Journal of Organometallic Chemistry, 59 (1973) 189–197

CARBON-13 NMR INVESTIGATIONS ON ORGANOTIN COMPOUNDS

TERENCE N. MITCHELL
Lehrstuhl für Organische Chemie der Universität Dortmund (B.R.D.)
(Received January 15th, 1973)

SUMMARY

The carbon-13 NMR spectra of 49 organotin compounds have been recorded and analysed. Variation of the groups attached to tin causes variations in the chemical shift of carbons α to tin of almost 150 ppm. Large variations are also observed for the coupling constant $^1J(^{119}\text{Sn}-^{13}\text{C})$, which, for the compounds investigated, lies between 240 and 1120 Hz; conclusions can readily be drawn from the magnitude of this coupling constant as to the hybridisation state and coordination number of the tin atom.

INTRODUCTION

A large amount of proton magnetic resonance data on organotin compounds can be found in the literature; attempts have been made to correlate tin–proton coupling constants with the structures of these compounds, and it is now generally accepted that the values of $J(^{119}\text{Sn–C–H})$ increase with increasing percent *s*-character of the Sn–C bond[1,2]. Tin-119 magnetic resonance data are also available for well over a hundred organotin compounds[3–5], but though a few compounds have been studied[6,7] no systematic study of the carbon-13 NMR spectra of organotins has as yet been reported. It therefore seemed appropriate to record and analyse the spectra of a range of typical organotin compounds in order to obtain basic information on the size of the chemical shifts and coupling constants involved. In particular the coupling constant $^1J(^{119}\text{Sn}-^{13}\text{C})$ should give more exact information on the hybridisation at the tin atom, and hence on the structure of the compounds, than the $^2J(^{119}\text{Sn–C–H})$ coupling constant (which in addition can only readily be measured for methyl- and ethyltin compounds).

EXPERIMENTAL

(*a*). *Preparation of compounds*

Almost all the compounds studied are described in the literature and were prepared by standard methods. Dibutyltin methoxide acetylacetonate* was obtained as a white crystalline solid, m.p. 64°, by cooling a 1/1 mixture of dibutyltin methoxide and dibutyltin bis(acetylacetonate) to −60°.

---

* Prepared by Mr. R. Knocke.

(*b*). *Recording of spectra*

Spectra were recorded using the pulse Fourier Transform technique with a Bruker-Physik HFX-10 instrument operating at a resonance frequency of 22.63 MHz (field strength 2.114 T) in conjunction with a Nicolet Instrument Corporation Series 1080 computer for data accumulation and processing. Proton noise decoupling was normally used, though off-resonance decoupling was in some cases necessary for assignment of the observed resonances.

The compounds were examined in 10 mm tubes as neat liquids or saturated solutions in suitable solvents (normally non-complexing). Deuterochloroform or hexadeuterobenzene served as internal lock, TMS as internal standard ($\delta = 0$).

RESULTS AND DISCUSSION

Tables 1–4 show the data obtained. Chemical shift values are accurate to ±0.1 ppm, coupling constants generally to ±2 Hz, though in some cases due to overlap of resonance lines the accuracy of the latter is only ±5 Hz.

Assignments of the propyl and isobutyl resonances were confirmed by off-resonance decoupling; in the butyl- and phenyltin compounds the carbons β and γ to tin cannot be distinguished from one another by this method, and assignments were made by analogy with present results and by comparison with literature values. Firstly, it has been shown[8] that in diphenyl- and dibutylmercury and in tetraphenyl- and tetrabutylphosphonium compounds ^3J(C–Sn) is larger than ^2J(C–Sn) though both are much smaller than ^1J(C–Sn). This is also the case in isobutyltin trichloride. Secondly the chemical shifts of the β and γ carbons were compared with those of substituted alkanes[9,10] and benzenes[11]. No attempt has been made to determine the

