Subvalent Group 4B Metal Alkyls and Amides. Part 6.[1] Oxidative Addition of an Alkyl or Aryl Halide to Bis[bis(trimethylsilyl)methyl]tin(II); Hydrogen-1 Nuclear Magnetic Resonance Data on the Tin(IV) Adducts and a Single-crystal *X*-Ray Study of Tris[bis(trimethylsilyl)methyl]chlorotin(IV)

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Addition of an alkyl or aryl halide RX to $Sn[CH(SiMe_3)_2]_2$, (1), occurs readily at 20 °C in C_6H_6 or n-C_6H_{14} to give $SnX[CH(SiMe_3)_2]_2R$, (2). Similarly $CH_2X'_2$ (X′ = Br or I) and (1) give $CH_2\{SnX'[CH(SiMe_3)_2]_2\}_2$, (3). A side-product of some of the former reactions is $SnX_2[CH(SiMe_3)_2]_2$; a radical mechanism is proposed with $SnX[CH(SiMe_3)_2]_2^{\cdot}$ as the intermediate, for which R· and RX are in competition. Infrared spectra support a covalent monomeric tin(IV) structure for the chlorides (2). Hydrogen-1, and in some cases ^{13}C, n.m.r. spectra for (2) or (3) in benzene or methylene chloride solutions are consistent with a monomeric C_s molecular structure, showing diastereotopically distinct $SiMe_3$ groups. Addition of $(CD_3)_2SO$ or C_5D_5N leads to collapse of these doublets or, for R = Bu^t, a decrease in their separation, suggestive (with i.r. data) of a stereochemically non-rigid, five-co-ordinate, tin compound. A single-crystal *X*-ray analysis of $SnCl[CH(SiMe_3)_2]_3$ shows a covalent monomeric structure with the three alkyl groups slightly flattened from the tetrahedral: Sn–Cl 2.380(3), Sn–C (av.) *ca.* 2.18 Å; C–Sn–Cl (av.) *ca.* 103.9, C–Sn–C (av.) *ca.* 114.4°.

IN Part 2[2] we reported that bis[bis(trimethylsilyl)methyl]tin, (1), behaves in solution as a singlet stannylene and undergoes various types of reaction, including oxidative addition to give the tin(IV) product. Thus it was shown that (1) and either methyl iodide or bis(trimethylsilyl)methyl chloride react readily at ambient temperature to afford the product of stannylene insertion

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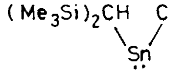
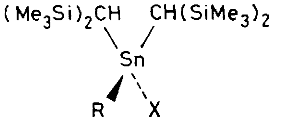
[1] Part 5, M. J. S. Gynane, D. H. Harris, M. F. Lappert, P. P. Power, P. Rivière, and M. Rivière-Baudet, *J.C.S. Dalton*, preceding paper.

[2] Part 2, J. D. Cotton, P. J. Davidson, and M. F. Lappert, *J.C.S. Dalton*, 1976, 2275.

into the carbon-halogen bond [2; RX = MeI or $(Me_3Si)_2CHCl$].

The ready formation of the organotin(IV) compound $SnCl[CH(SiMe_3)_2]_3$, containing three of the unusually bulky ligands $[CH(SiMe_3)_2]^-$,[3] was a little surprising,


(1)


(2)

$$CH_2\{Sn[CH(SiMe_3)_2]_2X'\}_2 \quad (3)$$

although the Group 4A transition-metal analogues $[MCl\{CH(SiMe_3)_2\}_3]$ (M = Zr or Hf, but not Ti) had been characterised.[4] However, the ^{119}Sn Mössbauer spectroscopic parameters for $SnX[CH(SiMe_3)_2]_3$ (X = Cl or Br) and $SnI[CH(SiMe_3)_2]_2Me$ appeared to be somewhat anomalous compared with other tin(IV) compounds.[5]

In a preliminary communication [6] we reported that: (*i*) the addition of an alkyl or phenyl halide to (1) [or its tin(II) isoelectronic amide analogue] is quite general and proceeds under mild conditions to give either the 1 : 1 or (with CH_2Br_2 or CH_2I_2) the 1 : 2 adduct, (2) or (3; X′ = Br or I); (*ii*) these reactions involve a free-radical path, from optical activity and e.s.r. evidence; and (*iii*) the adducts (2) have diastereotopically distinct $SiMe_3$ groups, but this dichotomy is lost on addition of $(CD_3)_2SO$ or C_5D_5N, probably due to the formation of a stereochemically non-rigid five-co-ordinate tin(IV)–base adduct. This paper provides full details of items (*i*) and (*iii*) and additionally the results of a single-crystal *X*-ray analysis particularly so as to clarify the Mössbauer anomalies, but also because there is a paucity of such data for organotin halides.[7]

