Subvalent Group 4B Metal Alkyls and Amides. Part I. The Synthesis and Physical Properties of Kinetically Stable Bis[bis(trimethysilyl)methyl]-germanium(II), -tin(II), and -lead(II) †

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Two methods are described for the synthesis of the unusual bivalent Group 4B metal alkyls $M[CH(SiMe_3)_2]_2$ (M = Ge, Sn, or Pb) from $Li[CH(SiMe_3)_2]$ in diethyl ether at 0 to −20 °C and (*a*) the metal(II) chloride (M = Sn or Pb) or (*b*) $M[N(SiMe_3)_2]_2$ (M = Ge or Sn). At ambient temperature in cyclohexane or benzene the solutions are yellow (Ge), red (Sn), or purple (Pb), and the compounds are monomeric and in a singlet electronic ground state. There are colour changes between the solid and the melt, and the compounds tend to become colourless at −196 °C. The crystal structure of the tin(II) alkyl shows a centrosymmetric dimer with a Sn–Sn bond (2.76 Å) similar in length to that in Sn_2Ph_6, and the two pairs of geminal alkyl groups in a mutually *trans* arrangement. The solid germanium compound is inferred to be structurally similar because of the presence of a strong polarised Raman line at 300 cm^{-1}. The monomer is believed to be angular with three approximately sp^2 hybridised orbitals at the metal, one of which is non-bonding; the dimer, with a Sn=Sn bent double bond, is formed by overlap of the non-bonding orbital of each monomer unit with the orthogonal vacant p_z orbital of the other.

AT the outset of these studies we were struck by the fact that the known kinetically stable alkyls or dialkylamides of main-group metals are found only for closed-shell metal configurations, even for those elements which are well known for their variable valencies. Thus, for example, the stable derivatives of tin or lead are species such as $SnMe_4$, $Sn(NMe_2)_4$, or $PbEt_4$, but not the

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† No reprints available.

corresponding bivalent compounds. This is curious because the lower valency state is firmly established, and indeed often more stable than the quadrivalent, with ligands such as chloride, a feature interpreted loosely in terms of the inert-pair effect,[1] an essentially thermodynamic approach.

The principal objective of these studies was to prepare and characterise alkyls and amides of subvalent main-group elements. Attention focused initially on known stable lower valencies and in the early parts of this series we describe the chemistry of some alkyls and amides of bivalent Group 4B elements. Thus this paper deals with the synthesis, physical properties, and, to an extent, structures of some thermally stable alkyls of Ge^{II}, Sn^{II}, and Pb^{II}, *i.e.* $M[CH(SiMe_3)_2]_2$, Part 2 with much of the extensive chemistry of the tin dialkyl and the lead analogue,[2] Part 3 with ^{119}Sn Mössbauer spectra of the tin compound and its various derivatives,[3] and Part 5 with the synthesis, physical properties, and photochemistry of the isostructural amides $M[N(SiMe_3)_2]_2$ (M = Ge, Sn, or Pb).[4] A more daunting challenge was to obtain stable paramagnetic derivatives of main-group elements. In Part 4 we report on the trivalent silicon, germanium, and tin species $M'[CH(SiMe_3)_2]_3$ (M′ = Si, Ge, or Sn) and $M''[N(SiMe_3)_2]_3$ (M″ = Ge or Sn),[5] and that paper also deals with related amides of Ge^{III} and Sn^{III} and metal(II) precursors.[4] The He(I) photoelectron spectra of many of the bivalent compounds have been recorded and assignments proposed.[6] Preliminary communications referring to some of the material of this paper have been published.[7,8]

A range of supposedly bivalent tin alkyls was described in the early literature,[9] generally prepared from tin(II) chloride and an alkylating agent. These are now known to be telomers $R(SnR_2)_xR$, cyclic oligomers such as $(R_2Sn)_6$, or polymers, in all of which tin is quadrivalent, demonstrated *inter alia* by ^{119}Sn Mössbauer spectroscopy. A plausible interpretation of these findings seemed to us to be that the dialkyl is initially formed but is kinetically unstable, and has both associative and dissociative low-energy decomposition paths, due to its high degree of co-ordinative unsaturation at tin and energetically accessible non-bonding and vacant orbitals. By contrast, for example, the various forms of tin(II) chloride are chloride-bridged polymers in which tin is in a high co-ordination number. We therefore sought to achieve kinetic stability for subvalent alkyls or amides by appropriate selection of ligand. The ligands $[CH(SiMe_3)_2]^-$ and $[N(SiMe_3)_2]^-$ were chosen on the basis of their substantial bulk which might be helpful in shielding the metal centre and thus affording resistance to associative reactions, and the impossibility of an intramolecular β-hydrogen shift and olefin or imine fragmentation. The presence of a large number of methyl groups was seen as a useful bonus in providing for ease of manipulation because of the likelihood of good hydrocarbon solubility. Similar arguments have been used by us [10] and others [11] in tackling the complementary problem of obtaining stable transition-metal alkyls and amides. With regard to the alkyls, significant results were obtained with $[CH_2SiMe_3]^-$ as ligand. However, we rejected its use in the present context, because: (*i*) it is particularly suitable for stabilising metal four-co-ordination, as in $M(CH_2SiMe_3)_4$ (M = Ti, Zr, Hf, V, or Cr) or $[M'(CH_2SiMe_3)_3]_2$ (M′ = Mo or W); (*ii*) $Sn(CH_2SiMe_3)_4$ [12] and $Sn(CH_2CMe_3)_4$ [13] are known; and (*iii*) $SnCl_2$ with $Mg(CH_2CMe_3)Cl$ affords $Sn_2(CH_2CMe_3)_6$ and not the dialkyl.[13]

