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Subvalent group 14 metal compounds

XI *. Oxidative addition reactions of organic halides or acid anhydrides (including $CH_{4-n}Cl_n$, PhBr, $BrN(SiMe_3)_2$, Bu^tCOCl, or $(CF_3CO)_2O$) to some bivalent group 14 metal amides or alkyls

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Abstract

Oxidative reactions are reported of alkyl or phenyl halides, the chloromethanes $CH_{4-n}Cl_n$ ($n = 2$, 3, or 4), or *N*-bromohexamethyldisilazane with (i) some bulky germanium(II), tin(II), or lead(II) amides, or (ii) bis[bis(trimethylsilyl)methyl]tin(II). Similar reactions with pivaloyl or benzoyl chloride, or trifluoroacetic anhydride, produced stable, yellow α-keto-germanes and -stannanes. The following new compounds have been isolated and characterised: $Sn(NR_2)_2(R')X$, ($R = SiMe_3$; $R'X =$ Bu^nCl, MeBr, EtBr, Pr^nBr, Bu^tBr, PhBr, MeI, EtI, Pr^iI, Bu^nI, PhI, CCl_4, $CHCl_3$, or CH_2Cl_2), $MBr(NR_2)_3$ ($M = Ge$, Sn, or Pb; $R = SiMe_3$), $SnBr(NR_2)(TMPPD)_2$ [$TMPPD = \overline{NCMe_2(CH_2)_3CMe_2}$]. $SnIMe(TMPPD)_2$, $Sn(CHR_2)_3I$, $M'(COR'')$-$Cl(TMPPD)_2$ ($M' = Ge$ or Sn, $R'' = Ph$ or Bu^t), $Sn(CHR_2)_2(COR'')Cl$, $M'(COCF_3)(NR_2)_2(OCOCF_3)$, $M'(COCF_3)(OCOCF_3)(TMPPD)_2$, and $M'(COCF_3)(NBu^t_2)_2(OCOCF_3)$. The α-keto-germanes and -stannanes are particularly noteworthy. The acyl chloride 1/1 adducts (which are sparingly soluble in hydrocarbons) show two carbonyl stretching modes in the region 1635–1690 cm^{-1} which is attributed to the presence of two isomers as a consequence of restricted rotation about the $M'\ddagger C(=O)R''$ bond. This effect is not observed in the bis(amido)metal 1/1 adducts with $(CF_3CO)_2O$ probably because the $^-OC(O)CF_3$ ligand, being sterically much more demanding than Cl^-, directs the formation of a single rotamer. The mass spectral fragmentation pattern of $GeBr[N(SiMe_3)_2]_3$ is reported. The halogenohydrocarbon addition reactions to the amides $M'(NR_2)_2$

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* For Part X, see ref. 5. No reprints available.

** Dedicated to Professor Luigi Sacconi in recognition of his important contributions to organometallic chemistry.

($R = SiMe_3$) are believed to involve a free radical pathway, with $^{\cdot}M'(NR_2)_2X$ as an intermediate. The reaction of $Sn(NR_2)_2$ with excess of PhBr is pseudo first-order, and is catalysed by a trace of EtBr. The uncatalysed reaction yields exclusively $SnBr(NR_2)_2Ph$ in C_6H_6, whereas in THF $SnBr_2(NR_2)_2$ is a significant by-product. Crystalline $SnBr[N(SiMe_3)_2]_3$ is a monomer, with Sn–Br 2.579(2) Å, Sn–N 2.056(7) Å, Br–Sn–N 102.4(2)°, and N–Sn–N′ 115.5(1)°; the nitrogen environment is trigonal planar.

Introduction

For some time we have been interested in the heavy main group 4 (Group 14: Ölander numbering) element (M) analogues of carbenes (MX_2), radicals ($^{\cdot}MX_3$), and alkenes ($X_2M{=}MX_2$); for a brief review, see ref. 1. The present paper is a contribution to the first of these topics, focusing on oxidative additions of halogeno-hydrocarbons (or acyl chlorides or anhydrides) to metal(II) amides or to a lesser extent to the alkyltin(II) $Sn(CHR_2)_2$ ($R = SiMe_3$).

The synthesis and physical properties of the monomeric coloured compounds $M(NR_2)_2$ (M = Ge, Sn, or Pb; $R = SiMe_3$), $M(NBu^tR)_2$, and $M'(NR'_2)_2$ (M' = Ge or Sn; $R' = SiEt_3$, $GeMe_3$, or $GePh_3$) was described in Part V [2]. Their photolyses to yield the persistent radicals $^{\cdot}M'(NR_2)_3$ [3], $^{\cdot}M'(NBu^tR)_3$ [2], and $^{\cdot}M'(NR'_2)_3$ [2] has also been reported. Part VII dealt with the role of $M(NR_2)_2$ in transition metal chemistry [4]; among the reaction types identified were those in which $M(NR_2)_2$ behaved as a terminally bound ligand, as in $[Cr(CO)_5\{M'(NR_2)_2\}]$, or as a coordinatively unsaturated fragment inserting into a transition metal–halogen bond, as in $[Fe(\eta\text{-}C_5H_5)(CO)_2\{Sn(NR_2)_2Cl\}]$. Part X reported the syntheses and structures of some bis(metallo)plumbylenes, such as $Pb[Mo(\eta\text{-}C_5Me_5)(CO)_3]_2$ [5]; that paper inter alia illustrated reactions of $Pb(NR_2)_2$ with protonic compounds HA (e.g., $A = Mo(\eta\text{-}C_5Me_5)(CO)_3$). A number of communications have dealt with other reactions of $M'(NR_2)_2$ and transition metal substrates [6]. The amides $M'(NR_2)_2$ have been shown to form 1/1 adducts with diazoalkanes [7]. The ^{119}Sn Mössbauer [8] and ^{119}Sn NMR [9] spectra of $Sn(NR_2)_2$ have been reported.

We have published a number of preliminary communications which have a bearing on the chemistry of group 14 metal(II) amides. These concerned: (i) oxidative addition of an alkyl or aryl halide (Bu^tCl, MeBr, MeI, or PhI) to $Sn(NR_2)_2$ [10], including (ii) the effect of changing the solvent in the $Sn(NR_2)_2$/PhBr system from C_6H_6 to THF and catalysis of the reaction by EtBr [11]; (iii) the similar reaction of $BrNR_2$ with $M(NR_2)_2$ to give $MBr(NR_2)_3$ [12]; (iv) synthesis of the monomeric orange (Ge) or red (Sn or Pb) bis(2,2,6,6-tetramethylpiperidinato)metal(II) complexes $M'(TMPPD)_2$ (M' = Ge or Sn) [13], the orange (Ge) or maroon (Sn) bis(di-t-butylamido) analogues [14b], and the orange $Sn(NHC_6H_2Bu^t_3\text{-}2,4,6)_2$ [14a]; and (v) the structures of the V-shaped molecules $M(NR_2)_2$, both in the gas phase (electron diffraction) (M = Ge [15], Sn [13], or Pb [15]) and in the crystal (M = Sn or Pb [15]), and of the crystalline $Ge(TMPPD)_2$ [14b].