RESULTS AND DISCUSSION

Oxidative-addition Reactions.—The conversion of a tin(II) compound into a tin(IV) product is well known,[2] insertion of $SnCl_2$ into a transition-metal–X bond (X = metal, Cl, or R) being particularly closely studied.[8] Such reactions may be classified as $s^2 \longrightarrow d^{10}$ oxidative additions, together with *inter alia* $Tl^I \longrightarrow Tl^{III}$, $Ge^{II} \longrightarrow Ge^{IV}$, and $Pb^{II} \longrightarrow Pb^{IV}$, to distinguish them from $d^6 \longrightarrow d^4$ (*e.g.* $Mo^0 \longrightarrow Mo^{II}$), $d^7 \longrightarrow d^6$ (*e.g.* $Co^{II} \longrightarrow Co^{III}$), $d^8 \longrightarrow d^6$ (*e.g.* $Rh^I \longrightarrow Rh^{III}$), or $d^{10} \longrightarrow d^8$ (*e.g.* $Pt^0 \longrightarrow Pt^{II}$).[9]

Tin(II) halides react with organic halides to give mono-organotin(IV) adducts; elevated temperatures are generally required and the yields are low.[10] Recently, oxidative-addition of organic halides RX, under mild conditions, to several organic tin(II) precursors has been reported {see also ref. 6 for reactions of (1) or $Sn[N(SiMe_3)_2]_2$}. Thus, reactive organic halides oxidatively add to $Sn(\eta\text{-}C_5H_5)_2$ or $Sn(pd)_2$ (pd = pentane-2,4-dionate) at room temperature, but in many cases oxidative coupling to give RR takes place; [11] n-alkyl iodides react with other tin(II) bis(1,3-diketonates) under mild conditions.[12] Either pyrolysis [13] or photolysis [14] of the tin(IV) polymer $(SnBu^n{}_2)_n$ in the presence of an alkyl halide RX yields $SnBu^n{}_2(X)R$, leading to the suggestion that RX is a trapping agent for the transient $SnBu^n{}_2$ monomer.

The reaction of the tin(II) alkyl (1) in benzene or hexane solution with an alkyl or aryl halide RX proceeds [equation (1)] rapidly at ambient temperature to give the 1 : 1 adduct (2). The methylene halides $CH_2X'_2$ similarly give [equation (2)] the 2 : 1 adducts (3).

$$\underset{(1)}{Sn[CH(SiMe_3)_2]_2} + RX \longrightarrow \underset{(2)}{SnX[CH(SiMe_3)_2]_2R} \quad (1)$$

$$(1) + CH_2X'_2 \longrightarrow \underset{(3)}{CH_2\{SnX'[CH(SiMe_3)_2]_2\}_2} \quad (2)$$

Details are shown in Table 1. From the data of Table 1 it is clear that the relative rates of reactions (1) and (2) decrease in the sequence I > Br > Cl. Additionally, for reaction (1) the alkyl halides (Br, Cl) are somewhat more reactive than the aryl halides, but there is no clear discrimination between primary, secondary, or tertiary alkyl halides. A minor product (0—15%) of mixing the reactants of equation (1) is $SnX_2[CH(SiMe_3)_2]_2$, (4). These results may be compared with others on some of the transition-metal systems; [15] thus in summary, three types of metal complex are isolable, *e.g.*[16] equation (3).

$$[Pt(PEt_3)_3] + Bu^nBr \xrightarrow[2h]{PhMe,\ 25\ ^\circ C} \left[\begin{array}{l} \longrightarrow trans\text{-}[PtBr(Bu^n)(PEt_3)_2],\ 95\% \\ \longrightarrow trans\text{-}[PtBr(H)(PEt_3)_2],\ 4\% \\ \longrightarrow trans\text{-}[PtBr_2(PEt_3)_2],\ 1\% \end{array}\right. \quad (3)$$

The following radical mechanism (Scheme) is consistent with the above observations. (It is further supported [6]

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[11] K. D. Bos, E. J. Bulten, and J. G. Noltes, *J. Organometallic Chem.*, 1975, **99**, 397.

[12] I. Wakeshima and I. Kijima, *J. Organometallic Chem.*, 1974, **76**, 37.

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[14] W. P. Neumann and A. Schwarz, *Angew. Chem. Internat. Edn.*, 1975, **14**, 812.

[15] *Cf.*, M. F. Lappert and P. W. Lednor, *Adv. Organometallic Chem.*, 1976, **14**, 345.