The only bivalent Group 4B organometallic compounds, *i.e.* having metal–carbon bonds, are the bis(cyclopentadienyls), organogermylenes such as 'GePhCl' [14] (the latter are not monomeric; *e.g.* they may be chloride-bridged oligomers), and stannacarbaboranes (in which the tin is in an unusual electronic environment) $B_9C_2{}^{1,2}Sn^3H_{11}$ [15] and $Sn(Ph\overline{CB_{10}H_{10}C})_2$.[16] The compound $Ge(\eta\text{-}C_5H_5)_2$ polymerises within 3 h at ambient temperature.[17] The tin and lead analogues are monomeric in the gas phase, and electron diffraction shows them to have an angular sandwich structure.[18] The lead compound is a polymer, with terminal and bridging ligands in the crystal;[19] the tin derivative also polymerises slowly (90% in 5 d at 20 °C) and probably has a similar structure.[20]

RESULTS AND DISCUSSION

We have used two methods of synthesis. Reaction between bis(trimethylsilyl)methyl-lithium and the appropriate metal(II) chloride [equation (1)] proved suitable

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[1] *Cf.*, R. S. Nyholm, *Proc. Chem. Soc.*, 1961, 273.

[2] Part II, J. D. Cotton, P. J. Davidson, and M. F. Lappert, following paper.

[3] Part III, J. D. Cotton, P. J. Davidson, J. D. Donaldson, M. F. Lappert, and J. Silver, *J.C.S. Dalton*, 1976, 2286.

[4] Part V, M. J. S. Gynane, D. H. Harris, M. F. Lappert, P. P. Power, P. Rivière, and M. Rivière-Baudet, *J.C.S. Dalton*, to be submitted.

[5] Part IV, A. Hudson, M. F. Lappert, and P. W. Lednor, *J.C.S. Dalton*, 1976, in the press.

[6] D. H. Harris, M. F. Lappert, J. B. Pedley, and G. J. Sharp, *J.C.S. Dalton*, 1976, 945.

[7] P. J. Davidson and M. F. Lappert, *J.C.S. Chem. Comm.*, 1973, 317.

[8] D. E. Goldberg, D. H. Harris, M. F. Lappert, and K. M. Thomas, *J.C.S. Chem. Comm.*, 1976, 261.

[9] For a critical account, see W. P. Neumann, *Angew. Chem. Internat. Edn.*, 1963, **2**, 165; A. K. Sawyer, in 'Organotin Compounds,' ed. A. K. Sawyer, Marcel Dekker, New York, 1972, vol. 3, p. 823.

[10] *Cf.*, P. J. Davidson, M. F. Lappert, and R. Pearce, *Accounts Chem. Res.*, 1974, **7**, 209.

[11] See, for example, G. Wilkinson, *Chimia*, 1973, **27**, 165; D. C. Bradley, *Chem. in Britain*, 1975, **11**, 393; and refs. therein.

[12] D. Seyferth, *J. Amer. Chem. Soc.*, 1957, **79**, 5881.

[13] H. Zimmer, I. Hechenbleikner, O. A. Homberg, and M. Danzik, *J. Org. Chem.*, 1964, **29**, 2632.

[14] *Cf.*, J. Satgé, M. Massol, and P. Rivière, *J. Organometallic Chem.*, 1973, **56**, 1.

[15] R. W. Rudolph and V. Chowdhry, *Inorg. Chem.*, 1974, **13**, 248.

[16] A. Yu. Aleksandrov, V. I. Bregadze, V. I. Goldanskii, L. I. Zakharkin, O. Yu. Okhlobystin, and V. V. Khrapov, cited by J. J. Zuckerman, *Adv. Organometallic Chem.*, 1970, **9**, 21.

[17] M. D. Curtis and J. V. Scibelli, *J. Amer. Chem. Soc.*, 1973, **95**, 924.

[18] A. Almenningen, A. Haaland, and T. Motzfeldt, *J. Organometallic Chem.*, 1967, **7**, 97.

[19] C. Panattoni, G. Bombieri, and U. Croatto, *Acta Cryst.*, 1966, **21**, 823.

[20] P. G. Harrison and M. A. Healey, *J. Organometallic Chem.*, 1973, **51**, 153.

for the tin(II) and lead(II), but not the germanium(II), alkyl. Using the bivalent metal amide [equation (2)],[21] provided a route to $Ge[CH(SiMe_3)_2]_2$, and was also successful for the tin(II) [and lead(II) (S. J. Miles, unpublished work)] alkyl. The metal amide–lithium alkyl route may well prove useful also in the transition-metal alkyl field, because a large range of dialkyl- and bis-(trimethylsilyl)amido-transition-metal complexes is available.

$$2Li[CH(SiMe_3)_2] + MCl_2 \xrightarrow[\text{0 to} -20^\circ\text{ C}]{OEt_2} M[CH(SiMe_3)_2]_2 + 2LiCl \quad (1)$$

M = Sn or Pb

$$2Li[CH(SiMe_3)_2] + M'[N(SiMe_3)_2]_2 \xrightarrow[\text{0 to} -20^\circ\text{ C}]{OEt_2} M'[CH(SiMe_3)_2]_2 + 2Li[N(SiMe_3)_2] \quad (2)$$

M′ = Ge or Sn (or Pb)