TABLE 1

CARBON-13 SPECTRAL DATA FOR METHYLTIN COMPOUNDS

Compound	δ(*C*)[a] (*ppm*)	^1J(*C–Sn*) (*Hz*)	*Additional data*
Me_4Sn	−9.6	340	
Me_6Sn_2	−10.2	244	^2J(C–Sn) 56 Hz
Me_3SnH	−11.8	352	
Me_3SnCl	0.0	386	
$Me_3SnCl \cdot Py$[b]	2.1	472	
Me_3SnBr	−0.1	372	
Me_3SnOEt	−3.1	416	$\delta(CH_2)$ 58.1, $\delta(CH_3)$ 19.5 ppm
Me_3SnNEt_2	−6.7	380	$\delta(CH_2)$ 46.5, $\delta(CH_3)$ 17.5 ppm J(C–N–Sn) 7, J(C–C–N–Sn) 14 Hz
Me_3SnCCl_3	−7.2	364	$\delta(CCl_3)$ 90.9 ppm
Me_2SnBr_2[c]	8.6	440	
$Me_2Sn(OEt)_2$	0.6	682	$\delta(CH_2)$ 59.3, $\delta(CH_3)$ 20.5 ppm
$Me_2Sn(Acac)_2$[d]	7.8	966	δ(CO) 190.8, δ(CH) 100.0, $\delta(CH_3)$ 27.8 ppm
$Me_2Sn(NEt_2)_2$	−5.9	472	$\delta(CH_2)$ 45.6, $\delta(CH_3)$ 17.5 ppm J(C–N–Sn) 12, J(C–C–N–Sn) 13 Hz

[a] Positive values denote shifts downfield from TMS (0 ppm). [b] In pyridine. [c] In methylene chloride. [d] In deuterochloroform. Py = pyridine, HAcac = acetylacetone.

TABLE 2

CARBON-13 SPECTRAL DATA FOR ETHYLTIN COMPOUNDS

Compound	*$\delta(C_\alpha)$ (ppm)*	*$\delta(C_\beta)$ (ppm)*	*$^1J(C\text{–}Sn)$ (Hz)*	*$^2J(C\text{–}Sn)$ (Hz)*	*Additional data*
Et_4Sn	0.0	11.1	320	22	
Et_6Sn_2	1.8	12.5	247	19	^2J(C–Sn–Sn) 41 Hz
Et_3SnH	−0.3	11.8	347	25	
Et_3SnCl	9.3	9.9	352	26	
Et_3SnBr	9.0	10.4	340	28	
Et_3SnI	7.9	11.4	326	29	
Et_3SnOAc[a]	8.1	9.9	370	25	δ(CO) 177, $\delta(CH_3)$ 21.3 ppm
Et_3SnNEt_2	3.6	10.2	370	25	$\delta(CH_2)$ 46.6, $\delta(CH_3)$ 17.4 ppm
Et_2SnBr_2[a]	19.6	10.1	400	40	

[a] In methylene chloride.

signs of the coupling constants measured; it is known[8] that ^1J(C–Sn) is positive and ^2J(C–Sn) negative for alkyltin compounds.

In the phenyltin compounds coupling through four bonds was observed; in the butyltin compounds such coupling was only visible for an aqueous solution (50% v/v) of butyltin trichloride: in all other cases it was too small ($<$ 10 Hz) to be measured. In the propyltin compounds investigated no coupling through three bonds was observed.

The advantages of carbon-13 spectroscopy over proton spectroscopy when studying organotin compounds include the following: (*a*), the differences in the coupling constant ^1J(C–Sn) are much greater than those in ^2J(H–Sn); (*b*), since the α-carbon of the alkyl or aryl group is directly bonded to tin, the variations in ^1J(C–Sn) more accurately reflect rehybridisation at the tin atom than do those in ^2J(H–Sn); (*c*), it is possible to measure ^1J(C–Sn) accurately for types of alkyl group (*e.g.* propyl, isobutyl, butyl, octyl) where ^2J(H–Sn) cannot be measured under normal conditions; (*d*), for such long-chain alkyl groups the identity of the compound and, within limits, its purity can be established without doubt: for example octyltin trichloride gives eight separate carbon resonances, at least four of which show measurable tin–carbon coupling. For no two octyltin compounds will all twelve measurable parameters be the same.