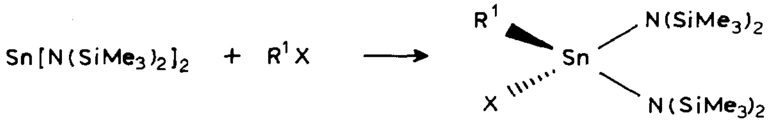
The present paper provides details relating to items (i), (ii), and (iii), as well as extensions into related oxidative additions of other organic halides to a wider range of group 14 metal(II) amides. A new departure, which promises to have some wider utility, concerns the similar reactions of acyl chlorides or anhydrides; these give rise to the somewhat elusive class of compound, the acylmetal(IV) complexes. Four new related reactions of the alkyltin(II) $Sn(CHR_2)_2$ are included: the formation of 1/1 adducts with R_2CHI, Bu^tCOCl, PhCOCl, and $(CF_3CO)_2O$; oxidative additions with other molecules R^1X were described in Part VI [16].

Alternative routes to acyl derivatives of Group 14 metals are difficult [17], partly because acyl analogues of Grignard or lithium reagents are not available. By regarding the bulky alkyl or amido ligands as protecting groups which prevent subsequent rearrangement of the new α-keto adducts $\rangle M'\{C(=O)R''\}X$ (R'',X = Bu^t,Cl; Ph,Cl; or CF_3,$OCOCF_3$), a convenient route to stable acyl-germanes or -stannanes becomes feasible.

Results and discussion

1. Reactions of halogenohydrocarbons or an N-bromoamine

Alkyl bromides or iodides reacted readily with $Sn(NR_2)_2$ ($R = SiMe_3$) to give oxidative addition products in 70–80% yield, as summarised in eq. 1 and Table 1. Although the corresponding reaction with n-butyl chloride occurred, the rate was much lower than with bromides or iodides. Completion times averaged 15 min for alkyl iodides and about 3 h for alkyl bromides. Thus, the qualitative reactivity order was: $R^1I > R^1Br \gg R^1Cl$ (where R^1 = alkyl). From Table 1 it will be noted that bromo- or iodo-benzene also added oxidatively to $Sn(NR_2)_2$, but PhCl did not react even after prolonged refluxing of a mixture of the reactants.



(1)

(R^1X = Bu^nCl ; MeBr , EtBr , Pr^nBr, Bu^tBr or PhBr ;
MeI , EtI , Pr^iI , Bu^nI or PhI ; CCl_4 , $CHCl_3$ or CH_2Cl_2)

Table 1

Oxidative addition products of $Sn[N(SiMe_3)_2]_2$ with alkyl or phenyl halides

$Sn[N(SiMe_3)_2]_2(R)(X)$ [a]		M.p. (°C)	$\delta(^1H)$ [b] (ppm)	$\nu(Sn-C)$ [c] (cm^{-1})	$\nu(SnN_2)$ [c] (cm^{-1})
R	X				
Bu^n	Cl	[a]	0.49	560(w)	406(s), 369(s), 340(s) [d]
Me	Br	36– 37	0.47	540(s)	415(s), 372(s)
Et	Br	48– 54	0.40	510(s)	413(s), 371(s)
Pr^n	Br	78– 84	0.46	590(m)	411(s), 371(s)
Bu^t	Br	160–180	0.47	510(w)	411(s), 374(s)
Ph	Br	42– 44	0.52	465(w)	412(s), 372(s)
Me	I	78– 84	0.46	535(s)	411(s), 371(s)
Et	I	94–104	0.55	506(s)	410(s), 371(s)
Pr^i	I	160–170	0.50	499(s)	411(s), 371(s)
Bu^n	I	126–128	0.55	500(s)	410(s), 371(s)
Ph	I	88– 92	0.60	459(s)	411(s), 371(s)

[a] All are white crystalline solids, except $Sn(Bu^n)(Cl)[N(SiMe_3)_2]_2$ which is waxy. [b] Of the $SiMe_3$ groups; for samples in C_6H_6 solution at 305 K at 60 MHz. [c] For samples as Nujol mulls. [d] $\nu(Sn-Cl)$.

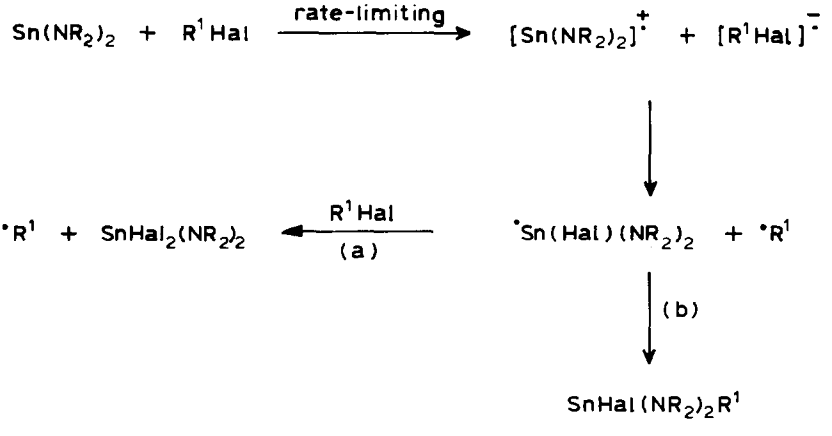
The reaction between $Sn(NR_2)_2$ and PhBr at 32° C (eight-fold excess (3.2 mol dm^{-3}) in C_6H_6: or with PhBr as solvent and reagent (10.47 mol dm^{-3})) was followed by ^1H NMR spectroscopy. A plot of $\log(a/(a-x))$ versus time was linear in each case, and led to rate constants $k = 6.87 \times 10^{-5}$ s^{-1} and 7×10^{-5} s^{-1}, respectively. In presence of 12 μmol dm^{-3} EtBr, each rate constant was approximately doubled. The corresponding reaction of $Sn(CHR_2)_2$ and a halogenohydrocarbon was appreciably faster, consistent with $Sn(CHR_2)_2$ being more electron-rich than $Sn(NR_2)_2$, as judged by their first ionisation potentials [18]. For example, $k = 9 \times 10^{-4}$ s^{-1} for the PhBr oxidative addition [11].

Solvent participation is illustrated by eq. 2.

$$\mathrm{Sn(NR_2)_2 + PhBr} \begin{cases} \xrightarrow{\text{in } C_6H_6} \mathrm{SnBr(NR_2)_2Ph} \\ \qquad\qquad \text{(only)} \\ \xrightarrow{\text{in THF}} \mathrm{SnBr(NR_2)_2Ph} + \mathrm{SnBr_2(NR_2)_2} \\ \qquad\qquad \text{(9 parts)} \qquad\qquad \text{(1 part)} \end{cases} \tag{2}$$

The above data, together with previously reported EPR results [10], are accommodated by a free radical reaction pathway, involving the sequences of Scheme 1. The initial step of electron-transfer is in accord with $Sn(NR_2)_2$ having a low first ionisation potential [18]. When THF is the solvent, reaction (a) (Scheme 1) becomes more important relative to (b), because THF readily reacts with Alk$^\cdot$ to yield AlkH. The catalysis by EtBr of the PhBr addition is attributed to initial $^\cdot SnBr(NR_2)_2$ formation (from $Sn(NR_2)_2 + EtBr$), abstraction by the latter of Br$^\cdot$ from PhBr to afford Ph$^\cdot$, which together with $^\cdot Sn(NR_2)_2Ph$, acts as the propagating species in a radical chain reaction.

