Subvalent Group 4B Metal Alkyls and Amides. Part 8.[1] Germanium and Tin Carbene Analogues MR_2 [M = Ge or Sn, R = $CH(SiMe_3)_2$]: Syntheses and Structures in the Gas Phase (Electron Diffraction); Molecular-orbital Calculations for MH_2 and $GeMe_2$†

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Bis[bis(trimethylsilyl)methyl]germanium, GeR_2 [R = $CH(SiMe_3)_2$], is conveniently prepared from $GeCl_2$(diox) (diox = 1,4-dioxane) (for which an improved synthesis, from $GeCl_4$ and $SnHBu^n{}_3$, is reported) and $2MgCl(R)(OEt_2)$, $MgR_2(diox)_{0.5}$, or $MgR_2(OEt_2)$ in OEt_2. The corresponding tin(II) alkyl is accessible from $SnCl_4$ and successively 2LiR (to yield $SnCl_2R_2$) and Li_2(cot) (cot = cyclo-octatetraene) in OEt_2. Gas-phase electron diffraction (g.e.d.) patterns, recorded with nozzle temperatures of 155 °C for GeR_2 and 120 °C for SnR_2, show that the gas consists of V-shaped monomers. Least-squares refinements of models of C_2 symmetry yielded the bond distances Ge–C 203.8(15) and Sn–C 222(2) pm and the angles CGeC 107(2) and CSnC 97(2)°. In GeR_2 the $-CH(SiMe_3)_2$ ligands are oriented so that the HC^iMC^iH moiety (C^i = inner, or methine, C) has a nearly planar *syn,syn* conformation but in SnR_2 the dihedral angles C^iMC^iH are *ca.* 15°. *Ab initio* molecular-orbital calculations with a better than DZ (double zeta) basis were carried out on the model compounds MH_2 and $GeMe_2$, and yielded the optimal bond distances Ge–H 158, Ge–C 202, and Sn–H 177 pm, and valence angles HGeH 93, CGeC 97, and HSnH 93°. Correlation of experimental and calculated structures shows that M^{II}–H and M^{II}–C bond distances are significantly larger (by 4—10 pm) than their M^{IV}–H and M^{IV}–C counterparts, and valence angles at M increase in the series $GeH_2 = SnH_2 < GeMe_2 = SnMe_2 < GeR_2 < SnR_2$. Both the long bond distances and the less-than-tetrahedral valence angles are rationalised by assuming the metal lone pair to occupy atomic orbitals of predominant *s* character and the M–H and M–C σ-bonding orbitals to be formed from metal atomic orbitals of predominant *p* character.

In Part 1 of this Series we described the first heavy-atom Main Group 4 analogues of the carbenes MR_2 [R = $CH(SiMe_3)_2$] [M = Ge (bright yellow), Sn (brick red), or Pb (purple)].[2] The germylenes and stannylenes were diamagnetic monomers in dilute solution in C_6H_6 or cyclo-C_6H_{12}, and were thus assumed to be V-shaped and in an electronic singlet ground state in a non-polar medium. (A preliminary *X*-ray structure of the tin compound was reported in Part 2,[3] and revised data and details for the germanium compound will appear in Part 9;[4] it is evident that in the crystal these species adopt a *trans*-folded quasi-olefinic structure, M_2R_4.)

In the original method of synthesis of MR_2 we attempted to employ the only generally available convenient metal(II) starting materials, the chlorides;[2] however, a published procedure[5] for $GeCl_2$(diox) (diox = 1,4-dioxane) proved in our hands to be unreliable. The $SnCl_2$ + 2LiR pathway was appropriate for SnR_2, but $GeCl_2$(diox) and LiR gave a paramagnetic green product from which GeR_2 was not isolated.[2] An alternative route, using $M[N(SiMe_3)_2]_2$ and 2LiR, was effective for both Ge and Sn, but involved a chemical separation of MR_2 and $2Li[N(SiMe_3)_2]$ [the latter removed as the tin(II) amide, after addition of $SnCl_2$].