At the start of this work satisfactory methods for the preparation of $Li(CH_2SiMe_3)$ [22] and $Li[C(SiMe_3)_3]$ [23a,b] [equation (3)] were known. The reaction of $(Me_3Si)_2CHCl$ with lithium chips in diethyl ether–tetrahydrofuran

$$(Me_3Si)_3CH + LiMe \longrightarrow Li[C(SiMe_3)_3] + MeH \quad (3)$$

(thf) was reported as giving $Li[CH(SiMe_3)_2]$ in *ca.* 50% yield,[23a] but a number of attempts to repeat this, before our work, had proved unsuccessful.[24a] An alternative method involving the metallation of $(Me_3Si)_2CH_2$ with LiMe [23a,b] was ruled out since an excess of LiMe is required and the yield of $Li[CH(SiMe_3)_2]$ is low (*ca.* 20%); the presence of an excess of LiMe or its decomposition products would be likely to prejudice the isolation of the alkyls. We found that $(Me_3Si)_2CHCl$ reacts readily with lithium powder in diethyl ether at reflux [equation (4)] to give bis(trimethylsilyl)methyllithium in virtually quantitative yield. The ease of

$$(Me_3Si)_2CHCl + 2Li \longrightarrow Li[CH(SiMe_3)_2] + LiCl \quad (4)$$

reaction is probably due to the high surface area of the powdered metal and similar results were obtained for two different types of lithium powder, suggesting that impurities were not responsible. (It is well known that the presence of small amounts of sodium can be beneficial to the preparation of organolithium compounds from lithium metal.) Reaction of $Li[CH(SiMe_3)_2]$ with excess of $SiMe_3Cl$ resulted in a 96% yield of $(Me_3Si)_3CH$. The reaction was usually followed by hydrolysing an aliquot portion and comparing the amounts of $(Me_3Si)_2CH_2$ and $(Me_3Si)_2CHCl$ by g.l.c. Solutions of the lithium reagent (0.5—0.7 mol dm^{-3} in diethyl ether) were estimated by total-base titration and could be stored under argon at −30 °C for several months without noticeable decomposition. It was found on repeating the preparation several times that closely controlled conditions were required to obtain consistently high yields of the lithium reagent.

The starting halide $(Me_3Si)_2CHCl$ was generally prepared from $(ClMe_2Si)CHCl_2$, a by-product in the preparation of $(Me_3Si)CH_2Cl$, as shown in equation (5).[24b]

$$\begin{tikzcd} SiMe_3Cl \arrow[r, "Cl_2"', "h\nu"'] \arrow[r, "Cl_2"] & (ClMe_2Si)CH_2Cl \arrow[d, "MgBrMe"] + (ClMe_2Si)CHCl_2 \quad (5) \\ & (Me_3Si)CH_2Cl \end{tikzcd}$$

The route to $(Me_3Si)_2CHCl$, shown in equation (6),

$$(ClMe_2Si)CHCl_2 \xrightarrow{MgBrMe} (Me_3Si)CHCl_2 \xrightarrow[SiMe_3Cl]{LiBu^n,\ -110\,^\circ C} (Me_3Si)_2CCl_2 \xrightarrow[(ii)\ EtOH]{(i)\ LiBu^n,\ -110^\circ\ C} (Me_3Si)_2CHCl \quad (6)$$

involved known reactions.[23a,c,25] [Low temperatures are necessary for the metallations with $LiBu^n$ because of the instability of the carbenoids of the type $=C(Cl)Li$ which are postulated as intermediates.] When $(ClMe_2Si)CHCl_2$ was not readily available, metallation of CH_2Cl_2 [equation (7)] was used to prepare $(Me_3Si)_2CCl_2$ which [25] could then be used, as in equation (6), to prepare $(Me_3Si)_2CHCl$.[23c]

$$CH_2Cl_2 \xrightarrow[2SiMe_3Cl]{2LiBu^n,\ -110^\circ\ C} (Me_3Si)_2CCl_2 \quad (7)$$

Reaction (1) gave the red $Sn[CH(SiMe_3)_2]_2$ in good yield. For the lead analogue, obtaining the pure crystalline material was much more difficult. This was in part due to the formation of metallic lead, and hence to a laborious work-up procedure involving finally multiple recrystallisations. The compound is very air- and photo-sensitive, especially when in solution, and non-reactive solvents are limited to hydrocarbons. As will be shown in Part 2,[2] the chemical properties of $Pb[CH(SiMe_3)_2]_2$ can be adequately studied, yielding more stable derivatives, by using the filtered solution product of reaction (1).

An intermediate stage in the development of the synthesis shown in equation (2) was an unsuccessful attempt to make a heteroleptic tin(II) alkylamide $Sn[CH(SiMe_3)_2][N(SiMe_3)_2]$ from $SnCl[N(SiMe_3)_2]$ and the lithium alkyl, possibly due to disproportionation [equation (8)]; certainly the homoleptic alkyl and amide

$$\begin{tikzcd} Li[CH(SiMe_3)_2] + SnCl[N(SiMe_3)_2] \arrow[r] & {} \\ Sn[CH(SiMe_3)_2][N(SiMe_3)_2] \ \text{not isolated} \arrow[d] \\ \tfrac{1}{2}Sn[CH(SiMe_3)_2]_2 + \tfrac{1}{2}Sn[N(SiMe_3)_2]_2 \quad (8) \end{tikzcd}$$

were isolated. However, the possibility of amide–alkyl exchange had to be explored. Reaction (2) was made into a useful synthesis by developing the separation procedure of equation (9), based in the final step on the

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[21] D. H. Harris and M. F. Lappert, *J.C.S. Chem. Comm.*, 1974, 895.