Treating $Sn(NR_2)_2$ with a chlorinated methane $CH_{4-n}Cl_n$ ($n = 2$, 3, or 4) at ambient temperature readily and exothermically gave the appropriate crystalline 1/1 adduct $Sn(CH_{4-n}Cl_{n-1})Cl(NR_2)_2$. Qualitatively the reactivity order was $CCl_4 > CHCl_3 > CH_2Cl_2$. Details on these adducts are in Tables 2 and 3; they were found to be moderately stable in air, hydrolysing slowly to release HNR_2. Their electron-impact mass spectra showed parent molecular ions.



Scheme 1. Proposed mechanistic pathway for oxidative addition of R^1Hal to $Sn(NR_2)_2$.

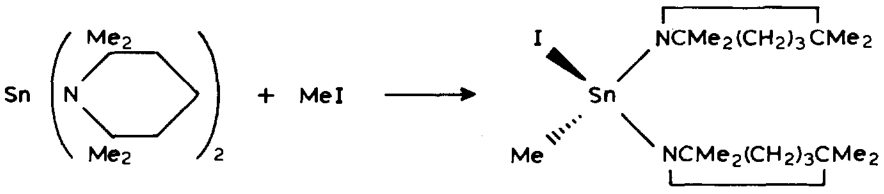
Table 2

Oxidative addition products of $Sn[N(SiMe_3)_2]_2$ with $CH_{4-n}Cl_n$: yields and characterisation

Complex	Colour	Yield (%) [a]	Analysis (Found (calcd.)(%))			M.p. (°C) [b]
			C	H	N	
$Sn(CH_2Cl)Cl(NR_2)_2$	white	90	29.3	7.1	4.9	44– 48
			(29.8)	(7.3)	(5.2)	
$Sn(CHCl_2)Cl(NR_2)_2$	white	95	27.3	6.6	4.9	120–125
			(27.9)	(6.7)	(5.0)	
$Sn(CCl_3)Cl(NR_2)_2$	white	96	26.0	6.1	4.1	105–107
			(26.3)	(6.1)	(4.7)	

[a] These are not optimised. [b] Under one atmosphere of argon in sealed capillaries and m.p.s are uncorrected.

Similarly, methyl iodide readily furnished a 1/1 adduct (Table 4) with $Sn(TMPPD)_2$ (eq. 3).



(3)

Oxidative addition of $BrN(SiMe_3)_2$ to $M(NR_2)_2$ in n-hexane at 25°C gave $MBr[N(SiMe_3)_2]_3$ (eq. 4 and Table 4); bis(2,2,6,6-tetramethylpiperidinato)tin(II) [$Sn(TMPPD)_2$] and $BrNR_2$ likewise yielded $SnBr(NR_2)(TMPPD)_2$ (eq. 5 and Table 4). The germanium and tin adducts had a high melting point and were surprisingly stable to air or moisture. They are the first well-characterised examples of a tetravalent Group 14 metal compound containing three sterically-demanding amido ligands attached to the central metal. A part of the mass spectral fragmentation pattern of $GeBr(NR_2)_3$ is shown in Scheme 2. The molecular ion was not detected, nor was $\{Ge[N(SiMe_3)_2]_3\}^+$, but $[N(SiMe_3)_3]^+$ was observed at *m/e* 233.

Table 3

^1H, ^{13}C, and ^{119}Sn NMR chemical shifts (ppm) of the complexes $Sn(CH_xCl_{3-x})Cl(NR_2)_2$ [a] ($x = 0$, 1, or 2; $R = SiMe_3$)

Complex	^1H [b]	^{13}C [c]	^{119}Sn [d]
$Sn(CH_2Cl)Cl(NR_2)_2$	0.45($SiMe_3$)	5.7($SiMe_3$)	−82
	3.38(CH_2Cl)	53.6(CH_2Cl)	
$Sn(CHCl_2)Cl(NR_2)_2$	0.50($SiMe_3$)	5.9($SiMe_3$)	−126
	4.02($CHCl_2$)	70.5($CHCl_2$)	
$Sn(CCl_3)Cl(NR_2)_2$	0.51($SiMe_3$)	6.4($SiMe_3$)	−188
		96.5(CCl_3)	

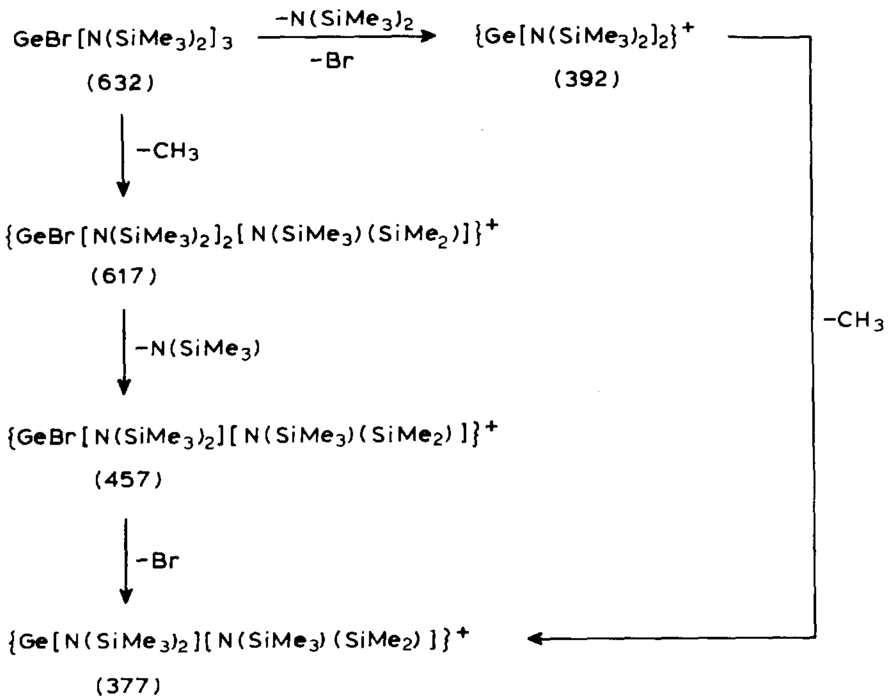
[a] Recorded in C_6D_6 at 305 K. [b] Recorded on a Varian T60 continuous wave NMR spectrometer. [c] Recorded at 25 MHz on a Bruker 80 MHz FT NMR spectrometer. [d] Recorded at 30 MHz on a Bruker 80 MHz FT NMR spectrometer; referenced to external $SnMe_4$.