In preliminary publications we have briefly described (*a*) a new synthesis of GeR_2 from $GeCl_2$(diox) [using MgCl(R)(OEt_2)],[6] (*b*) a reductive route to SnR_2 (from $SnCl_2R_2$),[7] (*c*) gas-phase electron diffraction (g.e.d.) data on gaseous GeR_2[8,‡] and SnR_2,[7] and (*d*) *ab initio* molecular-orbital (m.o.) calculations on MH_2.[7,8]

We now provide: (*i*) an improved method for preparing $GeCl_2$(diox), (*ii*) details on (*a*)—(*d*), (*iii*) further alternative pathways to GeR_2 from $GeCl_2$(diox) [using $MgR_2(OEt_2)$ or $MgR_2(diox)_{0.5}$], and (*iv*) m.o. calculations on GeH_2 and $GeMe_2$.

Results and Discussion

The synthetic data referred to in (*i*)—(*iii*) are summarised in the Scheme. In general, because of the availability or ease of preparation of starting materials, we recommend the use of $SnCl_2$ + 2LiR and $GeCl_2$(diox) + $2MgCl(R)(OEt_2)$. The Grignard reagent is readily prepared from RCl and magnesium powder in refluxing OEt_2, and is obtained as a crystalline solid (70%) by removal of OEt_2, extraction with n-C_6H_{14}, and cooling the extract to −30 °C. [An account of the *X*-ray structure of this compound, as well as of $MgR_2(OEt_2)$ and $MgR_2(diox)_{0.5}$, and the preparation of the two dialkyls, will be presented elsewhere.[9]] The reductive dechlorination route to SnR_2, from the new compound $SnCl_2R_2$ and Li_2(cot) (cot = cyclo-octatetraene) may, as a model, have some generality in those systems where lower-oxidation-state precursors are not available; the synthesis of SiR_2 is under investigation.

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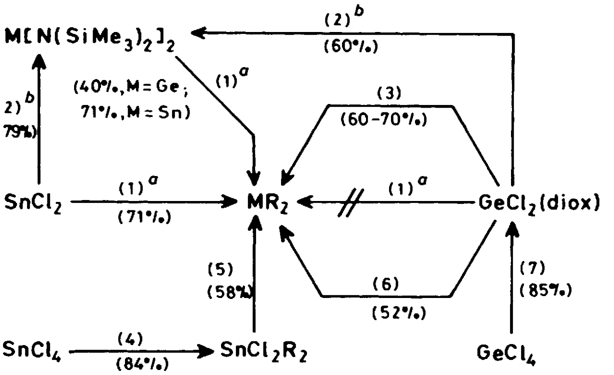
† *Non-S.I. units employed:* eV ≈ 1.60 × 10^{-19} J; Torr ≈ 133 Pa.

‡ This paper was also printed, with incorrect page order, in *J. Organomet. Chem.*, 1984, **276**, C1.



Scheme. Alternative syntheses for bis[bis(trimethylsilyl)methyl]germanium and -tin MR_2 [R = $CH(SiMe_3)_2$]; the routes[2] from $M[N(SiMe_3)_2]_2$ involve a tedious separation procedure. (1) 2LiR, OEt_2; (2) $2Li[N(SiMe_3)_2]$; (3) $MgR_2(OEt_2)$, OEt_2; or $MgR_2(diox)_{0.5}$, OEt_2; (4) 2LiR, n-C_6H_{14}; (5) $Li_2(cot)$; (6) $2MgCl(R)(OEt_2)$, OEt_2; (7) $SnHBu^n{}_3$, diox, OEt_2-n-C_6H_{14}. [a] Ref. 2. [b] M. J. S. Gynane, D. H. Harris, M. F. Lappert, P. P. Power, P. Rivière, and M. Rivière-Baudet, *J. Chem. Soc., Dalton Trans.*, 1977, 2004. Percentage yields are given in parentheses