From the data recorded a series of observations can be made. Firstly, in all cases large chemical shift variations were only observed for carbon atoms α to tin: in the two phenyltin compounds investigated, the α-carbon shift variation was very small compared to the corresponding variation ($R_3SnX \rightarrow R_2SnX_2$) in the alkyltin compounds. Secondly, in the ethyltin halides the variation of the α-carbon chemical shift parallels the electronegativity change on going from chlorine to iodine. Thirdly, in the alkyltin series the coupling constant ^1J(C–Sn) decreases slightly in the order Me $>$ Et $>$ Pr $>$ Bu; an exception is provided by the ditins, where practically no variation is observed. Fourthly, this coupling constant increases in the order $R_4Sn < R_3SnHal < R_2SnHal_2 < RSnHal_3$, paralleling the increase in ^2J(H–Sn) in the methyltin compounds; the differences are however much larger.

It now seems established that the increase in ^2J(H–Sn) on going from Me_4Sn

TABLE 3

CARBON-13 SPECTRAL DATA FOR BUTYLTIN COMPOUNDS

Compound	$\delta(C_\alpha)$	$\delta(C_\beta)$	$\delta(C_\gamma)$	$\delta(C_\delta)$	${}^1J(C\text{–}Sn)$	${}^2J(C\text{–}Sn)$	${}^3J(C\text{–}Sn)$	*Additional data*
	(*ppm*)				(*Hz*)			
Bu_4Sn	9.1	29.6	27.6	13.7	310	25	52	
Bu_6Sn_2	10.3	31.0	27.8	13.7	241	16	53	${}^2J$(C–Sn–Sn) 40 Hz
Bu_3SnH	8.3	30.2	27.3	13.6	355	22	53	
Bu_3SnBr	17.2	28.5	26.9	13.6	330	23	60	
Bu_3SnOMe	14.1	28.4	27.4	13.7	370	20	62	$\delta(OCH_3)$ 54.3 ppm
Bu_6Sn_2O	16.6	28.5	27.4	13.7	370	20	60	
Bu_2SnH_2	6.9	30.6	26.9	13.6	375	24	57	
Bu_2SnCl_2[a]	27.0	27.0	26.3	13.5	424	36	85	
$Bu_2SnCl_2\cdot 2Py$[b]	38.4	28.4	26.0	13.6	860	45	150	
$i\text{-}Bu_2SnCl_2$	38.5	25.9	25.7		405	39	78	
$Bu_2Sn(OMe)_2$	19.5	27.8	27.2	13.8	642	30	85	$\delta(OCH_3)$ 52.0
$Bu_2Sn(O\text{-}t\text{-}Bu)_2$	21.4	[c]	[c]	13.6	496	[c]	[c]	$\delta(OC)$ 70.3, $\delta(OCC)$ 34.1 ppm
$Bu_2Sn(O\text{-}i\text{-}Pr)_2$	19.2	27.5	27.0	13.6	520	38	88	$\delta(OCH)$ 66.5, $\delta(CH_3)$ 27.8 ppm
$Bu_2Sn(OCycl)_2$	19.4	[c]	[c]	13.6	515	[c]	[c]	$\delta(OCH)$ 72.8, $\delta(OCC)$ 38.2 ppm
$Bu_2Sn(OAc)_2$	25.0	27.0	26.5	13.6	630	35	92	$\delta(CO)$ 181, $\delta(CH_3)$ 20.0 ppm
$Bu_2Sn(Acac)_2$	27.7	27.4	26.5	13.9	914	41	130	$\delta(CO)$ 191, $\delta(CH)$ 99.8 ppm
$Bu_2Sn(H)Cl$	17.6	28.1	26.6	13.6	397	27	70	
$Bu_2Sn(OMe)Cl$[a]	26.3	27.2	26.7	13.7	622	36	94	$\delta(OCH_3)$ 52.0 ppm
$Bu_2Sn(OAc)Cl$	26.1	27.0	26.5	13.6	516	34	90	$\delta(CO)$ 182, $\delta(CH_3)$ 20.0 ppm
$Bu_2Sn(OAc)OMe$[a]	24.9	27.4	27.0	13.8	666	37	110	$\delta(CO)$ 179, $\delta(CH_3)$ 21.6, $\delta(OCH_3)$ 52.7 ppm
$Bu_2Sn(Acac)OMe$	27.7	27.8	27.0	14.0	904	38	119	$\delta(CO)$ 191, $\delta(CH)$ 100, $\delta(OCH_3)$ 51.9 ppm
$BuSnCl_3$	33.7	26.7	25.4	13.1	645	40	120	
$BuSnCl_3$[d]	44.8	28.8	26.2	14.8	1120	72	230	${}^4J$(C–Sn) 14 Hz
$i\text{-}BuSnCl_3$	44.1	26.2	24.9		627	50	106	