Table 4

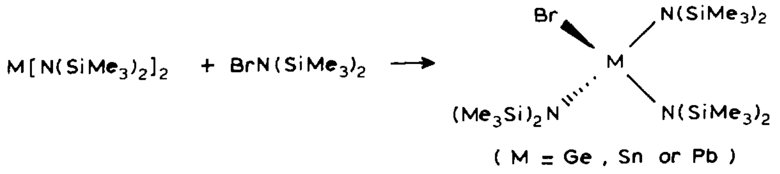
Oxidative addition products and some of their physical properties

Compound	Colour	Yield [a] (%)	M.p. (B.p./Torr) (θ_c/°C)	$\nu(MN_2)$ [b] [$\nu(SnC_2)$] (cm^{-1})	$\nu(CO)$ [b,c] (cm^{-1})	$\delta(^1H)$ (ppm)	$\delta(^{19}F)$ [d] (ppm)
$GeBr[N(SiMe_3)_2]_3$	white	20	208–210	380 m, 410 w		0.65	
$SnBr[N(SiMe_3)_2]_3$	white	100	228–229	365 s, 401 s		0.58	
$PbBr[N(SiMe_3)_2]_3$	orange	40	(120/0.5)	–		0.33	
$SnBr[N(SiMe_3)_2](TMPPD)_2$	yellow	87	134–135	365 m, 380 m		0.80 [e], 0.70 [f], 0.45 [g], 0.25 [g]	
$SnI(Me)(TMPPD)_2$	yellow	85	(110/0.1)	380 w, 415 w			
$Sn[CH(SiMe_3)_2]_3I$	white	72	195	–		–	
$Ge(COPh)Cl(TMPPD)_2$	yellow	38	impure	–	1640 s, 1690 w,sh	–	
$Sn(COPh)Cl(TMPPD)_2$	yellow	63	115–118	–	1635 m, 1655 w,sh	–	
$Ge(COBu^t)Cl(TMPPD)_2$	orange	20	impure	–	1640 m, 1670 m	–	
$Sn(COBu^t)Cl(TMPPD)_2$	yellow	20	122–123	–	1655 m, 1675 m	–	
$Sn(COPh)Cl(NBu^t_2)_2$	yellow	[h]		–	1640 m,br, 1660 sh	–	
$Sn[CH(SiMe_3)_2]_2(COPh)Cl$	yellow	90	64–66	[495 m]	1620 m, 1635 sh	–	
$Sn[CH(SiMe_3)_2]_2(COBu^t)Cl$	yellow	70	42	[480 m, 495 m]	1652 s, 1688 m	–	
$Ge(COCF_3)[N(SiMe_3)_2]_2(OCOCF_3)$	white	67	142–144	–	1765 m, 1710 m	–	−74.0, −75.8
$Sn(COCF_3)[N(SiMe_3)_2]_2(OCOCF_3)$	yellow	43	81–83	–	1770 m, 1700 m, br	[i]	−75.2 [i], −75.4 [i]
$Ge(COCF_3)(OCOCF_3)(TMPPD)_2$	yellow	67	82–84	–	1760 m, 1700 m	–	−72.3, −77.0
$Sn(COCF_3)(OCOCF_3)(TMPPD)_2$	yellow	87	55–57	–	1735 m, 1680 m	–	−74.5, −76.5
$Ge(COCF_3)(NBu^t_2)_2(OCOCF_3)$	yellow	30	121–122	–	1760 m, 1708 m	–	−70.5, −76.8
$Sn(COCF_3)(NBu^t_2)_2(OCOCF_3)$	yellow	[h]	[h]	–	1750 m, 1680 m	–	−73.0, −76.0

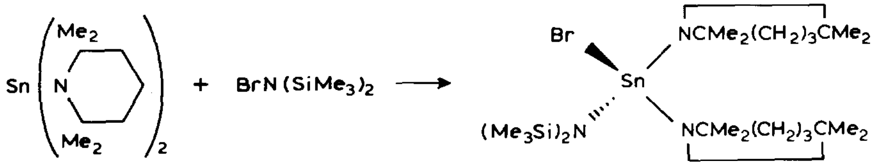
[a] After purification; not optimised. [b] For compounds as Nujol mulls or neat liquids. [c] $\nu(CO)$ for $PhCOCl$; 1735 s, 1775 m; for Bu^tCOCl; 1780 s, 1830 m; for $(CF_3CO)_2O$: 1785 m, [d] Relative to $CFCl_3$. [e] Of $SiMe_3$. [f] Of CH_3's in TMPPD. [g] Of CH_2's in TMPPD. [h] Not isolated. [i] See Table 5.



Scheme 2. Mass spectral fragmentation pattern of $GeBr(NR_2)_3$. (Numbers are m/e values of the most intense peak in each band of isotopic ions.)

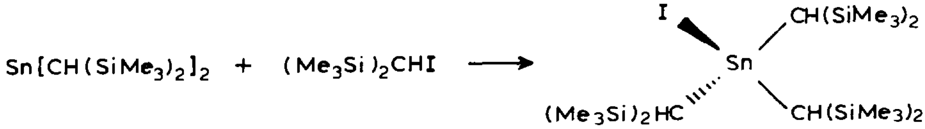


(4)



(5)

It is likely that the alkyl isoelectronic with $SnBr[N(SiMe_3)_2]_3$, namely $SnBr[CH(SiMe_3)_2]_3$, will be accessible. Thus, it has already been shown that the corresponding chloride $SnCl(CHR_2)_3$ (which has been X-ray characterised) is formed from $Sn(CHR_2)_2$ and RCl [16], and we now demonstrate that the iodide is formed in analogous fashion (eq. 6).



(6)

2. *Reactions of carboxylic acid chlorides or anhydrides*

Compounds of main group metals having an α-keto function are rare. Corresponding transition metal acyls are often accessible by a CO insertion into the appropriate alkylmetal; however, this requires that an alkylmetal carbonyl be formed as an intermediate. Main group elements (except one or two boron hydride derivatives) do not form carbonyls; hence this route is not viable. Neither are acyl analogues of Grignard reagents available as alternative precursors for acylmetal complexes. However, transition metal acyls have also been obtained by oxidative addition of a carboxylic acid chloride or anhydride to a low oxidation state transition metal substrate. For example $(CF_3CO)_2O$ and *trans*-$[Ir(CO)Cl(PPh_3)_2]$ gave $[Ir(CO)(COCF_3)Cl(OCOCF_3)(PPh_3)_2]$ [19], and reactions of various platinum(0) (d^{10}), rhodium(I) (d^8), or iridium(I) (d^8) complexes with acid chlorides are well documented [20].

We now show that formally s^2 germanium(II) or tin(II) substrates undergo similar oxidative additions (eqs. 7–11). The characterisation of the acylgermanium(IV) or -tin(IV) adducts is summarised in Table 4, with fuller NMR details on $Sn(COCF_3)(NR_2)_2(OCOCF_3)$ in Table 5.

The mechanism of the reaction probably involves initial metal-centred nucleophilic attack at the carbonyl carbon atom, followed by an intramolecular rearrangement of the tetrahedral intermediate, as shown in Scheme 3 ($X = Cl$ or $OCOCF_3$).