Electron Diffraction Data Collection, Structure Solution, and Refinement for MR_2 [M = Ge *or* Sn, R = $CH(SiMe_3)_2$].—The g.e.d. patterns of MR_2 were recorded on Balzers Eldigraph KDG-2 with nozzle and reservoir temperatures of about 155 (Ge) or 120 °C (Sn). Exposures were made with nozzle-to-plate distances of about 50 and 25 cm. The structure analysis was based on six 50-cm and eight 25-cm plates for M = Ge, and five 50-cm and three 25-cm plates for M = Sn. The data were processed by standard procedures.[10]

The complex atomic scattering factors, $f'(s)$, were calculated from analytical representations of the atomic potential[11] using a published program.[12] Molecular intensities were modified by multiplying them by $s/|f'_C(s)| \times |f'_M(s)|$ (M = Ge or Sn). Average molecular intensity curves extended from s = 20 to 135 nm^{-1} with increment Δs = 1.25 nm^{-1} (50 cm) and from 40 to 270 nm^{-1} with increment 2.50 nm^{-1} (25 cm).

A molecular model of MR_2 is illustrated in Figure 1, wherein we denote methyl C atoms as *outer* (C^o) and methine C atoms (*i.e.* those bonded to M) as *inner* (C^i). Structure refinements were based on the following assumptions: (*i*) all methyl groups have local C_{3v} symmetry with the three-fold axes coinciding with the Si–C^o bonds; (*ii*) all trimethylsilyl groups have local C_3 symmetry with the three-fold axes coinciding with the Si–C^i bonds; (*iii*) both $C(SiMe_3)_2$ fragments have local C_2 symmetry with the symmetry axes bisecting angle SiC^iSi; (*iv*) the molecule has C_2 symmetry with the symmetry axes bisecting angle C^iMC^i; (*v*) the bond distances Si–C^i are longer than Si–C^o by 1.5 pm, as found in gaseous $CH_2(SiMe_3)_2$[13] and $CH(SiMe_3)_3$;[14] (This is, presumably, an intra-ligand strain-relieving effect.) and (*vi*) the bond distances C^i–H and C^o–H are equal and angle MC^iH is 116°.

The molecular structure of each of the MR_2 molecules was then defined by eleven independent parameters: the bond distances M–C, Si–C (mean) ($\equiv \langle Si–C \rangle$), and C–H; the valence angles CMC, MCSi, SiC^iSi, C^iSiC^o, and SiC^oH; and the dihedral angles $\varphi(C^iMC^iH)$, $\varphi(SiC^iSiC^o)$, and $\varphi(C^iSiC^oH)$. The last of these proved difficult to refine; refinements were therefore carried out with fixed values ranging from 0 to 60°, and the best fits were obtained with eclipsed (φ = 0°, Ge) or nearly eclipsed (φ = 10°, Sn) methyl groups.

Ten structure parameters were refined by least-squares calculations[15] from the intensity data under the constraints of a geometrically consistent r_2 structure along with sixteen root-mean-square vibrational amplitudes (l). The best values are listed in Table 1. The estimated standard deviations have been multiplied by a factor of three to include additional uncertainty due to data correlation and possible errors introduced by the above assumptions (*i*)—(*vi*), and non-refined amplitudes. We do not indicate error limits for the dihedral angles: not only do the best values depend on the magnitude of non-refined vibrational amplitudes, but their meaning is nebulous unless assumptions (*ii*)—(*iv*) are strictly valid.