[a] In methylene chloride. [b] In pyridine. [c] Assignments uncertain. [d] In water (50% v/v). HOCycl = cyclohexanol.

to $MeSnCl_3$ in non-complexing solvents is related to the increase in *s*-character of the Sn–C bond[2]. In complexing solvents, *e.g.* acetone, dimethyl sulphoxide, dimethylformamide, water or pyridine, the coupling constants of methyltin halides increase[1,12–14], corresponding to the formation of weak or strong complexes; trimethyltin halides are pentacoordinated in such complexes, dimethyltin dihalides hexacoordinated: the crystal structure of the complex $Me_3SnCl \cdot$ pyridine has been found[15] to be a trigonal bipyramid, the three methyl groups lying in a plane. It has been further suggested that in this complex the Sn–C bonds have sp^2 character, the Sn–Cl and Sn–N bonds being *dp* hybridised[16–18]. In most complexes with hexacoordinate tin *e.g.* $Me_2SnCl_2 \cdot$ 2,2′-bipyridine, $Me_2SnCl_2 \cdot$ 2 pyridine[19] or dimethyltin bis(acetylacetonate)[20] the methyl groups are *trans* to each other; however, Mössbauer evidence suggests that in diphenyltin bis(acetylacetonate) the methyl groups are *cis*[21]. In the *trans*-oriented compounds the Sn–C bonds should be approximately *sp*-hybridised[16–18].

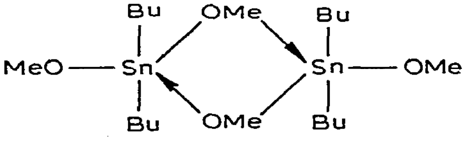
The coupling constant ^1J(C–Sn) shows a corresponding increase on adding complexing solvents to the pure liquid or to a solid halide. Thus in pure trimethyltin chloride the coupling constant is 372 Hz, but on adding an excess of pyridine it increases to 472 Hz. Similarly for dibutyltin dichloride in methylene chloride the value is 424 Hz, in acetone 480 Hz and in pyridine 860 Hz. Pure butyltin trichloride gives a value of 645 Hz, but in water (50% v/v) it increases to 1120 Hz; in this case it seems likely that the tin is hexacoordinated. Dimethyl- and dibutyltin bis(acetylacetonate), where the tin is also hexacoordinated, show values of 966 and 916 Hz respectively.

Tables 1–4 indicate that the coupling constant ^1J(C–Sn) has values in the following ranges: 300–340 Hz for tetraalkyltins, 330–390 Hz for 4-coordinated and 450–480 Hz for 5-coordinated trialkyltin compounds, 370–480 Hz for 4-coordinated and 900–970 Hz for 6-coordinated dialkyltin compounds.

In the light of these values for compounds whose structure is certain, and in view of the fact that butyltin compounds are in several respects more suitable for study than methyltin compounds, it was decided to study a number of dibutyltin compounds whose structure is unknown or uncertain.