[22] J. W. Connolly and G. Urry, *Inorg. Chem.*, 1963, **2**, 645.

[23] (*a*) M. A. Cook, D.Phil. Thesis, University of Sussex, 1970; (*b*) M. A. Cook, C. Eaborn, A. G. Jukes, and D. R. M. Walton, *J. Organometallic Chem.*, 1970, **24**, 529; (*c*) M. A. Cook, C. Eaborn, and D. R. M. Walton, *ibid.*, 1971, **29**, 389.

[24] (*a*) J. D. Walsh, M.Sc. Thesis, University of Sussex, 1971; (*b*) R. H. Krieble and J. R. Elliot, *J. Amer. Chem. Soc.*, 1945, **67**, 1810.

[25] W. R. Bamford and B. C. Pant, *J. Chem. Soc.* (*C*), 1967, 1470.

greater hydrocarbon-solubility of the amide compared with the alkyl. A comparison between reactions (1)

$$\begin{aligned}&M'[CH(SiMe_3)_2]_2 + 2Li[N(SiMe_3)_2] \xrightarrow{SnCl_2,\ 0^\circ C,\ OEt_2} \\ &\quad Sn[N(SiMe_3)_2]_2 + 2LiCl\downarrow + M'[CH(SiMe_3)_2]_2 \quad (9)\\ &M' = Ge \text{ or } Sn\end{aligned}$$

and (2) for the tin compound shows that the latter has the advantage in that control of reaction conditions (*e.g.* temperature) are not so critical, whereas for the former at $>$*ca.* 0 °C reduction to metallic tin is a significant side reaction. However, work-up is obviously more tedious for reaction (2).

TABLE 1

Some physical data for GeR_2, SnR_2,[a] and PbR_2 [$R = CH(SiMe_3)_2$]

	GeR_2	SnR_2 [a]	PbR_2 [b]
Colour: (1) of crystals at 20 °C	Bright yellow	Brick-red	Purple
(2) of solution in hexane	Yellow	Deep magenta	
(3) of melt	Orange–red	Very deep red	
(4) at −196 °C	Colourless	Pale yellow	Colourless
M.p. (θ_c/°C) (*in vacuo*)	179—181	135—137	43—45
Sublimation θ_c/°C (P/mmHg)	110 (10^{-3})	70 (10^{-3})	Decomp.
Molecular weight:			
(1) mass spectrometrically (calc. values in parentheses)	392 (391.4)	438 (437.5)	
(2) by cryoscopy in C_6H_6	[c]	448 [d]	
(3) by cryoscopy in C_6H_{12} [e]	420	435	
^1H N.m.r. (τ) [f] ($Si-CH_3$)	9.51	9.68	9.78
($M-CH$)	6.40	8.10	8.85
Raman (cm^{-1})	300vs	[h]	
P.e. (eV) [i] (M lone pair)	7.75	7.42	7.25
(C–M–C bonding orbital)	8.87	8.33	7.98
U.v., $\lambda_{max.}$/ nm [j]	414 (970) 302 (1 450) 227 (19 600)	495 (610) 332 (910) 239 (32 750)	

[a] Also available are ^{119}Sn Mössbauer,[3] diamagnetic (Faraday method on solid), and e.s.r. (no signal in absence of light, *cf.* ref.5) and single-crystal *X*-ray analysis.[8] [b] The sample was believed to be too reactive as vapour or solution to record the mass spectrum or cryoscopic molecular weight. [c] Insufficiently soluble. [d] Average of two separate determinations (16.79 g l^{-1} of C_6H_6, M 422; 15.15 g l^{-1} of C_6H_6, M 449). [e] The cryoscopic constant in cyclohexane is high; consequently depressions of *ca.* 1 °C were observed. [f] In C_6H_6. [g] Sample as solid: ν(Ge–Ge)?, *cf.* 273 cm^{-1} for Ge_2Me_6. [h] Sample (solid) decomposed in laser beam. [i] Data from ref. 6. [j] Hexane solution; absorption coefficients ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$) are given in parentheses.

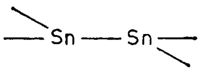
There seems no ready explanation for the failure to isolate the germanium(II) alkyl from reaction (1). The nature of the deep-green solution obtained in that system is unknown. It was originally believed to be $Ge[CH(SiMe_3)_2]_3^{\bullet}$ or a mixture of this with the dialkyl, because of the strong colours associated with the tin(II) and lead(II) alkyls and the e.s.r. characterisation.[5] However, the pure germanium(II) alkyl is now available from reaction (2), and is bright yellow, affording on photolysis in hexane a yellow solution which showed a strong e.s.r. signal due to the germanium(III) alkyl; however, an alternative method of generating $Ge[CH(SiMe_3)_2]_3^{\bullet}$ gave a colourless solution.[5]

The available physical properties are summarised in Table 1, with vibrational spectroscopic results in Table 2.

Cryoscopy in benzene or cyclohexane showed that the tin(II) and germanium(II) alkyls are monomeric in these solvents, thus ruling out alternative formulations such as telomeric $R(R_2Sn)_nR$ (which might give similar analytical figures if n is large) or cyclic $(R_2Sn)_m$. The molecular weight could only be studied over a narrow range of concentrations, since at higher concentrations than those reported in Table 1 crystallisation occurred as the freezing point of the solvent was approached, and for the *germanium compound a very dilute solution was used and hence the result is only approximate.* The volatility of these two compounds and their mass spectra suggest that the vapour is that of the monomer.