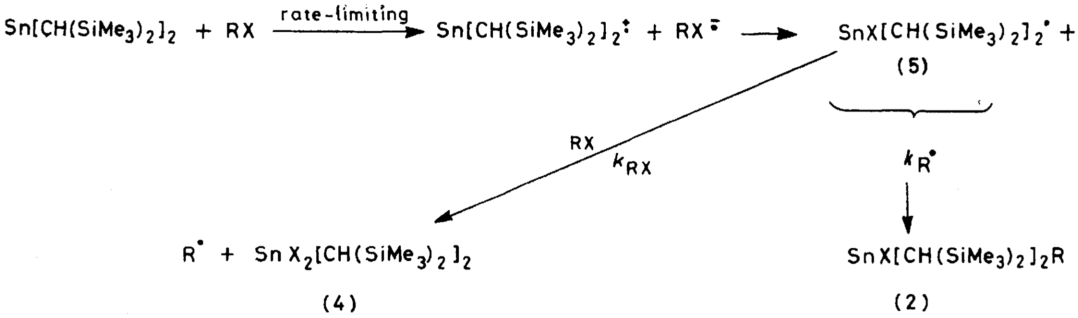
[16] A. V. Kramer, J. A. Labinger, J. S. Bradley, and J. A. Osborn, *J. Amer. Chem. Soc.*, 1974, **96**, 7145.

TABLE 1

Synthesis of tin(IV) compounds $SnX[CH(SiMe_3)_2]_2R$, (2), and $CH_2\{SnX'[CH(SiMe_3)_2]_2\}_2$, (3), and their characterisation

RX in (2) [X′ in (3)]	Solvent [a]	Time (t/h) for complete reaction [b]	Yield (%) of (2) or (3) [c]	M.p. (θ_c/°C) [B.p. (θ_c/°C), 10^{-3}mmHg]	Analysis (%) [d] C	Analysis (%) [d] H
MeI	*e*	<0.1	83	71—72	31.3 (31.1)	7.10 (7.15)
EtI	*e*	<0.1	81	76—77	32.4 (32.4)	7.25 (7.30)
Pr^iI	*e*	<0.1	71	78—79	34.1 (33.6)	7.35 (7.45)
Bu^nI	*e*	<0.1	72	[131]	34.9 (34.8)	7.55 (7.60)
PhI	*f*	<0.1	62	[125]	37.4 (37.4)	6.75 (6.75)
MeBr	*e*	*ca.* 1	86	80—81	33.6 (33.8)	7.90 (7.75)
EtBr	*e*	*ca.* 1	81	52—53	36.0 (35.2)	7.95 (7.95)
Pr^nBr	*e*	*ca.* 1	65	[126]	36.8 (36.4)	8.10 (8.10)
Bu^tBr	*e*	*ca.* 1	82	78—79	37.7 (37.6)	8.40 (8.45)
PhBr	*f*	*ca.* 10	63	[121]	40.2 (40.4)	7.80 (7.30)
Pr^iCl	*e*	*ca.* 4	57	[120]	34.1 (33.7)	7.35 (7.45)
Bu^nCl	*e*	*ca.* 4	68	[125]	40.2 (40.8)	8.20 (8.95)
Bu^tCl	*e*	*ca.* 4	54	[130]	39.7 (40.8)	8.60 (8.95)
$(Me_3Si)_2CHCl$	*e*	*ca.* 2	89	198—202	40.1 (39.9)	9.10 (9.10)
PhCl	*f*	*ca.* 80	49	[128]	43.7 (43.6)	7.70 (7.90)
[I]	*f*	<0.1	67	222—224	30.8 (30.5)	7.10 (6.90)
[Br]	*f*	*ca.* 1	72	156—158	33.3 (33.2)	7.35 (7.50)

[a] Concentration in the range 0.05—0.07 mol dm^{-3}. [b] Approximate; estimated visually from the time taken to discharge the red colour of $Sn[CH(SiMe_3)_2]_2$, (1), and refers to reaction at *ca.* 20 °C. [c] Refers to isolated and purified product (2) or (3). [d] Calculated values are given in parentheses. [e] $n-C_6H_{14}$. [f] C_6H_6.



SCHEME Mechanism of oxidative addition of RX to a tin(II) alkyl

by e.s.r. data {for the system (1)–EtBr or $-Pr^nBr$, the radical Et• or Pr^n• can be spin-trapped by nitrosodurene at *ca.* 20 °C as the nitroxide; for the system (1)–EtBr at −60 °C, a tin(III) species, probably $SnBr[CH(SiMe_3)_2]_2$•, is detected} and optical-activity observations {for the system (1)-(+)-$n-C_6H_{13}(Me)CHCl$, the *racemic* product $SnCl[CH(SiMe_3)_2]_2[CH(Me)C_6H_{13}-n]$ is obtained}; details of these experiments with results on kinetics, initiation, and inhibition will be published later.[17]) The relative proportions of the tin(IV) mono- (2) or di-halide species (4) is thus governed by competition for the tin(III) species by R• or RX, as measured by the relative rate constants $k_{R\cdot}$ and k_{RX}. In general, the geminate radical-pair combination reaction is expected to be dominant unless RX is particularly bulky. For the platinum case, in comparison, the $[PtX(R)(PEt_3)_2]$ adduct is only generally observed for a primary alkyl RX system, except for activated halides such as $MeCH(Br)CO_2Et$.[15] A hydrido-tin(IV) compound was not observed in the present system, in contrast to the platinum situation, but a hydrogen-atom abstraction by a tin(III) species from RX is likely to be energetically unfavourable because Sn–H bonds are

[17] M. J. S. Gynane, M. F. Lappert, and S. J. Miles, unpublished work.

rather weak. An ionic mechanism is out of the question for the phenyl halide reactions.