Dibutyltin dimethoxide

From infrared[22], cryoscopic[23], and ^{119}Sn NMR measurements[5] it has been suggested that dibutyltin dimethoxide has the structure (I):



(I)

The coupling constant ^1J(C–Sn) for this compound (pure liquid) is 642 Hz, which is intermediate between those of Bu_2SnCl_2 and $Bu_2Sn(Acac)_2$: this supports the 5-coordinated structure (I). Further support for this structure is given by low-temperature PMR[24] and mass spectrometric[25] investigations in this laboratory; the di-

TABLE 4

CARBON-13 SPECTRAL DATA FOR MISCELLANEOUS ORGANOTIN COMPOUNDS

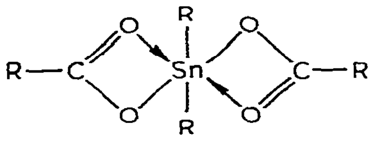
Compound	$\delta(C_\alpha)$	$\delta(C_\beta)$	$\delta(C_\gamma)$	$^1J(C\text{–}Sn)$	$^2J(C\text{–}Sn)$	$^3J(C\text{–}Sn)$	*Additional data*
Pr_4Sn	12.3	20.9	19.2	316	30	[a]	
Pr_3SnBr	20.2	19.8	18.3	331	32	[a]	
Pr_2SnBr_2[b]	29.9	19.5	17.4	390	32	[a]	
$OcSnCl_3$	33.4	[c]	[c]	650	[c]	[c]	
Ph_3SnCl[d]	137.5	136.1	129.2	610	49	68	$\delta(C_\delta)$ 130.5 ppm, ^4J(C–Sn) 12 Hz
Ph_2SnCl_2[b]	137.0	134.9	129.7	785	63	90	$\delta(C_\delta)$ 131.8 ppm, ^4J(C–Sn) 16 Hz

[a] Not observed. [b] In methylene chloride. [c] Assignments uncertain. [d] In deuterochloroform. Oc=octyl.

methoxide shows two methoxy resonances (coordinated and uncoordinated) at low temperatures, and volatilises as dimeric units in the mass spectrometer. More hindered alkoxides show lower values: 520, 515 and 496 Hz for the diisopropoxide, bis(cyclohexyloxide) and di-tert-butoxide respectively. Infrared[22] and ^{119}Sn NMR[5] evidence suggest that the latter is monomeric. Dimethyltin dimethoxide shows a value of 682 Hz, similar to that of the dibutyltin compound.

Organotin acetates

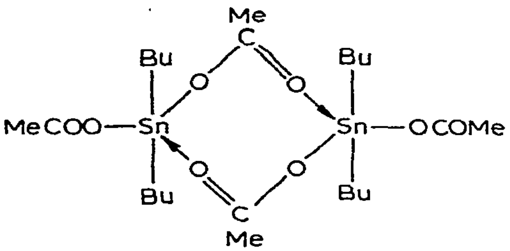
The structure of organotin carboxylates has been the subject of much discussion in the literature[26]. Using infrared spectroscopy as a basis it has been suggested[27,28] that trialkyltin carboxylates are polymeric in the solid state with bridging carboxylate groups, and monomeric in dilute solution; in both cases the tin should be pentacoordinate. Dialkyltin dicarboxylates have been suggested[29] to be monomeric with hexacoordinate tin (II):



(II)

The low solubility of trialkyltin acetates render them rather unsuitable for ^{13}C investigation; however, the spectrum of triethyltin acetate showed a value of ^1J(C–Sn) of 370 Hz, 102 Hz lower than that of trimethyltin chloride in pyridine. This suggests either a rather low tendency for the tin to be pentacoordinate or a very distorted trigonal bipyramidal structure. The carbonyl carbon shows a chemical shift of 177 ppm, compared with 177.3 ppm for pure acetic acid, thus favouring the former conclusion.