Further rearrangement of the acylmetal(IV) adduct, via a metaloxycarbene $M(NR_2)_2(O\ddot{C}RR)X$, as often occurs with an α-keto-silane or -germane [17], was not observed, presumably because of the bulky groups attached to the metal.

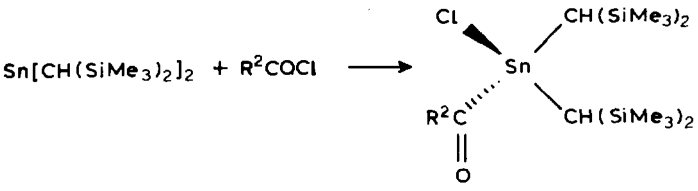
Two carbonyl stretching modes were observed in the IR spectra of the acyl(chloro)-germanes and -stannanes. This is attributed to the presence of two

Table 5

^{1}H, ^{19}F, ^{13}C and ^{119}Sn NMR chemical shifts (ppm) and coupling constants (Hz) for the complex $Sn(COCF_3)(NR_2)_2(OCOCF_3)$ ($R = SiMe_3$)

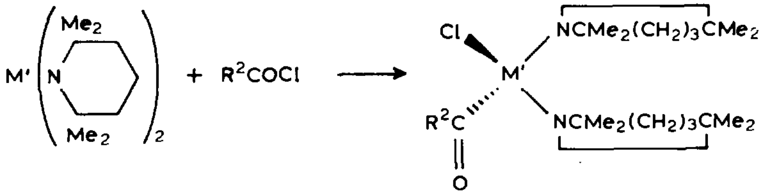
Nucleus	δ (ppm) [a]	J (Hz)	Assignment
^{1}H [b]	0.15(s)		$SiMe_3$
^{19}F [c]	−75.2(s)	3.7	$OCOCF_3$ [d]
	−75.4(s)	50.8	$COCF_3$ [d]
^{13}C [e]	217.7(q)	41.2	$O\mathit{C}OCF_3$
	160.2(q)	41.5	$\mathit{C}OCF_3$ [f]
	116.2(q)	296.7	$OCO\mathit{C}F_3$
	116.0(q)	287.4	$CO\mathit{C}F_3$
^{119}Sn [g]	−278(q)	50.0 [h]	

[a] All spectra were recorded at 305 K. ^{1}H and ^{19}F NMR were recorded in toluene-d_8, ^{13}C and ^{119}Sn NMR in 10% toluene-d_8/toluene. Positive chemical shifts are in all cases to high frequency (s, singlet; q, quartet). [b] Recorded at 80 MHz on a Bruker WP80 FT NMR spectrometer. [c] Recorded at 75 MHz on a Bruker WP80 FT NMR spectrometer; referenced to external $CFCl_3$. [d] Assignment based on the magnitude of $J(^{19}F, ^{119}Sn)$, obtained from the ^{119}Sn satellites. [e] Recorded at 90 MHz on a Bruker WM360 FT NMR spectrometer. [f] Assignment based on the shielding effect of tin relative to oxygen, shifting the $\mathit{C}OCF_3$ carbonyl carbon resonance to lower frequency (upfield). [g] Recorded at 30 MHz on a Bruker WP80 FT NMR spectrometer; referenced to external $SnMe_4$. [h] Only $^3J(^{119}Sn, ^{19}F)$ observed; $^4J(^{119}Sn, ^{19}F)$ of $OCOCF_3$ obliterated by the natural line width of the signal.



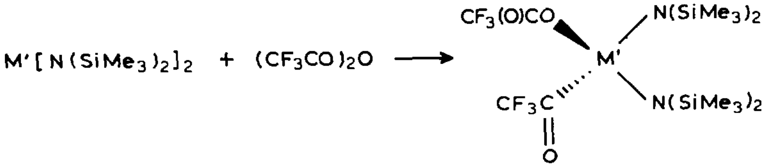
(7)

(R = Ph or Bu^t)



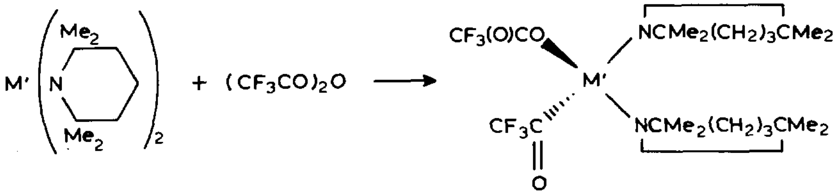
(8)

(M' = Ge or Sn ; R^2 = Ph or Bu^t)



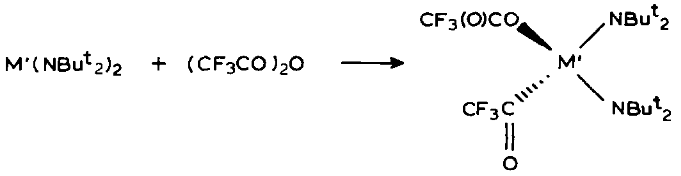
(9)

(M' = Ge or Sn)



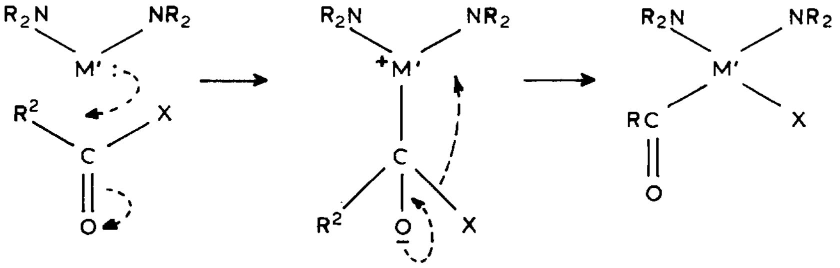
(10)

(M' = Ge or Sn)



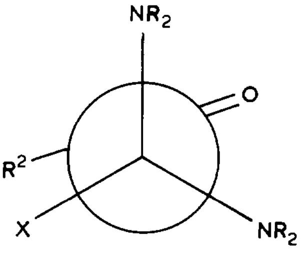
(11)

(M' = Ge or Sn)

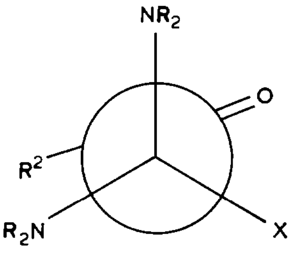


Scheme 3. Proposed mechanistic pathway for oxidative addition of $R^2C(O)X$ to $M'(NR_2)_2$.

conformers, due to restricted rotation about the $M\ddagger C(=O)R$ bond, as shown in the Newman projections (Ia) and (Ib) for the amides:



(Ia)



(Ib)

In the case of the corresponding adducts from $(CF_3CO)_2O$, only a single $\nu(CO)$ band attributable to the acyl $CF_3C(=O)^-$ ligand was found (a second carbonyl stretching mode is due to the trifluoroacetato ligand). This difference is ascribed to the existence of a preferred single rotamer, corresponding to Ia, because $^-OC(O)CF_3$ has much greater steric requirements than Cl^-. α-Prochiral, such as $CHCl_2COCl$, or α-chiral acid chlorides show two carbonyl stretching modes in solution or in the liquid phase, attributed to similar conformational effects [21]. In benzoyl chloride the carbonyl doublet has been ascribed to Fermi resonance involving coupling of $\nu(CO)$ with the first overtone of $\nu(C{-}Cl)$ [22]; such coupling cannot be operative in the new acyl-germanium(IV) and -tin(IV) adducts. The assignment of the two ^{19}F signals in $Sn(COCF_3)(NR_2)_2(OCOCF_3)$ is based on the magnitudes of the $^{119}Sn{-}^{19}F$ coupling constants (Table 5). For the remaining acylmetal carboxylates, the two ^{19}F signals are designated by analogy.