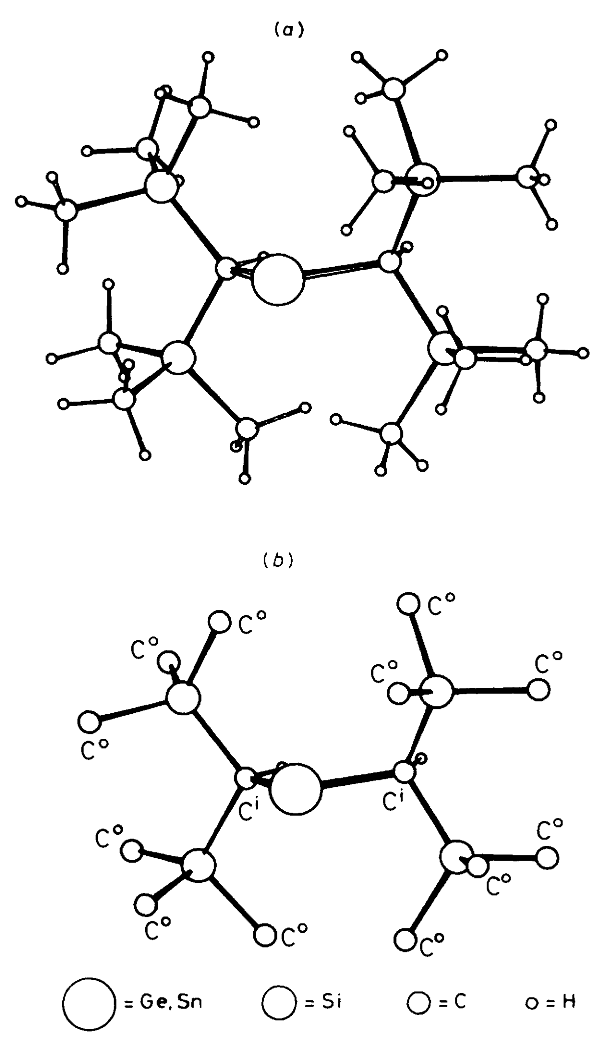


Figure 1. Molecular models of MR_2 [M = Ge or Sn, R = $CH(SiMe_3)_2$] (C_2 symmetry), including (*a*) or omitting (*b*) hydrogen atoms, and distinguishing (*b*) between methine (C^i = inner) carbons and methyl (C^o = outer) carbons

In Figures 2 and 3 we show experimental radial distribution curves and residual curves calculated for the best model. We consider the agreement to be satisfactory.

Molecular Orbital Calculations.—The *ab initio* m.o. calculations were carried out with the program DISCO[16] employing Gaussian-type basis functions. For Sn we used a (15, 11, 6) basis contracted to ⟨10, 8, 4⟩,[17] for Ge a (14, 11, 5) basis contracted to ⟨8, 7, 3⟩,[18] for Si a (10, 6, 1) basis contracted to ⟨6, 4, 1⟩,[19,20] for C a (7, 3) basis contracted to ⟨4, 2⟩,[20] and for H a (4) basis contracted to ⟨2⟩.[21]

The structures of GeH_2 and SnH_2 were optimised under C_{2v}

Table 1. Structure parameters for MR_2 [M = Ge or Sn, R = $CH(SiMe_3)_2$]: estimated standard deviations are in parentheses in units of the last digit; non-refined parameters are given in square brackets[a]

	Ge		Sn	
M	r_a	l	r_a	l
Bond distances (pm)				
M–C^i	203.8(15)	[5.5]	222(2)	4.5(14)
Si–C^i	189.6(3)	[5.6]	189.7(3)	6.4(3)
Si–C^o	188.1(3)	[5.3]	188.2(3)	6.2(3)
C–H	110.5(5)	7.8(9)	110.4(7)	8.6(8)
Non-bonded distances (pm)				
Within a $SiMe_3$ group				
$C^o \cdots C^o$	303(1)	9(2)	300(1)	[9.5]
Si ··· H	250(2)	13(1)	251(2)	11(2)
Within a $CH(SiMe_3)_2$ group				
Si ··· Si	316(1)	11(1)	318(2)	14(1)
$C^i \cdots C^o$	313(1)	8(2)	316(1)	[9]
Si ··· C^o	479(1)	11(2)	486(2)	12(4)
Si ··· C^o	402(2)	10(2)	373(4)	30(4)
Si ··· C^o	353(2)	11(3)	392(4)	
$C^o \cdots C^o$	358 to 625	[13 to 35]	351 to 631	[13 to 35]
Distances involving M and interligand distances (pm)				
M ··· Si	324(1)	10(1)	338(1)	12(1)
M ··· C^o	349(2)	21(3)	376(4)	40(4)
M ··· C^o	359(3)		385(5)	
M ··· C^o	400(2)	19(2)	396(3)	
M ··· C^o	413(3)		406(4)	
M ··· C^o	487(2)	13(2)	510(1)	14(4)
M ··· C^o	491(2)		511(2)	
Si ··· Si	532(4)	[20]	538(5)	[20]
Si ··· Si	616(4)	[15]	593(5)	[15]
Si ··· Si	622(4)	[15]	645(5)	[15]
Valence angles (°)				
C^iMC^i	107(2)		97(2)	
MC^iSi	110.6(6)		109.7(7)	
MC^iH	[116]		[116]	
C^iSiC^o	111.6(6)		113.2(5)	
SiC^iSi	113.0(5)		114.0(3)	
SiC^oH	111(1)		111(1)	
Dihedral angles (°)[b]				
C^iMC^iH	2		15	
SiC^iSiC^o	40		68	
C^iSiC^oH	0		10	
R^c/%	4.9		6.5	

