. Chem. Soc.*, (1961) 1470.
68 R. Bock, S. Gorbach and H. Oeser, *Angew. Chem.*, 70 (1958) 272.

69 R. T. SKEEL AND C. E. BRICKER, *Anal. Chem.*, 33 (1961) 428.
70 H. VERITY SMITH, *Organotin Stabilizers*, The Tin Research Institute, Greenford, 1959.
71 See e.g. *U.S. Patent* 2,604,460, (1952), *Chem. Abstr.*, 46 (1952) 10685 and patents quoted in ref. 70.
72 A. H. FRYE, R. W. HORST AND M. A. PALIOBAGIS, *J. Polymer Sci.*, *A*, 2 (1964) 1765, 1785, 1801.