Interestingly, the germyl and stannyl ketones reported here are yellow (Table 4), just like the monosilylated ketones [17]. This colour is characteristic of a pronounced bathochromic effect on the $n \rightarrow \pi^*$ transition of the carbonyl group of a silyl or germyl substituent α to the carbonyl group [23].

From a synthetic viewpoint, therefore, it is plausible that the oxidative additions of an acyl chloride or trifluoroacetic anhydride described here may provide a convenient way of forming stable keto-germanes and -stannanes having reactive functional groups. In particular with $M'(NR_2)_2$ as substrate, the $^-NR_2$ ligands in the metal(IV) adducts are, in principle, readily displaceable, and hence may be used as protecting groups.

3. *X-Ray crystal structure of $SnBr[N(SiMe_3)_2]_3$*

The molecular structure and atom numbering scheme for $SnBr[N(SiMe_3)_2]_3$ is shown in Fig. 1, and bond distances and angles are in Table 6; further details are in ref. 37. There are a few earlier examples of four coordinate tris[bis(trimethylsilyl)amido]metal complexes [24]; these include $[Cr(NO)(NR_2)_3]$ [25] and $[La(NR_2)_3(O{=}PPh_3)]$ [26].

The crystal data for $SnBr(NR_2)_3$ are very similar to those for $[Cr(NO)\{N(SiMe_3)_2\}_3]$ with the unit constants a differing by 0.53 Å and α by 2.58° [25]. The difference lies in the coordination about the central metal atom. In the Cr structure, the distortion from a trigonal bipyramid is of the order of 9°. In $SnBr(NR_2)_3$ an even more tetrahedral appearance is seen with a Br–Sn–N angle of 102.4(2)° (Table 6), and a N–Sn–N′ angle of 115.5(1)°. These angles are similar to those found in $Sn[CH(SiMe_3)_2]_3Cl$ [16], where Cl–Sn–C angles averaged 103.9° and C–Sn–C, 114.4°.

$SnBr[N(SiMe_3)_2]_3$ is a monomeric covalent molecule. This can be seen from the Sn–Br bond distance of 2.519(2) Å which compares favourably with the 2.505 Å found in $SnBr_2Et_2$ [27] and the 2.630 Å in $SnBr(CH_2C_6H_4NMe_2-o)Ph_2$ [28].

The average Sn–N bond distance of 2.056(7) Å is similar to that reported in $Sn[N(Bu^t)SiMe_2NBu^t]_2$ (2.033(5) Å) [29] or (gaseous, electron-diffraction) $Sn(NMe_2)_4$ (2.045 Å) [30].

The average N–Si bond distance of 1.758(8) Å is significantly longer than in $[Cr(NO)\{N(SiMe_3)_2\}_3]$ (1.72 Å) [25], $[La\{N(SiMe_3)_3\}(O{=}PPh_3)]$ (1.67 Å) [26], $[Co\{N(SiMe_3)_2\}_2(PPh_3)]$ (1.71 Å), $[Ni\{N(SiMe_3)_2\}(PPh_3)_2]$ (1.71 Å) [31], or

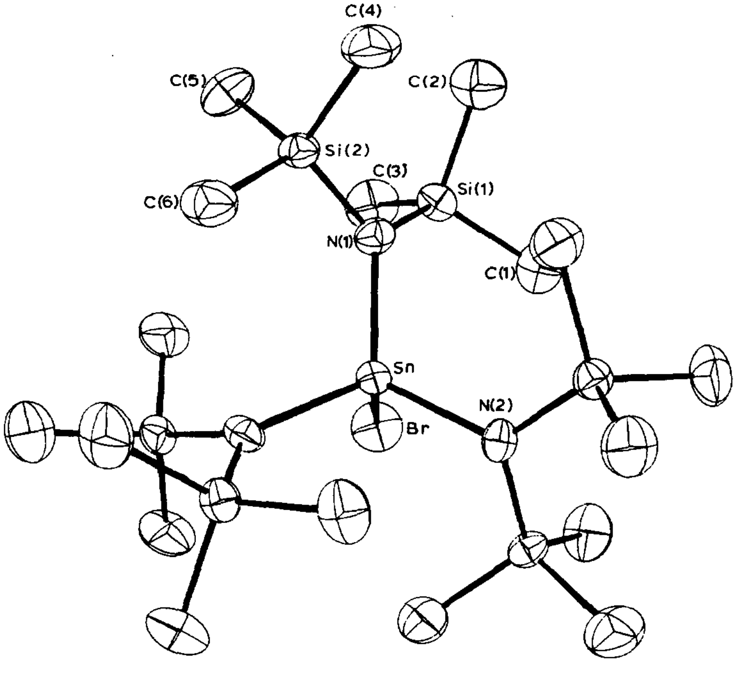


Fig. 1. The molecular structure and atom numbering scheme for $SnBr[N(SiMe_3)_2]_3$.

Table 6

Intramolecular distances and angles, with estimated standard deviations in parentheses for $SnBr[N(SiMe_3)_2]_3$ [37]

(a) Bonds (Å)			
Sn–Br	2.519(2)	Si(1)–C(2)	1.85(1)
Sn–N	2.056(7)	Si(1)–C(3)	1.83(1)
N–Si(1)	1.758(7)	Si(2)–C(4)	1.87(1)
N–Si(2)	1.759(7)	Si(2)–C(5)	1.86(1)
Si(1)–C(1)	1.88(1)	Si(2)–C(6)	1.85(1)
(b) Angles (°)			
Br–Sn–N	102.4(2)	N–Si(2)–C(4)	111.0(4)
N–Sn–N	115.5(1)	N–Si(2)–C(5)	111.8(4)
Sn–N–Si(1)	123.7(4)	N–Si(2)–C(6)	112.9(5)
Sn–N–Si(2)	117.2(4)	C(1)–Si(1)–C(2)	104.3(5)
Si(1)–N–Si(2)	118.6(4)	C(1)–Si(1)–C(3)	106.7(5)
N–Si(1)–C(1)	113.1(4)	C(2)–Si(1)–C(3)	107.4(5)
N–Si(1)–C(2)	113.3(4)	C(4)–Si(2)–C(5)	103.8(5)
N–Si(1)–C(3)	111.5(4)	C(4)–Si(2)–C(6)	106.3(6)
		C(5)–Si(2)–C(6)	110.6(5)

$[Fe\{N(SiMe_3)_2\}_3]$ (1.731 Å) [32]. This may be due to greater $\ddot{\mathrm{N}}\overset{\curvearrowright}{-}\mathrm{Si}$ π-interaction in the tin compound.