[a] Abbreviations: C^i = inner (*i.e.* methine) carbon atom, C^o = outer (*i.e.* methyl) carbon atom (see Figure 1). In both molecules MR_2, Si–C^i bonds were assumed to be 1.5 pm longer than Si–C^o. [b] Estimated standard deviations of the dihedral angles are not cited, *cf.* text. [c] $R = [\Sigma w(I_{obs.} - I_{calc.})^2/\Sigma wI_{obs.}^2]^{\frac{1}{2}} \cdot 100\%$.

symmetry. The conformation of $GeMe_2$ was assumed to be such that (*i*) a HCGeCH fragment has a planar *anti,anti* conformation, (*ii*) the valence angles at C are fixed at tetrahedral values, and (*iii*) the C–H bond distances are fixed at 109 pm; the Ge–C bond distance and CGeC valence angle were optimised.

When this project was initiated *ab initio* m.o. calculations with geometry optimisation of GeH_2 and SnH_2 had already been published by Olbrich;[22] Trinquier and co-workers had provided the results of *ab initio* valence-only m.o. calculations on GeH_2 and $GeMe_2$ with two different Me-group conformations,[23] and the related species $HGeGeH_3$;[23,24] the result of structure optimisation for $SnMe_2$ had also appeared.[25] Our conclusions, together with the published data, on the equilibrium structures of MH_2 and MMe_2 are summarised in Table 2.

Table 2. Equilibrium structural parameters for germylenes and stannylenes MX_2 obtained by *ab initio* m.o. calculations

MX_2	M–X/pm	XMX/°	Ref.
GeH_2	157	93	22
	160	93	23
	158	93	This work
$GeMe_2$	202	98	23
	202	97	This work
SnH_2	176	93	22
	177	93	This work
$SnMe_2$	220	96	25

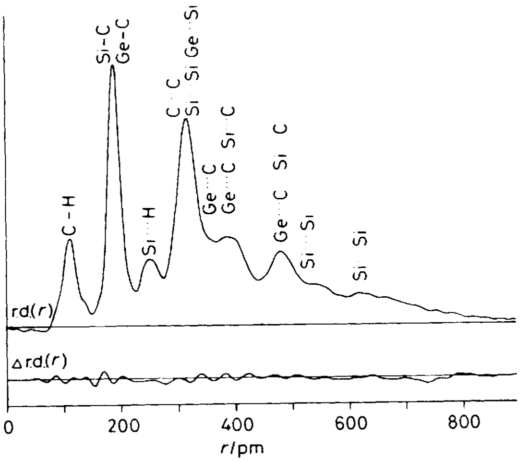


Figure 2. Experimental radial distribution (r.d.) curve for bis[bis(trimethylsilyl)methyl]germanium, GeR_2 [R = $CH(SiMe_3)_2$], and the residual curve Δr.d.(r) = exptl. r.d. − calc. r.d. corresponding to the best theoretical model (artificial damping factor k = 20 pm^2)