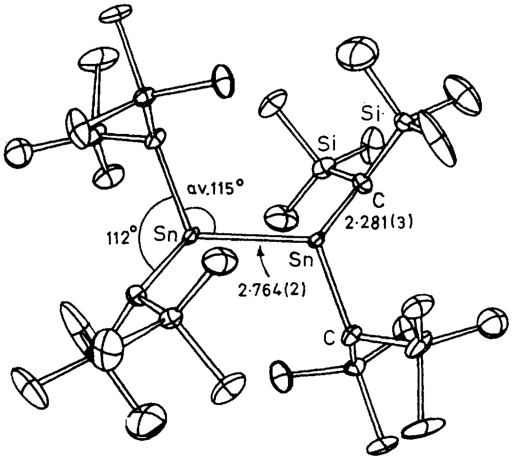
The tin(II) dialkyl is moderately soluble in hexane, benzene, or diethyl ether, but reacts rapidly with chlorinated solvents. Solutions are extremely air-sensitive, the red colour disappearing to give a colourless solution, but the solid is markedly more stable and can be handled briefly in the air without significant decomposition. This difference in stability appears to be greater than normally found for air-sensitive compounds and this may well be explained by the unusual dimeric solid-state structure of the compound (see below). Similarly, the colours of crystalline $Sn[CH(SiMe_3)_2]_2$ and its solutions are noticeably different; single crystals are pale brick-red, whereas solutions are deep magenta-red. The dialkylgermanium compound is appreciably less soluble in hydrocarbons, possibly because in the solid state the dimer (an *X*-ray crystal structure is in progress) has a stronger metal–metal bond than the tin analogue. Both solutions (the alkyl is extremely soluble in hexane) and crystals of the lead alkyl are very air-sensitive and the solid compound cannot be handled, even briefly, in the air.

A single-crystal *X*-ray analysis of $Sn[CH(SiMe_3)_2]_2$ shows the compound to be a centrosymmetric dimer (I);[8]



(I)

details are in the Figure. The crystals are diamagnetic at room temperature (Faraday method). The tin–tin bond length is similar to that found in tetrahedral tin or Sn_2Ph_6.[26] The sum of the angles at tin is 342°, compared with 360° expected for pure sp^2 hybridisation at Sn or 327° for sp^3. This led us to look for a Sn–H bond. However, this was ruled out by (*a*) detailed *X*-ray considerations, (*b*) the absence of ν(Sn–H) in the i.r. spectrum, (*c*) the failure to detect a Sn-*H* resonance in the ^1H n.m.r. spectrum, (*d*) the molecular weight, and (*e*) the conversion of a solution in benzene into $[Cr(CO)_5\{Sn[CH(SiMe_3)_2]_2\}]$, the crystal structure of which confirms trigonal tin.[2]



Crystal and molecular structure of $Sn[CH(SiMe_3)_2]_2$

The Raman spectrum of solid $Ge[CH(SiMe_3)_2]_2$ showed a strong polarised band at 300 cm^{-1} which is assigned to ν(Ge–Ge); this compound is therefore expected to have a similar structure to that of its tin analogue in the crystal. It has not yet been possible to record the Raman spectra of (*a*) the solid tin alkyl or (*b*) a solution of the germanium compound, because for (*a*) there was decomposition in the laser beam (see ref. 5, for the photochemical reaction) and for (*b*) the solution was too dilute. The ^1H n.m.r. spectra of the metal(II) alkyls strongly suggest that the compounds are diamagnetic, and therefore exist in a singlet rather than triplet electronic ground state. There were two sharp singlets in the expected 18 : 1 ratio, the C*H* resonance occurring somewhat downfield from the SiCH_3 signal (see Table 1).

The most striking feature associated with the bivalent Group 4B alkyls is their strong colours at ambient or higher temperatures, despite there being no obvious chromophore. This is surely associated with the open-shell metal electronic structure. The moderate absorption coefficient (600—1 000 dm^3 mol^{-1} cm^{-1}) found for the visible spectral absorption band does not suggest a forbidden electronic transition (*e.g.* singlet ⟶ triplet), nor a charge-transfer mechanism. Nevertheless, it was the latter explanation which we proposed earlier for Sn^{II} or Pb^{II},[7] implicating the essentially metal non-bonding orbital and the neighbouring Si 3*d* vacant orbital. We took this view because from photoelectron spectra (see Table 1)[6] the expected energy of this transition is of the appropriate magnitude. Coupled with the reversible thermochromic behaviour, the compounds being colourless at −196 °C suggests thermally accessible neighbouring electronic singlet states. This is certainly consistent with the diamagnetism (examined closely only for the tin compound) inferred from (*a*)

TABLE 2

Infrared absorptions (cm^{-1}) of GeR_2, SnR_2 [R = $CH(SiMe_3)_2$], $(SiMe_3)_2CH_2$, and $(SiMe_3)_2CHCl$ in the range 240—1 350 cm^{-1}