Spectroscopic Studies of $SnX[CH(SiMe_3)_2]_2R$, (2), *and* $CH_2\{SnX'[CH(SiMe_3)_2]_2\}_2$, (3).—The data are summarised in Table 2. The highest peak observed in the mass spectra was $[P - 15]^+$, where P^+ represents the parent monomeric molecular cation.

Infrared spectra were examined over the range 250—4 000 cm^{-1}. This permits the identification of tin–carbon (510 ± 20 cm^{-1}, and additionally 460 ± 10 cm^{-1} for R = Ph) and tin–chlorine (327 ± 3 cm^{-1}) stretching modes, but not ν(Sn–Br) or ν(Sn–I). By comparison,[7] vibrational modes for $SnXMe_3$ are (cm^{-1}): $\nu_{asym}(SnC_3)$, 544; ν_{sym} (SnC_3), 514; ν(SnCl), 315—330; ν(SnBr), 219—234; and ν(SnI), 177—189. For $SnXMe_3$ (X = Cl, Br, or I), there is i.r. as well as other spectroscopic evidence to show that the solids associate, contain five-co-ordinate tin, and depolymerise on melting or dissolution in an inert solvent. For compounds (2), on the other hand, a similar structural change does not accompany the phase change. For these compounds a monomeric formulation is proposed with C_s molecular symmetry and four-co-ordination at tin. Strong support derives both from the n.m.r. and *X*-ray data for the solution and solid [for the case of RX = $(Me_3Si)_2CHCl$] (see below), respectively.

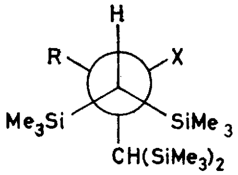
TABLE 2

Spectroscopic data for the tin(IV) compounds (2) and (3)

RX in (2) [X′ in (3)]	^{1}H N.m.r. chemical shifts (τ) [a]			I.r. (cm^{-1}) [b]	
	$SiMe_3$	HC–Sn	R–Sn	ν(Sn–C)	ν(Sn–Cl)
MeI	9.53 9.71 [c,d]	9.66	8.81	529s, 509s, 497s	
EtI	9.54 9.71 [c]	9.69	8.48	510s, br, 498s, br	
Pr^{i}I	9.41 9.54	9.47	8.41	498s, br	
Bu^{n}I	9.46 9.63 [e]	9.58	8.23 8.86	596m, 505s, br, 498s, br	
PhI [f]	9.76 9.90		2.20 2.65	500s, 460s	
MeBr	9.54 9.71	9.78	8.98	539m, 512s, 503s	
EtBr	9.56 9.75	9.80	8.48	512vs, br, 501vs, br	
Pr^{n}Br	9.48 9.63	9.70	8.33 9.23	595m, br, 508m, br	
Bu^{t}Br	9.53 9.64 [d,g]	9.68	8.49	500m, 481m	
PhBr	9.75 9.89		2.17 2.48	502s, 459s	
Pr^{i}Cl	9.59 9.66	9.73	8.43	510s, br	330s
Bu^{n}Cl	9.59 9.73		8.40 8.85	595m, br, 510m, br	330m
Bu^{t}Cl	9.51 9.60 [d,h]	9.71	8.48	505m, br, 490m, 475 (sh)	328m
$(Me_3Si)_2CHCl$	9.57	9.65		505m, 490s, 471m	325s
PhCl [f]	9.78 9.90		2.26 2.58	505m, br, 455m	329m
[I]	9.44 9.51		8.91	499s, 480w, 470s, 499w	
[Br]	9.50 9.55	9.60	9.36	504s, 470s	

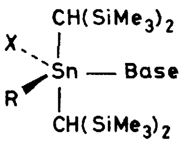
[a] In C_6H_6 solution, unless otherwise stated. [b] Capillary film or Nujol mull. [c] Splitting remained unchanged between 30 and 100 °C. [d] Doublet coalesced into singlet on addition of $(CD_3)_2SO$. [e] Doublet coalesced into singlet on addition of C_5D_5N. [f] N.m.r in CH_2Cl_2. [g] Splitting decreased from 6.2 to 3.4 Hz on addition of C_5D_5N. [h] Splitting decreased from 5.0 to 3.8 Hz on addition of C_5D_5N.