Pure dibutyltin diacetate has ^1J(C–Sn) 630 Hz, comparable with the value found for the dimethoxide (642 Hz), where the tin is pentacoordinate. In view of this an analogous structure (III) can be postulated, involving bridging and non-bridging carboxylate groups:

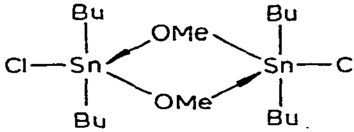


(III)

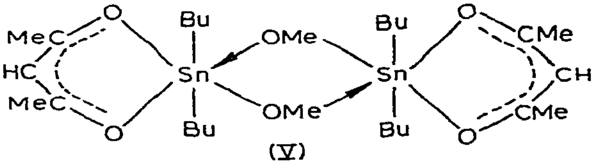
The infrared spectrum of neat dibutyltin diacetate shows bands which have been assigned[29] as due to bridging (1570 cm^{-1}) and non-bridging (1605 cm^{-1}) carboxylate groups: the former band is absent in dilute solutions. The ^{13}C spectrum shows only one carbonyl resonance at 181 ppm, indicating that the carboxyl group has some "anionic" character. Presumably a rapid exchange of carboxyl groups takes place at the operating temperature of the spectrometer (50°), leading to equivalence of the carbonyl carbons. Mössbauer evidence has been interpreted[30] as indicating a distorted octahedral structure of type (II) in the solid state; however, it seems rather unlikely that the (relatively small) distortion suggested would lead to a decrease of ca. 300 Hz in the coupling constant ^1J(C–Sn) compared to the regular octahedral $Bu_2Sn(Acac)_2$. In this respect it will be interesting to study $Ph_2Sn(Acac)_2$ in which the phenyl groups are *cis*[21].

Dibutyltin compounds with two functional groups

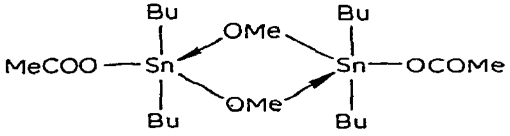
Table 3 includes the data obtained for five dibutyltin compounds with two functional groups. In the light of these values dibutyltin methoxide chloride is suggested, in agreement with literature reports[31], to be dimeric with bridging methoxide groups and pentacoordinate tin (IV), and dibutyltin acetylacetone methoxide dimeric



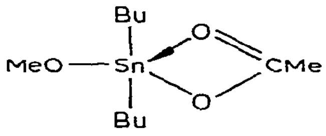
(IV)



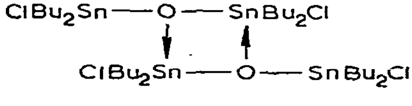
(V)



(VI)



(VII)



$$\begin{array}{ccc} \mathrm{ClBu_2Sn}-\mathrm{O} & - & \mathrm{SnBu_2Cl} \\ \downarrow & & \uparrow \\ \mathrm{ClBu_2Sn} & - & \mathrm{O}-\mathrm{SnBu_2Cl} \end{array}$$

(VIII)

with bridging methoxide groups and hexacoordinate tin (V); dibutyltin acetate methoxide apparently has pentacoordinate tin, and structures (VI) or (VII) can be written, though the dimeric structure (VI) seems more likely.

In all three cases, only four butyltin carbon resonances were observed; this suggests that in concentrated solution or in the neat liquid only the dimeric form is present at 50°. In tetrabutyldichlorostannoxane, which is apparently dimeric in concentrated solution[32], two signals were observed for the α, β and γ carbons, corresponding to four- and five-coordinate tin (VIII); unfortunately the coupling constants could not be accurately determined, due to line overlapping.

Dibutyltin hydride chloride and dibutyltin acetate chloride are apparently at 50° in very rapid equilibrium with the dihydride and the dichloride or diacetate respectively; all chemical shifts and coupling constants are those obtained by taking the arithmetic mean of those for the dihydride and dichloride or diacetate. It is planned to study the spectra of these and similar systems as a function of temperature.

ACKNOWLEDGEMENT

The author thanks Mr. M. A. Ardjmandian for his tireless help in recording the spectra, and Mr. J. Kleffner for preparing a number of compounds investigated. Thanks are also due to several colleagues, in particular Mr. R. Knocke, for providing samples of compounds, and to Professor W. P. Neumann for encouragement and discussions.