	GeR_2 [b]				
Assignment [a]	I.r.	Raman	SnR_2 [c]	$(SiMe_3)_2CH_2$ [c]	$(SiMe_3)_2CHCl$ [d]
$\delta_{sym}(CH_3)$	1 293w, br		1 305m, br		1 260 (sh)
	1 258 (sh)	1 262vw, br	1 260 (sh)	1 250s	1 254s
	1 251s	1 246vw, br	1 249s		
$\nu_{asym}(Si_2C)$	1 014 (sh)	1 016m	1 010m, br	1 051s	1 042s
	998s	1 002w			
$\rho_{asym}(CH_3)$	971m	979vw	921w		
	842vs, br	840vw, br	840vs, br	840vs, br	848vs, br
$\rho_{sym}(CH_3)$	768s	765vw	774s	784m	773m
	722w		724vw	765m	768 (sh)
				735vw	716m
					700m
$\nu_{asym}(SiC_3)$	683 (sh)	685w, br	688 (sh)	690s	690 (sh)
	670 (sh)	677w, br			
	666s		666m	660vw	
ν_{asym}(Ge–C) (?)	643 (sh)				
	613w	620m, br			632w
$\nu_{sym}(SiC_3)$		539vw	610 (sh)	612w	618w
			588w	590w	
$\nu_{sym}(Si_2C)$	511m	517m	500 (sh)	555w	528w
	472w	480m	480w		
			462 (sh)		
$\delta_{asym}(SiC_3)$	346vw	350w			
ν(Ge–Ge)		300vs			
$\delta_{sym}(SiC_3)$	282w, br				

[a] ν = Stretching vibration; δ = deformation mode, ρ = low-frequency deformation mode *e.g.* 'wagging.' [b] Nujol mull (i.r.); solid sample in sealed evacuated ampoule (Raman). [c] Hexane solution. [d] Capillary film.

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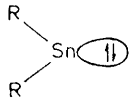
[26] H. J. Haupt, F. Huber, and H. Preut, *Z. anorg. Chem.*, 1973, **396**, 81.

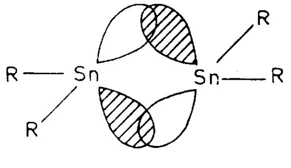
magnetic-susceptibility measurements (at 20 °C), (*b*) sharp ^{1}H n.m.r. spectra, and (*c*) the absence of e.s.r. signals under anaerobic and dark conditions (*cf.* ref. 5).

A plausible bonding scheme for the monomer (vapour or solution) and dimer (crystal) is shown for Sn in (II) and (III), respectively. (An alternative valence-bond representation is $R_2\overset{\cdot\cdot}{\underset{-}{Sn}}-\underset{+}{Sn}R_2 \longleftrightarrow R_2\underset{+}{Sn}-\overset{\cdot\cdot}{\underset{-}{Sn}}R_2$.) The proposal that in the dimer there is a weak but multiple metal–metal bond is necessary to account for some of the physical properties mentioned above; a solution to this apparent paradox may be the suggestion that there is a bent double bond, consistent also with the representations in (II) and (III) and structural data shown in the Figure. The angular structure for the monomer is supported by (*a*) the singlet electronic properties of the solutions, and (*b*) the demonstration that two bulky $[CH(SiMe_3)_2]^-$ ligands at tin can be accommodated by such an arrangement; thus the C–Sn–C angle in $[Cr(CO)_5\{Sn[CH(SiMe_3)_2]_2\}]$ is 98°.[2] The dimer (III) is envisaged as formed from the monomer (II) by a pairwise orbital-overlap scheme involving the filled sp_xp_y non-bonding orbital of one monomer unit with the vacant p_z orbital of the other.



(II)

sp_xp_y hybrid orbitals, p_z orbital vacant



(III)

Bent SnSn double bond

EXPERIMENTAL

Since nearly all the complexes were air and moisture sensitive, rigorous exclusion of air and moisture was maintained at all times. Experiments were made in all-glass apparatus under an atmosphere of high-purity argon. Pure argon (Air Products Ltd.) was passed consecutively through activated B.A.S.F. catalyst at 130 °C (to remove oxygen), phosphorus pentachloride on vermiculite (to remove water), ground potassium hydroxide (to remove carbon dioxide), and activated No. 4A molecular sieve (to remove water). The pure dry argon was delivered to the apparatus through copper tubing, an all-glass two-way manifold (also connected to a vacuum source), and short lengths of P.V.C. (Portex 13) tubing required for flexibility. Before use, all the apparatus was evacuated and filled with argon, and the procedure was repeated several times. Solvents were distilled under nitrogen immediately prior to use, from P_4O_{10}, Na–Ph_2CO, NaH, or Na–K. Rigorous degassing under reduced pressure, followed by filling of the reaction vessel with argon, removed final traces of oxygen. Schlenk-tube manipulations were used.

Infrared spectra were recorded between CsI plates on a Perkin-Elmer 457 spectrometer. Raman spectra were obtained by Dr. M. J. S. Gynane on a Cary 81 instrument with a Kr^+ laser source. Mass spectra were recorded on an A.E.I. MS9 instrument, by the direct-inlet procedure. Hydrogen-1 n.m.r. continuous-wave spectra were obtained on the Varian HA100 instrument, and ^{13}C Fourier-transform spectra on a Jeol PFT 100 MHz spectrometer at an observing frequency of 25 MHz. Ultraviolet spectra were determined on a Unicam SP 800 spectrophotometer, using vacuum-line techniques for introducing the sample into the u.v. cell. Similarly, e.s.r. spectra were recorded by Dr. P. W. Lednor on a Varian E3 instrument with a V-4540 variable-temperature unit. Cryoscopic molecular weights were determined in a closed system by the Beckmann procedure.

Bis(trimethylsilyl)methyl-lithium.—Bis(trimethylsilyl)-methyl chloride (16.4 cm^3, 75 mmol) in diethyl ether (25 cm^3) was added dropwise during 1 h to lithium powder (1.565 g, 225 mmol) in refluxing diethyl ether (75 cm^3). The mixture was heated under reflux for 24 h during which time most of the lithium had reacted and a purple precipitate was produced. After cooling to room temperature, filtration (twice) through celite yielded a colourless solution of bis(trimethylsilyl)methyl-lithium which also contained a small amount of suspended lithium chloride. A portion (1 cm^3) of this solution was added to hydrochloric acid (10 cm^3, 0.1 mol dm^{-3}) and titration with sodium hydroxide (0.1 mol dm^{-3}) using phenolphthalein as indicator showed the concentration of the solution to be 0.67 mol dm^{-3}.