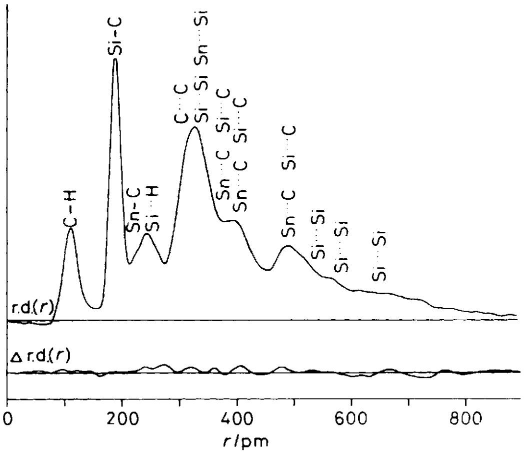


Figure 3. Experimental radial distribution curve for bis[bis(trimethylsilyl)methyl]tin, SnR_2 [R = $CH(SiMe_3)_2$], and the residual curve. Details as in Figure 2

Discussion of the Structures of MR_2 [M = Ge *or* Sn, R = $CH(SiMe_3)_2$], MH_2, *and* MMe_2.—As shown in Figure 1 and Table 1, the molecules MR_2 [M = Ge or Sn, R = $CH(SiMe_2)_2$] are V-shaped with CMC angles substantially

Table 3. Compilation of experimentally determined XMX angles and M–X bond lengths for germylenes GeX_2 and stannylenes SnX_2 [X = a monohapto anionic ligand, R = $CH(SiMe_3)_2$]

MX_2	XMX/°	⟨M–X⟩/pm	Method[a]	Ref.
GeR_2	107(2)	203.8(15)	g.e.d.	This work
SnR_2	97(2)	222(2)	g.e.d.	This work
$Ge[N(SiMe_3)_2]_2$	101(1.5)	189(1)	g.e.d.	26
$Sn[N(SiMe_3)_2]_2$	96	209(1)	g.e.d.	27
$Sn[N(SiMe_3)_2]_2$	104.7(2)	209(1)	*X*-ray	26
$Ge(NCMe_2[CH_2]_3CMe_2)_2$	111.4(5)	188	*X*-ray	28
$Ge(OCBu^t_3)_2$	85.9(4)	186(3)	*X*-ray	29
$Ge(OC_6H_2Bu^t_2\text{-}2,6\text{-}Me\text{-}4)_2$	92.0(4)	180.5(10)	*X*-ray	30
$Sn(OC_6H_2Bu^t_2\text{-}2,6\text{-}Me\text{-}4)_2$	88.8(4)	200.5(10)	*X*-ray	30
$Sn(SC_6H_2Bu^t_3\text{-}2,4,6)_2$	85.4(1)	243.5(1)	*X*-ray	31
GeF_2	97.15(3)	173.21(1)	Microwave	*a*
$GeCl_2$	100.3(5)	218.6(4)	g.e.d.	*b*
$SnCl_2$	99(1)	234.7(7)	g.e.d.	*c*

[a] H. Takeo and R. F. Curl, *J. Mol. Spectrosc.*, 1972, **43**, 21. [b] G. Schultz, J. Tremmel, I. Hargittai, I. Berecz, S. Bohátka, N. D. Kagramanov, A. K. Maltsev, and O. M. Nefedov, *J. Mol. Struct.*, 1979, **55**, 207. [c] I. Ischenko, L. S. Ivashkevich, E. Z. Zazarin, V. P. Spiridanov, and A. A. Ivanov, 6th Austin Symp. on Gas Phase Molecular Structure, 1976, abstracts, p. 89.

smaller than tetrahedral. Moreover, there is a significant CMC angle contraction with increasing atomic number of M (*i.e.* CGeC > CSnC). Both these features appear to be general for other germylenes and stannylenes MX_2, Table 3,[26–31] although in one case, $Ge(NCMe_2[CH_2]_3CMe_2)_2$,[28] the angle at M is marginally greater than 109°. [To date there is only one example, involving a pentahapto ligand X^-, in $Sn(\eta\text{-}C_5Ph_5)_2$, where there is linear geometry at M, *i.e.* centroid–Sn–centroid is 180°.[32]]

Each of the monohapto ligands X^- is exceedingly bulky, whence the kinetic stability of these heavy-atom carbene analogues MX_2 with respect to oligomerisation to yield $(MX_2)_n$. Steric effects must clearly also play an important role in influencing the magnitude of the XMX angle in MX_2. The XMX angle contraction for M = Sn with respect to M = Ge may be steric in origin.