We associate the presence of equal-intensity doublets at *ca.* τ 9.9 in the ^{1}H n.m.r. spectra of (2) [except [2] RX = $(Me_3Si)_2CHCl$] or (3) in benzene or methylene dichloride at 30 °C (or at 30—100 °C for RX = EtI) with the two magnetically distinct diastereotopic $SiMe_3$ environments, a consequence of the prochiral, stereochemically rigid, approximately tetrahedral, tin centre of discrete monomeric molecules (6). Other examples of molecules $SnA[CH(SiMe_3)_2]_2B$ showing this phenomenon are found elsewhere.[2] Further evidence for the solution structure comes from ^{13}C n.m.r. data on one of the adducts $SnI[CH(SiMe_3)_2]_2Et$ (Table 2) showing a doublet for the $Si(CH_3)_3$ ^{13}C signal. The addition of the strong donor bases [$^2H_6$]dimethyl sulphoxide (dmso) or [$^2H_5$]pyridine to solutions of (2) or (3) caused either the coalescence of the doublet or, for (2; RX = Bu^{t}Cl or Bu^{t}Br), a decrease in the splitting. Similar effects have been noticed for addition of base to other diastereotopic tin(IV) compounds



(6)

and were found to be second order in added pyridine.[18] For (2; RX = EtI) in C_5D_5N the $SiMe_3$ sharp singlet showed no change for the range +35 to −40 °C. At least three possible intermediates may be envisaged: (*i*) a stereochemically non-rigid, five-co-ordinate, donor–acceptor base adduct; (*ii*) a five-co-ordinate bipyramidal adduct of structure (7); or (*iii*) an ionic complex, (8).



(7)

$$[\mathrm{Sn}\{\mathrm{CH}(\mathrm{SiMe}_3)_2\}_2\mathrm{R}]\mathrm{X}$$

(8)

As there are no significant shifts in the ^1H n.m.r. spectra, possibility (*iii*) is the least likely. For the chloro-compounds [2; RX = Bu^tCl or $(Me_3Si)_2CHCl$] in solution with base, ν(Sn–Cl) was identified as an i.r. band at 318 cm^{-1}; this may be compared with 250 cm^{-1} in solid $SnClMe_3(C_5H_5N)$,[7] which however, dissociates even in non-polar benzene.[19] In general, for trigonal-bipyramidal five-co-ordinate complexes of main-group elements, the most electronegative ligands are found in axial positions;[20] however, fluxional behaviour in these systems is common. Hence intermediate (*i*) is the most plausible and dissociates into its components in solution. However, such a compound, if formed at all, must have a very weak donor–acceptor interaction, at least in $SnCl[CH(SiMe_3)_2]_3{\cdot}py$, because, after dissolving the chloride in pyridine and allowing excess of pyridine to evaporate at 20 °C, crystals of pure $SnCl[CH(SiMe_3)_2]_3$ were recovered.

Crystal and Molecular Structure of $SnCl[CH(SiMe_3)_2]_3$.—*Crystal data.* $C_{21}H_{57}ClSi_6Sn$, $M = 632.35$, Orthorhombic, $a = 31.305(5)$, $b = 18.331(3)$, $c = 12.320(2)$ Å, $U = 7\,069.5$ Å^3, $Z = 8$, $D_c = 1.188$ g cm^{-3}, $F(000) = 2\,960$. Mo-K_α radiation, $\lambda = 0.710\,69$ Å, $\mu(\text{Mo-}K_\alpha) = 10.07$ cm^{-1}. Space group *Pbca* (D_{2h}^{15}, No. 61) from systematic absences: $hk0$ for $h \neq 2n$, $0kl$ for $k \neq 2n$, and $h0l$ for $l \neq 2n$. Weissenberg and precession photographs were used to establish the space group and cell constants, which were refined by least-squares methods from the 2θ values measured using a GE XRD-6 automated diffractometer for 28 reflections. Scattering factors, including anomalous scattering corrections for tin, were taken from ref. 21.

The white data crystal had dimensions 0.37 × 0.33 × 0.27 mm and was mounted with the *a* axis parallel to the ϕ axis of the diffractometer, which was equipped with a scintillation counter and pulse-height analyser. Zirconium-filtered Mo-K_α radiation was used and the stationary crystal–stationary-counter method was employed. Counts were taken for 30 s and a background curve was derived from measurements taken with the crystal at different orientations. The intensities of three standard reflections (060, 062, 004) were monitored after every 100 measurements. These diminished by <7% during the course of data collection and were used to scale the data to a common level. Standard deviations were estimated from counting statistics. Of 6 228 independent reflections measured (2θ < 50°), 3 646 with intensities >3σ were considered observed and used for the structure determination. Lorentz and polarisation factors were applied to the derivation of structure amplitudes.