REFERENCES

1 J. R. Holmes and H. D. Kaesz, *J. Amer. Chem. Soc.*, 83 (1961) 3903.
2 E. V. Van den Berghe and G. P. Van der Kelen, *J. Organometal. Chem.*, 11 (1968) 479.
3 A. G. Davies, P. G. Harrison, J. D. Kennedy, T. N. Mitchell, R. J. Puddephatt and W. McFarlane, *J. Chem. Soc. C*, (1969) 1137.
4 P. G. Harrison, S. E. Ulrich and J. J. Zuckerman, *J. Amer. Chem. Soc.*, 93 (1971) 5398.
5 W. McFarlane, J. C. Maire and M. Delmas, *J. Chem. Soc., Dalton Trans.*, (1972) 1862.
6 W. McFarlane, *J. Chem. Soc. A*, (1967) 528.
7 W. McFarlane, *J. Chem. Soc. A*, (1968) 1630.
8 F. J. Weigert and J. D. Roberts, *J. Amer. Chem. Soc.*, 91 (1969) 4940.
9 D. M. Grant and E. G. Paul, *J. Amer. Chem. Soc.*, 86 (1964) 2984.
10 G. C. Levy and G. L. Nelson, *Carbon-13 Nuclear Magnetic Resonance for Organic Chemists*, Wiley-Interscience, New York, 1972, p. 47.
11 See ref. 10, p. 81.
12 T. F. Bolles and R. S. Drago, *J. Amer. Chem. Soc.*, 88 (1966) 5730.
13 G. Matsubayashi, Y. Kawasaki, T. Tanaka and R. Okawara, *Bull. Chem. Soc. Jap.*, 40 (1967) 1566.
14 B. K. Hunter and L. W. Reeves, *Can. J. Chem.*, 46 (1968) 1399.
15 R. Hulme, *J. Chem. Soc.*, (1963) 1524.
16 R. J. Gillespie and R. S. Nyholm, *Quart. Rev., Chem. Soc.*, 11 (1957) 339.
17 N. A. Matwiyoff and R. S. Drago, *Inorg. Chem.*, 3 (1964) 337.
18 E. V. Van den Berghe, L. Verdonck and G. P. Van der Kelen, *J. Organometal. Chem.*, 16 (1969) 497.
19 I. R. Beattie and G. P. McQuillan, *J. Chem. Soc.*, (1963) 1519.
20 Y. Kawasaki, T. Tanaka and R. Okawara, *Bull. Chem. Soc. Jap.*, 37 (1964) 903.
21 B. W. Fitzsimmons, N. J. Seeley and A. W. Smith, *Chem. Commun.*, (1968) 390.
22 J. Mendelsohn, J. Pommier and J. Valade, *C. R. Acad. Sci., Paris, Ser. C*, 263 (1966) 921.
23 I. P. Goldshtein, N. N. Zemlyanski, O. P. Shamagina, E. N. Gurýanova, E. M. Panov, N. A. Slovokhotova and K. A. Kocheshkov, *Proc. Acad. Sci. USSR*, 163 (1965) 715.

24 R. Knocke, unpublished results.
25 R. Knocke and H. P. Ritter, unpublished results.
26 See for example; R. Okawara and M. Ohara, in A. K. Sawyer (Ed.), *Organotin Compounds*, (Vol. 2), Dekker, New York, 1971, p. 253.
27 M. J. Janssen, J. G. A. Luijten and G. J. M. van der Kerk, *Recl. Trav. Chim. Pays-Bas*, 82 (1963) 90.
28 R. A. Cummins and P. Dunn, *Aust. J. Chem.*, 17 (1964) 185.
29 Y. Maeda and R. Okawara, *J. Organometal. Chem.*, 10 (1967) 247.
30 A. G. Maddock and R. H. Platt, *J. Chem. Soc. A*, (1971) 1191.
31 A. C. Chapman, A. G. Davies, P. G. Harrison and W. McFarlane, *J. Chem. Soc. C*, (1970) 821.
32 A. G. Davies, L. Smith, P. J. Smith and W. McFarlane, *J. Organometal. Chem.*, 29 (1971) 245.