It is, therefore, surprising that *ab initio* m.o. calculations for MH_2 and MMe_2 (Table 2) do not reveal any difference in the valence angles of MH_2 and MMe_2. This result may lend even greater weight to the steric criterion for accounting for the XMX trends in MX_2: *i.e.* there is increased ligand–ligand repulsion in the compound with the shorter M–X bond.

The highest occupied molecular orbital (h.o.m.o.) in each of GeH_2, $GeMe_2$, and SnH_2 is an a_1 metal-centred lone-pair orbital. The energy of this orbital increases rapidly with increasing valence angle. Calculated h.o.m.o. energies are −9.0 eV for GeH_2, −8.2 eV for $GeMe_2$, and −8.2 eV for SnH_2. The angular structures may therefore be rationalised as due to the steric requirements of the lone-pair electrons. First ionisation potentials for GeR_2 (7.75 eV) and SnR_2 (7.42 eV) have been measured by He I photoelectron spectroscopy.[33]

From Tables 1 and 2 it is evident that the experimentally determined equilibrium M–C bond distances in MR_2 [M = Ge or Sn, R = $CH(SiMe_3)_2$] are very similar to those calculated for MMe_2, and are significantly longer than in tetravalent molecules. The most direct experimental comparisons are for (*i*) Ge–C in GeR_2 [203.8(15) pm, g.e.d.] and $GeR_2(H)OEt$ [196(1) pm, *X*-ray[34]], (*ii*) Sn–C in SnR_2 [222(2) pm, g.e.d.] and $SnClR_3$ [218(1) pm, *X*-ray[35]], and (*iii*) M–C g.e.d. data on MMe_4 [M = Ge, 194.5(3) pm;[36] M = Sn, 214.4(2) pm[37]]. Similar trends have been noted for *N*-, *O*-, and *S*-centred ligands X^-, in that M–X bond lengths are greater in heavy-atom Group 4 metal carbene analogues MX_2 (*cf.* Table 3) than in metal(IV) amides, alkyl- or aryl-oxides, or arylthiolates. Moreover, calculated equilibrium Ge–H bond distances in a molecule containing divalent and tetravalent germanium likewise indicate that the bonding radius of M^{II} is 4—6 pm greater than the bonding radius of M^{IV}.[24] Both the less-than-tetrahedral valence angles, $HM^{II}H$ and $CM^{II}C$, and the difference between metal-(II) and -(IV) bond distances may be rationalised by assuming the electron lone pair on M^{II} to occupy an atomic orbital of predominant *s* character, and the M^{II}–H and M^{II}–C σ-bonding orbitals to be formed from metal(II) atomic orbitals of predominant *p* character.

The conformation of the best model for $M[CH(SiMe_3)_2]_2$, where the HC^iMC^iH fragments are close to a planar *syn,syn* conformation (Figure 1), comes close to maximising *interligand* distances. The shortest interligand $C^o \cdots C^o$ distance is calculated as 360 pm in GeR_2 and 370 pm in SnR_2. Rigid rotation of one ligand by 180° into a conformation where the HC^iMC^iH fragment is close to a planar *syn,anti* conformation (as in crystalline Sn_2R_4[4]) yields contacts of 260 (Ge) and 280 (Sn) pm.

In the parent molecule RH of the ligand, R^-, angle SiC^iSi is 123.2(9)°.[13] Introduction of a third large substituent (MR) bonded to C^i reduces the angle to 113 or 114° in GeR_2 or SnR_2, respectively.

Experimental

All the manipulative operations were carried out as described in Part 2.[3] Spectroscopic instrumentation was as outlined previously.[1] Bis(trimethylsilyl)methyl chloride, RCl, was prepared according to the modification[38] of our earlier[2] recipe.