TABLE 3

Final atomic co-ordinates (fractional, ×10^4), with standard deviations in parentheses

	x	*y*	*z*
Sn	1 347.5(2)	37.8(4)	2 083.2(5)
Cl	1 966.6(9)	130(2)	3 196(2)
Si(1)	1 564(1)	−74(2)	−674(3)
Si(2)	2 039(1)	−1 187(2)	944(3)
Si(3)	605(1)	1 415(2)	1 701(3)
Si(4)	1 556(1)	1 906(2)	2 289(3)
Si(5)	1 008(1)	−554(2)	4 636(3)
Si(6)	567(1)	−1 316(2)	2 604(4)
C(1)	1 561(3)	−577(7)	656(8)
C(2)	1 196(3)	1 161(5)	1 705(8)
C(3)	880(3)	−493(5)	3 136(9)
C(11)	1 967(5)	690(9)	−720(13)
C(12)	1 721(7)	−710(11)	−1 842(12)
C(13)	1 008(5)	267(9)	−1 008(12)
C(21)	1 947(5)	−1 686(8)	2 260(12)
C(22)	2 569(4)	−676(10)	976(12)
C(23)	2 063(7)	−1 924(4)	−135(15)
C(31)	434(5)	1 766(9)	3 082(11)
C(32)	500(4)	2 117(7)	611(11)
C(33)	233(4)	634(8)	1 353(14)
C(41)	1 573(5)	1 934(8)	3 831(11)
C(42)	1 381(6)	2 848(8)	1 880(12)
C(43)	2 112(5)	1 795(9)	1 755(12)
C(51)	1 469(5)	−1 175(9)	4 965(12)
C(52)	529(5)	−881(9)	5 429(14)
C(53)	1 125(5)	374(9)	5 174(12)
C(61)	−17(5)	−1 182(9)	2 936(16)
C(62)	748(5)	−2 226(7)	3 210(15)
C(63)	584(5)	−1 459(9)	1 095(15)

Structure solution and refinement. The co-ordinates of the tin atom in the asymmetric unit were determined from a three-dimensional Patterson map. An initial Fourier synthesis phased with this atom revealed all but the methyl carbon atoms, which were placed by a subsequent Fourier map. With all the atoms having isotropic temperature factors, the structure was refined by full-matrix least-squares methods to an agreement factor *R* of 0.131. Anisotropic refinement reduced *R* to 0.070. An empirical weighting scheme of the form $w^{-1} = 40 - 0.1|F| + 0.001|F|^2$ was then introduced to give constant errors in the different ranges of $|F_o|$ values. Convergence was obtained at *R* 0.069 with *R′*, the weighted residual, 0.084. A final difference-Fourier synthesis showed residual electron density in the vicinity of the tin atom to a maximum value of 1.9 eÅ^{-3}, and although some hydrogen atoms were located no attempt was made to include them in the refinement. All the computations were carried out on the IBM 360-75 system in the University of Waterloo Computing Centre.

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[19] I. R. Beattie and G. P. McQuillan, *J. Chem. Soc.*, 1963, 1519.

[20] *Cf.*, E. L. Muetterties and R. A. Schunn, *Quart. Rev.*, 1966, **20**, 245.

[21] 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1962, vol. 3.

The programs used have been described in detail elsewhere.[22]

Final positional parameters are listed in Table 3, bond lengths and angles in Table 4. Structure-factor tables and anisotropic thermal parameters are in Supplementary Publication No. SUP 22035 (25 pp.).*