Synthesis of Bis[bis(trimethylsilyl)methyl]tin(II), SnR_2.—(a) *From* $SnCl_2$. Bis(trimethylsilyl)methyl-lithium (19.8 mmol, 30 cm^3 of a 0.66 mol dm^{-3} diethyl ether solution) was added during 1 h to anhydrous tin(II) chloride (1.877 g, 9.9 mmol) in diethyl ether (25 cm^3) at 0 °C. As each drop of lithium reagent was added a deep red colour was produced which immediately dispersed to give a pale yellow solution. Approximately halfway through the addition the solution began to change in colour to orange and finally deep red. After stirring for 2 h at 0 °C, and at room temperature for 3 h, the solution was filtered and the solvent was removed under high vacuum to yield a red solid. Recrystallisation (twice) from hexane at −30 °C gave red crystals of *bis[bis(trimethylsilyl)methyl]tin*(II) (3.100 g, 71%), m.p. 135—137 °C (Found: C, 38.2; H, 8.6; Sn, 27.0. $C_{14}H_{38}Si_4Sn$ requires C, 38.4; H, 8.8; Sn, 27.1%).

(b) *From [bis(trimethylsilyl)amido]chlorotin*(II), $[SnCl(NR'_2)]_x$. Dropwise addition, at 0 °C, of bis(trimethylsilyl)-methyl-lithium (1.30 mmol, 3.9 cm^3 of a 0.33 mol dm^{-3} diethyl ether solution) to the chlorotin amide[27] (0.424 g, 1.35 mmol), prepared *in situ* from tin(II) chloride (0.256 g, 1.35 mmol) and bis(trimethylsilyl)amidolithium–diethyl ether (0.325 g, 1.35 mmol) in diethyl ether (25 cm^3), resulted in an immediate reaction. As each drop of lithium reagent was added, a strong red colour was produced, which rapidly dispersed to give a straw-yellow solution. After approximately half-addition, the reaction mixture became orange and finally red. The mixture was allowed to reach room temperature, stirred for 1 h, then left to settle overnight. Removal of the red supernatant layer by syringe followed by removal of volatiles [20 °C (10^{-2} mmHg)] * gave a red crystalline solid mixed with an orange oil. Repeated extractions with hexane and cooling (−30 °C) gave red crystals of bis[bis(trimethylsilyl)methyl]-tin(II) (0.201 g, 71%), m.p. 134—136 °C (authentic ^{1}H n.m.r. spectrum) (Found: C, 37.9; H, 8.9; N, 0.0%). Removal of volatiles from the orange mother liquor and

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* 1 mmHg ≈ 13.6 × 9.8 Pa.

[27] E. H. Amonoo-Neizer, R. A. Shaw, D. O. Skovlin, and B. C. Smith, *Inorg. Synth.* 1966, **8**, 19.

microdistillation [b.p. *ca.* 60 °C (10^{-3} mmHg)] gave yellow bis[bis(trimethylsilyl)amido]tin(II) (0.174 g, 61%), m.p. (*in vacuo*) 37—38 °C (authentic ^{1}H n.m.r. and i.r. spectra).[21]

(c) *From bis[bis(trimethylsilyl)amido]tin*(II), $Sn(NR'_2)$.[21] Similarly, dropwise addition, at 0 °C, of the alkyl-lithium (4.20 mmol, 12.7 cm^3 of a 0.33 mol dm^{-3} diethyl ether solution) to the tin amide (0.927 g, 2.11 mmol), prepared *in situ* from tin(II) chloride (0.400 g, 2.11 mmol) and $Li[N(SiMe_3)_2]\cdot OEt_2$ (1.019 g, 4.22 mmol) in diethyl ether (30 cm^3), gave an immediate reaction with eventual formation of a deep red solution. Filtration, followed by removal of volatiles [20 °C (10^{-2} mmHg)], gave a red solid. Extraction with hexane and cooling (−30 °C) afforded a mixture of colourless and red crystals. Repeated careful recrystallisations from hexane effected separation and identification (^{1}H n.m.r., m.p.) of the two products as $Li[N(SiMe_3)_2]\cdot OEt_2$ (0.245 g, 24%), m.p. 110—112 °C [lit.,[27] m.p. 110—115 °C (decomp.)], and bis[bis(trimethylsilyl)methyl]tin(II) (0.175 g, 19%), m.p. 135—137 °C. Crystals of the tin alkyl were found to be suitable for *X*-ray studies. Higher yields (*ca.* 70%) of SnR_2 were obtained when the work up was simplified by addition of $SnCl_2$ to the reaction mixture, as described in detail for the synthesis of GeR_2 (see below).

Lack of Reaction between $Sn[N(SiMe_3)_2]_2$ *and Tetramethyltin*(IV).—Addition of a tetramethyltin (0.27 cm^3, 2.0 mmol) solution in benzene (5 cm^3) to the tin amide (0.339 g, 1.0 mmol) in benzene (5 cm^3), at ambient temperature, gave no observable reaction. Heating the reaction mixture to reflux temperature and monitoring by ^{1}H n.m.r. indicated that no reaction had occurred after 2 h.