Some key structural parameters for tin di[bis(trimethylsilyl)]amides are summarised in Table 7.

Experimental

General procedures

Experiments were carried out under high purity dinitrogen or argon using a high vacuum manifold and Schlenk tube techniques. Solvents were freshly distilled, dried, and degassed. Except for the data in Tables 3 and 5 (see footnotes thereto),

Table 7

Some structural parameters for crystalline bis(trimethylsilyl)amidotin compounds ($R = SiMe_3$)

Compound	*l*(Sn–N) (Å)	*l*(Si–N) (Å)	N–Sn–N (°)	Ref.
$SnBr(NR_2)_3$	2.056(7)	1.758(8)	115.5(1)	37
$Sn(NR_2)_2$	2.096(1)	1.742(6)	104.7(2)	15
$[Pd\{Sn(NR_2)_2\}_3]$	2.08(2)	1.72	107(1)	[b]
$[Pt\{Sn(NR_2)_2\}_3]$	2.1(2)	1.8(2)	104(1)	6a
$[(Pd\{\mu\text{-}Sn(NR_2)_2\}(CO))_3]$	2.03(8)	1.75 [b]	105(1)	6d
$[(Pt\{\mu\text{-}Sn(NR_2)_2\}(CO))_3]$	2.05(2)	1.76 [b]	108(1)	6d
$[Rh(\eta^6\text{-}C_6H_5Ph)(\eta\text{-}C_8H_{14})\text{-}\{SnCl(NR_2)_2\}]$ [a]	2.086(9)	1.74(1) [c]	108.3(2) [c]	6c
trans-$[(Pt(\mu\text{-}Cl)(PEt_3)\text{-}\{Sn(NR_2)_2Cl\})_2]$	2.088(8)	[d]	[d]	6a

[a] C_8H_{14} = cyclooctene. [b] M.C. Misra, D. Phil. thesis, University of Sussex, 1986. [c] S.M. Hawkins, ibid., 1985. [d] Not recorded.

^1H NMR spectra were recorded on a Perkin–Elmer R12 or a Varian T60 spectrometer, both operating at 60 MHz, and the Perkin–Elmer R32 was used to obtain ^{19}F NMR spectra. A Perkin–Elmer 597 instrument was used to record IR spectra of samples either between CsI plates (as Nujol mulls or neat liquids) or in KBr cells (as dilute solutions). Samples were prepared in a dry-box or glove-bag thoroughly purged with dry dinitrogen. Mass spectra were measured on an AEI MS30 spectrometer, using samples in sealed tubes which fitted directly into the probe where they were broken. Melting points were determined with an electrothermal melting point apparatus and are uncorrected. The following starting materials were prepared by literature methods: $BrN(SiMe_3)_2$ [33], $Ge[N(SiMe_3)_2]_2$ [2], $Pb[N(SiMe_3)_2]_2$ [2], $Sn[CH(SiMe_3)_2]_2$ [34], $Ge(TMPPD)_2$ [13,35], $Sn(TMPPD)_2$ [13,35], $Ge(NBu^t_2)_2$ [14b,35], $Sn(NBu^t_2)_2$ [14b,35], and $CH(I)(SiMe_3)_2$ [36].

Colours, yields, melting and boiling points, and IR and NMR data for the new compounds are recorded in Tables 1–5.

Reactions of bis[bis(trimethylsilyl)amido]tin(II) with alkyl or phenyl halides

In a typical experiment, iodomethane (0.2 g, 1.4 mmol) in n-hexane (10 ml) was added dropwise with stirring to an orange solution of $Sn[N(SiMe_3)_2]_2$ (0.62 g, 1.4 mmol) in n-hexane (20 ml). The solution was decolourised within 30 min. After stirring for 2 h, volatile components were pumped off, leaving an oily residue which sublimed (100 °C/10^{-2} Torr) to afford the white solid bis[bis(trimethylsilyl)amido]-(iodo)methyltin(IV) (0.6 g, 70%). Analysis: Found: C, 26.9; H, 6.9; N, 4.8. $C_{13}H_{39}IN_2Si_6Sn$ calcd.: C, 26.8; H, 6.7; N, 4.7%. Its m.p., $\delta(^1H)$ NMR, ν(Sn–C), and $\nu(SnN_2)$ values are recorded in Table 1, together with those of other oxidative addition products obtained by a similar procedure.

Preparation of bis[bis(trimethylsilyl)amido](chloro)chloromethyltin(IV) compounds

Bis[bis{trimethylsilyl}amido]tin(II) (0.80 g, 1.82 mmol) was added to tetrachloromethane (14.20 g, 0.09 mol) with stirring at ambient temperature. An exothermic reaction took place to yield a colourless solution. The excess tetrachloromethane was removed in vacuo to produce a white precipitate of the 1/1 adduct $Sn(CCl_3)Cl(NR_2)_2$ ($R = SiMe_3$). Analysis: Found: C, 26.0; H, 6.1; N, 4.1. $C_{13}H_{36}Cl_4N_2Si_4Sn$, calcd.: C, 26.3; H, 6.1; N, 4.7%.

Bis[bis{trimethylsilyl}amido]tin(II) (0.90 g, 2.05 mmol) and trichloromethane (10.60 g, 0.13 mol) similarly yielded the 1/1 adduct $Sn(CHCl_2)Cl(NR_2)_2$ ($R = SiMe_3$) (1.08 g, 95%). Analysis: Found: C, 27.3; H, 6.6; N, 4.9. $C_{13}H_{37}Cl_3N_2Si_4Sn$ calcd.: C, 27.9; H, 6.7; N, 5.0%.

Likewise, bis[bis{trimethylsilyl}amido]tin(II) (0.95 g, 2.16 mmol) and dichloromethane (17.50 g, 0.20 mol) gave the 1/1 adduct $Sn(CH_2Cl)Cl(NR_2)_2(R = SiMe_3)$ (1.02 g, 90%). Analysis: Found: C, 29.3; H, 7.1; N, 4.9. $C_{13}H_{38}Cl_2N_2Si_4Sn$ calcd.: C, 29.8; H, 7.3; N, 5.2%.

Bromotris[bis(trimethylsilyl)amido]-germanium(IV), -tin(IV), and -lead(IV)

Addition of $BrN(SiMe_3)_2$ (0.97 g, 4.1 mmol) to a solution of $Ge[N(SiMe_3)_2]_2$ (1.59 g, 4.1 mmol) in pentane (10 ml) caused a rapid, exothermic reaction to take place; the orange colours of both reagents were discharged and a white precipitate was formed. Recrystallisation of this precipitate from hot toluene gave white needles of bromotris[bis(trimethylsilyl)amido]germanium(IV). Analysis: Found: C, 34.2, H, 8.46. $C_{18}H_{54}BrN_3GeSi_6$ calcd.: C, 34.2; H, 8.50%. The crystalline tin(IV) analogue (Fig. 1) was prepared similarly.