TABLE 4

Bond lengths and angles, with standard deviations in parentheses *

(*a*) Lengths (Å)			
Sn–Cl	2.380(3)	Si(2)–C(22)	1.905(15)
Sn–C(1)	2.192(11)	Si(2)–C(23)	1.897(20)
Sn–C(2)	2.164(10)	Si(3)–C(31)	1.896(15)
Sn–C(3)	2.185(10)	Si(3)–C(32)	1.889(14)
C(1)–Si(1)	1.880(11)	Si(3)–C(33)	1.895(14)
C(1)–Si(2)	1.902(12)	Si(4)–C(41)	1.901(14)
C(2)–Si(3)	1.908(10)	Si(4)–C(42)	1.882(15)
C(2)–Si(4)	1.911(10)	Si(4)–C(43)	1.870(17)
C(3)–Si(5)	1.894(11)	Si(5)–C(51)	1.883(18)
C(3)–Si(6)	1.914(11)	Si(5)–C(52)	1.888(17)
Si(1)–C(11)	1.886(17)	Si(5)–C(53)	1.863(16)
Si(1)–C(12)	1.917(18)	Si(6)–C(61)	1.890(15)
Si(1)–C(13)	1.894(17)	Si(6)–C(62)	1.914(15)
Si(2)–C(21)	1.883(15)	Si(6)–C(63)	1.878(19)
(*b*) Angles (°)			
Cl–Sn–C(1)	104.5(3)	C(22)–Si(2)–C(23)	109.3(7)
Cl–Sn–C(2)	103.6(2)	C(2)–Si(3)–C(31)	110.8(5)
Cl–Sn–C(3)	103.6(2)	C(2)–Si(3)–C(32)	109.7(5)
C(1)–Sn–C(2)	112.5(3)	C(2)–Si(3)–C(33)	114.4(5)
C(1)–Sn–C(3)	116.8(3)	C(31)–Si(3)–C(32)	110.9(6)
C(2)–Sn–C(3)	113.9(3)	C(31)–Si(3)–C(33)	106.6(6)
Sn–C(1)–Si(1)	116.6(1)	C(32)–Si(3)–C(33)	104.3(6)
Sn–C(1)–Si(2)	113.1(1)	C(2)–Si(4)–C(41)	114.3(5)
Si(1)–C(1)–Si(2)	116.6(1)	C(2)–Si(4)–C(42)	112.5(5)
Sn–C(2)–Si(3)	116.4(1)	C(2)–Si(4)–C(43)	109.8(5)
Sn–C(2)–Si(4)	118.0(1)	C(41)–Si(4)–C(42)	104.6(6)
Si(3)–C(2)–Si(4)	113.5(1)	C(41)–Si(4)–C(43)	109.2(6)
Sn–C(3)–Si(5)	117.6(1)	C(42)–Si(4)–C(43)	106.0(6)
Sn–C(3)–Si(6)	119.4(1)	C(3)–Si(5)–C(51)	114.1(5)
Si(5)–C(3)–Si(6)	113.3(1)	C(3)–Si(5)–C(52)	110.8(5)
C(1)–Si(1)–C(11)	113.2(6)	C(3)–Si(5)–C(53)	109.5(5)
C(1)–Si(1)–C(12)	110.9(5)	C(51)–Si(5)–C(52)	107.8(7)
C(1)–Si(1)–C(13)	110.3(5)	C(51)–Si(5)–C(53)	108.9(6)
C(11)–Si(1)–C(12)	104.9(7)	C(52)–Si(5)–C(53)	105.2(6)
C(11)–Si(1)–C(13)	111.3(6)	C(3)–Si(6)–C(61)	108.6(6)
C(12)–Si(1)–C(13)	105.9(7)	C(3)–Si(6)–C(62)	113.6(5)
C(1)–Si(2)–C(21)	109.0(5)	C(3)–Si(6)–C(63)	115.8(6)
C(1)–Si(2)–C(22)	113.6(5)	C(61)–Si(6)–C(62)	108.4(6)
C(1)–Si(2)–C(23)	108.6(7)	C(61)–Si(6)–C(63)	105.1(7)
C(21)–Si(2)–C(22)	110.8(6)	C(62)–Si(6)–C(63)	104.8(7)
C(21)–Si(2)–C(23)	105.3(7)		

* Closest intermolecular contact 3.74 Å. No intermolecular Sn–Cl contact <4.0 Å.

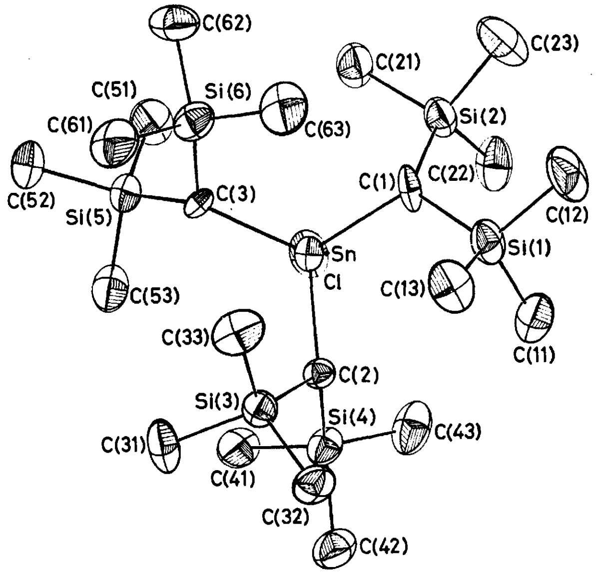
Discussion of structure. Despite considerable interest in the structural chemistry of organotin halides,[7,23] the available diffraction data are quite limited. Table 5 provides a comparison between some of the salient structural parameters obtained here for $SnCl[CH(SiMe_3)_2]_3$ (see also Table 4 and the Figure) and previously for other tri(σ-hydrocarbyl)tin chlorides and for $SnXMe_3$ (X = Br or I). Electron-diffraction analysis of $SnXMe_3$ (X = Cl, Br, or I) showed that in the gas phase the compounds are discrete monomeric distorted tetrahedra.[24] *X*-Ray studies are available only for $SnFMe_3$ among aliphatic compounds and show[25] a covalent polymeric structure in which F atoms alternate with $SnMe_3$ groups, the tin being approximately trigonal bipyramidal. Tin-119 Mössbauer and n.q.r. studies on trimethyltin halides show that in the solid state the compounds are associated (F ≫ Cl > Br > I), and from vibrational spectroscopy are found to be depolymerised (I > Br > Cl ≫ F) on melting or in solvent.[7]

TABLE 5

Comparative structural data for some organotin(IV) halides $SnXR_3$

	Bond/Å		Angle/°	
Compound	*l*(Sn–X)	*l*(Sn–C) (av.)	C–Sn–X (av.)	C–Sn–C (av.)
$SnCl[CH(SiMe_3)_2]_3$ [a]	2.38	2.18	103.9	114.4
$SnClPh_3$ [b]	2.32	2.12	106.4	112.3
$SnClMe_3$ [c]	2.37	2.17	108	*d*
$SnBrMe_3$ [c]	2.49	2.17	109.5	*d*
$SnIMe_3$ [c]	2.72	2.17	109.5	*d*

[a] From the present *X*-ray data (Table 4). [b] From *X*-ray data of ref. 26. [c] From electron-diffraction data of ref. 24. [d] Assumed[24] to be tetrahedral.