Synthesis of Bis[bis(trimethylsilyl)methyl]lead(II), PbR_2.—Bis(trimethylsilyl)methyl-lithium (10 mmol, 17.2 cm^3 of a 0.58 mol dm^{-3} diethyl ether solution) was added during 50 min to anhydrous lead(II) chloride (1.39 g, 5 mmol) in diethyl ether (15 cm^3) at 0 °C. As the first few drops were added, a purple colour was produced which rapidly dispersed to give a yellow solution. After stirring at 0 °C for 30 min, and at room temperature for 30 min, the solution was filtered from the dark solid produced. Solvent was removed from the yellow solution under high vacuum to give a yellow oil which gave a purple oily solid as the last traces of diethyl ether were removed. Recrystallisation (4 times) from hexane at −78 °C gave purple crystals of *bis[bis(trimethylsilyl)methyl]lead*(II) (0.068 g, 3%), m.p. 43—45 °C (Found: C, 31.7; H, 7.1; Pb, 39.7. $C_{14}H_{38}PbSi_4$ requires C, 32.0; H, 7.3; Pb, 39.4%).

Reaction of $Li[CH(SiMe_3)_2]$ *with Germanium*(II) *Iodide*.—The lithium reagent (3.98 mmol, 7.2 cm^3 of a 0.55 mol dm^{-3} solution in diethyl ether) was added during 23 min to germanium(II) iodide (0.649 g, 1.99 mmol) in diethyl ether (15 cm^3) at −25 °C. During mixing, the colour changed from yellow, through orange and brown, to green. After allowing to warm slowly to room temperature, the solution was filtered, and solvent was removed under high vacuum to give a deep green oil. This was soluble in hexane, but no product could be isolated. The e.s.r. spectrum showed a strong signal of $GeR_3^{\bullet}$.

Reaction of $Li[CH(SiMe_3)_2]$ *with Germanium*(II) *Chloride–Dioxan*.—The lithium reagent (4.43 mmol, 8.05 cm^3 of a 0.55 mol dm^{-3} diethyl ether solution) diluted with diethyl ether (10 cm^3) was added during 20 min to germanium(II) chloride–dioxan (0.513 g, 2.215 mmol) in diethyl ether (15 cm^3) at 25 °C. During the reaction the colour changed from pale yellow, through orange and yellow, to pale green. As the solution was slowly warmed to room temperature, the green colour deepened. Filtration, followed by removal of solvent under high vacuum, yielded an oily green solid, which contained $GeR_3^{\bullet}$ (e.s.r.). Attempts at recrystallisation from hexane yielded small amounts of colourless crystals, but no green product.

Synthesis of Bis[bis(trimethylsilyl)methyl]germanium(II), GeR_2.—Dropwise addition, at 0 °C, of $Li[CH(SiMe_3)_2]$ (2.80 mmol, 8.5 cm^3 of a 0.33 mol dm^{-3} diethyl ether solution) to bis[bis(trimethylsilyl)amido]germanium(II) [21] (0.563 g, 1.43 mmol), prepared *in situ* from germanium(II) chloride–dioxan (0.332 g, 1.43 mmol) and $Li[N(SiMe_3)_2]\cdot OEt_2$ (0.694 g, 2.87 mmol) in diethyl ether (25 cm^3), gave an immediate reaction with gradual formation of a bright yellow solution. Filtration, followed by removal of volatiles [20 °C (10^{-2} mmHg)] gave a yellow and white solid mixture. Extraction with hexane and repeated recrystallisations failed effectively to separate the mixture. Sublimation [60 °C (10^{-3} mmHg)] on to a cooled (0° C) probe afforded sufficient pure crystals to permit their identification (^{1}H n.m.r., m.p.) as bis(trimethylsilyl)amidolithium, m.p. 69—70 °C (lit.,[27] 71—72 °C).

Similarly, $Li[CH(SiMe_3)_2]$ (5.00 mmol, 15.1 cm^3 of a 0.33 mol dm^{-3} diethyl ether solution) and $Ge[N(SiMe_3)_2]_2$ (0.996 g, 2.5 mmol) reacted at 0 °C in diethyl ether (30 cm^3) to give a bright yellow reaction mixture. Slow addition of solid tin(II) chloride (0.474 g, 2.5 mmol) at 0 °C gave an orange-red solution with a white precipitate. The mixture was allowed to reach room temperature, stirred for 1 h, and left to settle overnight. Separation, by syringe, of the red supernatant liquid and removal of volatiles [20 °C (10^{-2} mmHg)] gave an oily red solid. Extraction with pentane and removal of volatiles [20 °C (10^{-2} mmHg)] gave an orange-red liquid identified (^{1}H n.m.r.) as $Sn[N(SiMe_3)_2]_2$ contaminated with traces of $Sn[CH(SiMe_3)_2]_2$. Further extractions with hexane gave deep yellow solutions from which, on cooling (−30 °C), bright yellow crystals of *bis[bis(trimethylsilyl)methyl]germanium*(II) were obtained (0.391 g, 40%), m.p. 179—181 °C [sublimes 110 °C (10^{-3} mmHg)] (Found: C, 42.9; H, 10.0; Ge, 18.3; N, 0.0; Si, 29.0. $C_{14}H_{38}GeSi_4$ requires C, 43.0; H, 9.8; Ge, 18.5; N, 0.0; Si, 28.7%) [*M* (mass spec.) 392; Calc. 391.4].

Tris[bis(trimethylsilyl)methyl]germanium(III), identified by e.s.r., was obtained either by irradiation (u.v.) of a hexane solution of GeR_2, or by addition of $Li[CH(SiMe_3)_2]$ to a hexane solution of GeR_2 without irradiation.

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