The reaction of $BrN(SiMe_3)_2$ (1.32 g, 5.5 mmol) with $Pb[N(SiMe_3)_2]_2$ (2.9 g, 5.5 mmol) in pentane (20 ml) yielded a viscous orange oil which was distilled at 120 °C/0.5 Torr to give bromotris[bis(trimethylsilyl)amido]lead(IV). Analysis: Found: C, 27.8; H, 6.45; N, 5.30. $C_{18}H_{54}BrN_3PbSi_6$ calcd.: C, 28.2; H, 7.04; N, 5.47%.

Bis(2,2,6,6-tetramethylpiperidinato)(iodo)methyltin(IV) [SnI(Me)(TMPPD)₂]

The deep red colour of $Sn(TMPPD)_2$ (0.95 g, 2.3 mmol) was discharged upon the addition of iodomethane (10 ml), to afford a pale yellow solution. After removal of solvent, distillation at 110 °C/1 Torr gave the bis(2,2,6,6-tetramethylpiperidinato)-(iodo)methyltin(IV), as a pale yellow oil. Analysis: Found: C, 41.8; H, 6.92; N, 5.33. $C_{19}H_{39}IN_2Sn$ calcd.: C, 42.4; H, 7.20; N, 5.17%.

Bromobis(2,2,6,6-tetramethylpiperidinato)[bis(trimethylsilyl)amido]tin(IV)

Addition of $BrN(SiMe_3)_2$ (0.28 g, 1.2 mmol) to $Sn(TMPPD)_2$ (0.47 g, 1.2 mmol) in pentane (30 ml) resulted in the immediate formation of a pale orange solution. Removal of solvent under reduced pressure afforded yellow solid bromobis(2,2,6,6-tetramethylpiperidinato)[bis(trimethylsilyl)amido]tin(IV). Analysis: Found: C, 44.0; H, 7.90. $C_{24}H_{54}BrN_3Si_2Sn$ calcd.: C, 45.1; H, 8.45%. The compound was extremely soluble in hydrocarbon or ether solvents, and attempts to obtain good quality crystals were unsuccessful.

Tris[bis(trimethylsilyl)methyl]iodotin(IV)

Iodobis(trimethylsilyl)methane (0.48 g, 1.90 mmol) reacted instantly with red $Sn[CH(SiMe_3)_2]_2$ (0.83 g, 1.90 mmol) discharging its colour. From the resulting solution colourless crystals of tris[bis(trimethylsilyl)methyl]iodotin(IV) were obtained. Analysis: Found: C, 34.9; H, 7.68. $C_{21}H_{57}ISi_6Sn$ calcd.: C, 34.9; H, 7.94%.

Reactions of metal(II) amides or alkyls with benzoyl or pivaloyl chloride

In a typical reaction, benzoyl chloride (0.83 g, 5.9 mmol) was added to $Sn(TMPPD)_2$ (2.36 g, 5.9 mmol) in tetrahydrofuran (30 ml). During ca. 16 h at ambient temperature, the initial deep red colour gradually changed to orange. The THF was removed in vacuo and the residual yellow-orange powder was extracted into diethyl ether. Concentration of this solution yielded canary yellow bis(2,2,6,6-tetramethylpiperidinato)(benzoyl)chlorotin(IV). Analysis: Found: C, 54.5; H, 6.82; N, 4.95. $C_{25}H_{41}ClN_2OSn$ calcd.: C, 55.6; H, 7.60; N, 5.20%.

Prepared in a similar way were (i) waxy bis(2,2,6,6-tetramethylpiperidinato)(benzoyl)chlorogermanium(IV), which was only characterised spectroscopically; (ii) yellow crystalline bis(2,2,6,6-tetramethylpiperidinato)(pivaloyl)chlorotin(IV) (Analysis: Found: C, 53.3; H, 8.39. $C_{23}H_{45}ClN_2OSn$ calcd.: C, 53.1; H, 8.66%); (iii) waxy bis(2,2,6,6-tetramethylpiperidinato)(pivaloyl)chlorogermanium(IV), which was characterised spectroscopically; (iv) yellow crystalline bis[bis(trimethylsilyl)methyl](benzoyl)chlorotin(IV) (Analysis: Found: C, 43.0; H, 6.92. $C_{21}H_{43}ClOSi_4Sn$ calcd.: C, 43.6; H, 7.51%); and (v) yellow crystalline bis[bis(trimethylsilyl)methyl](pivaloyl)chlorotin(IV) (Analysis: Found: C, 40.7; H, 8.33. $C_{19}H_{47}ClOSi_4Sn$ calcd.: C, 40.9; H, 8.49%.

Reactions with trifluoroacetic anhydride

In a representative reaction, trifluoroacetic anhydride (0.38 g, 1.8 mmol), as a 25% w/v solution in pentane, was added to Ge(TMPPD)$_2$ (0.64 g, 1.8 mmol) in pentane (10 ml). The solution turned pale yellow almost immediately. Filtration, followed by evaporation to dryness of the filtrate in vacuo, gave the pale yellow solid [bis(2,2,6,6-tetramethylpiperidinato)](trifluoroacetyl)trifluoroacetatogermanium(IV). Analysis: Found: C, 46.1; H, 6.67; N, 4.95. $C_{22}H_{36}F_6GeN_2O_3$ calcd.: C, 46.9; H, 6.40; N, 4.97%. Prepared similarly were the following crystalline analogues: (i) [bis(2,2,6,6-tetramethylpiperidinato)](trifluoroacetyl)trifluoroacetatotin(IV) (Analysis: Found: C, 41.9; H, 6.36; N, 4.40. $C_{22}H_{36}F_6N_2O_3Sn$ calcd.: C, 43.4; H, 5.91; N, 4.60%); (ii) bis[bis(trimethylsilyl)amido](trifluoroacetyl)trifluoroacetatogermanium(IV) (Analysis: Found: C, 30.9; H, 5.45; N, 4.29. $C_{16}H_{36}F_6GeN_2O_3Si_4$ calcd.: C, 31.9, H, 5.98; N, 4.65%); (iii) bis[bis(trimethylsilyl)amido](trifluoroacetyl) trifluoroacetatotin(IV) (Analysis: Found: C, 29.3; H, 5.19. $C_{16}H_{36}F_6N_2O_3Si_4Sn$ calcd.: C, 29.6; H, 5.55%; (iv) bis[(di-t-butyl)amido](trifluoroacetyl)trifluoroacetatogermanium(IV) (Analysis: Found: C, 44.1; H, 7.54; N, 5.07. $C_{20}H_{36}F_6GeN_2O_3$ calcd.: C, 44.6; H, 6.69; N, 5.20%); and (v) waxy impure bis[(di-t-butyl)amido](trifluoroacetyl)trifluoroacetatotin(IV), which was characterised spectroscopically.

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