Perspective view of the molecular structure of $SnCl[CH(SiMe_3)_2]_3$ showing the atomic numbering and thermal ellipsoids

It is now found (Table 4) that in the *crystal* $SnCl[CH(SiMe_3)_2]_3$ has a molecular geometry similar to that of the *gaseous* trimethyltin halides (Cl, Br, or I). Essentially, the arrangement about the tin atom is tetrahedral with distortions towards planarity of the SnC_3 fragment. However, there is no concomitant lengthening of the Sn–Cl bond length compared with previously observed organotin(IV) chlorides (2.32—2.40 Å).[23] This tallies with the complete lack of close-range intermolecular Sn · · · Cl interactions (no contacts <4.0 Å). We there-

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1976, Index issue.

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[24] H. A. Skinner and L. E. Sutton, *Trans. Faraday Soc.*, 1944, **40**, 164.

[25] H. C. Clark, R. J. O'Brien, and J. Trotter, *J. Chem. Soc.*, 1964, 2332; K. Yasuda, Y. Kawasaki, N. Kasai, and T. Tanaka, *Bull. Chem. Soc. Japan*, 1965, **38**, 1216.

fore conclude that in the solid state $SnCl[CH(SiMe_3)_2]_3$ is a monomeric covalent molecule. The reluctance to associate as, for example, in $SnClMe_3$ is attributable to steric factors. Consistent with this proposal, and with the absence of specific electronic effects, is the close similarity (Table 5) of the structural parameters for $SnCl[CH(SiMe_3)_2]_3$ and $SnClPh_3$.[26]

Finally a comment on the Mössbauer data for compounds of type (2) is justified. The isomer-shift values (1.24—1.48 mm s^{-1} relative to SnO_2 at 20 °C) are generally similar to those of other trialkyltin halides but the Δ values are somewhat lower (2.05—2.24 mm s^{-1}; *cf.* $SnIBu^n_3$, 2.96 mm s^{-1}).[5] We suggest that the Δ value for $SnCl[CH(SiMe_3)_2]_3$ provides a lower limit standard for a monomeric, covalent, pseudo-tetrahedral tin environment. Such a standard is essential when assessing the importance of intermolecular association in trialkyltin compounds.[27] It is of interest that Δ values (mm s^{-1}) for the series $SnX(CH_2CMe_2Ph)_3$ (X = Cl, 2.65; Br, 2.64; I, 2.40) are only slightly higher confirming the postulate that these compounds are essentially unassociated because of the presence of the bulky alkyl group CH_2CMe_2Ph.[27]

EXPERIMENTAL

All the synthetic experiments were carried out under rigorously anaerobic conditions, as described in Part 2.[2] Spectroscopic instrumentation was as previously.[2,28] Bis[bis(trimethylsilyl)methyl]tin was prepared as in Part 1.[28]

Preparations.—Organotin(IV) *Halides* $SnX[CH(SiMe_3)_2]_2R$, (2). Typically, the reactants bis[bis(trimethylsilyl)methyl]tin and the organic halide RX (stoicheiometrically 1 : 1, scale *ca.* 0.3 mmol) were mixed in n-hexane or benzene (*ca.* 5 cm^3) and stirred at ambient temperature until the red colour due to the tin reagent had been discharged. Volatile material was removed at *ca.* 20 °C (10^{-3} mmHg).* Further purification of the organotin(IV) halide (2) was by sublimation [70—100 °C (10^{-3} mmHg) on to a −78 °C probe] or distillation [120—130 °C (10^{-3} mmHg)], as appropriate. Further details are in Tables 1 and 2.

Bis(*organostannyl*)*methane Derivatives* $CH_2\{SnX'[CH(SiMe_3)_2]_2\}_2$ (3; X′ = Br *or* I). The methylene dihalide ($CH_2X'_2$, X′ = Br or I) in benzene (*ca.* 10 cm^3) was slowly added dropwise to $Sn[CH(SiMe_3)_2]_2$ (stoicheiometrically 1 : 2, scale *ca.* 0.3 mmol) with stirring at ambient temperature until the red colour was discharged. Volatiles were removed at *ca.* 20 °C (10^{-3} mmHg) and the residual *bis*(*organostannyl*)*methylene*, (3), was purified by recrystallisation (n-C_6H_{14}) at −30 °C.

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[6/2231 *Received, 6th December,* 1976]

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* Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa.

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[27] R. H. Platt, *J. Organometallic Chem.*, 1970, **24**, C23.

[28] Part 1, P. J. Davidson, D. H. Harris, and M. F. Lappert, *J.C.S. Dalton*, 1976, 2268.