Preparations.—$GeCl_2$(diox). Tri-n-butyltin hydride (52.4 g) (freshly prepared by $Li[AlH_4]$ reduction of $SnClBu^n_3$, distilled, and analysed by gas chromatography–mass spectrometry (g.c.–m.s.)] was added to germanium(IV) chloride (38.5 g) and 1,4-dioxane (30.35 cm^3) in a mixture of diethyl ether (100 cm^3) and n-hexane (100 cm^3) at ambient temperature. Mixing was mildly exothermic and a white precipitate was immediately formed. This was filtered off, washed with n-hexane, freed from solvent *in vacuo*, and identified as the essentially pure $GeCl_2$(diox) (35.0 g, 85%). In repeat experiments, the yield was found to be somewhat variable, but not less than 60%.

Bis(trimethylsilyl)methylmagnesium chloride–diethyl ether (1/1). Bis(trimethylsilyl)methyl chloride (2.57 g, 13.2 mmol) was added dropwise to a suspension of magnesium powder (0.50 g, 20.6 mmol) in refluxing diethyl ether (50 cm^3). After refluxing the mixture for 4 h, volatiles were removed *in vacuo*, and the residual white powder was extracted into n-hexane (70 cm^3). The extract was filtered through Celite. Cooling of the filtrate to -30 °C afforded white crystals of the required *Grignard compound* (2.27 g, 70%), m.p. 126—127 °C (Found: C, 43.8; H, 4.95. $C_{11}H_{29}ClMgOSi_2$ requires C, 45.1; H, 4.95%). The hydrogen-1 n.m.r. spectrum (C_6D_6) showed the following signals (p.p.m. relative to 7.27 p.p.m. for C_6D_5H), with relative intensities and assignments in parentheses: -1.45 (1, CH), 0.52 [18, $Si(CH_3)_3$], triplet centred at 1.0 (6, CH_2CH_3), and quartet centred at 3.62 (4, CH_2CH_3). The carbon-13 n.m.r. spectrum (C_6D_6) showed the following signals (p.p.m. relative to 128.0 p.p.m. for C_6D_6) (assignments in parentheses): -0.025 (CH), 4.84 [$Si(CH_3)_3$], 13.41 (CH_2CH_3), and 65.29 (CH_2CH_3).

Tetra-alkyldigermene Ge_2R_4 [$R = CH(SiMe_3)_2$]. Bis(trimethylsilyl)methylmagnesium chloride–diethyl ether (1/1) (1.14 g, 3.89 mmol) was added in portions during 0.5 h to a solution of germanium(II) chloride–dioxane (1/1) (0.45 g, 1.94 mmol) in diethyl ether (20 cm^3). The formation of a fluffy white precipitate was virtually instantaneous with a concomitant colour change from colourless, through yellow, finally to a deep red. The mixture was heated under reflux for 6 h, whereafter volatiles were removed *in vacuo* and the red-orange waxy solid was repeatedly extracted with toluene. Filtration through Celite afforded a clear orange-yellow filtrate, from which volatiles were again removed *in vacuo*. The residual solid was recrystallised twice from n-hexane, affording bright yellow crystals of the compound Ge_2R_4 (0.59 g, 75%), m.p. 182 °C (lit.,[2] 179—181 °C).

Similarly, the dialkylmagnesium reagents [$(MgR_2)_2(\mu\text{-diox})$] or $MgR_2(OEt_2)$ were used to produce Ge_2R_4 in 60—70% yields.

Qualitative differences were observed in the rate of appearance of the red colour (and hence presumably of Ge_2R_4) depending on the nature of the magnesium reagent employed: $MgR_2(diox)_{0.5} \gg MgR_2(OEt_2) > MgCl(R)(OEt_2)$.

A solution of the Grignard reagent, *i.e.* MgCl(R) in OEt_2, can also be used to produce Ge_2R_4, but this is not the preferred procedure from the standpoint of yield or purity of product.

Bis[bis(trimethylsilyl)methyl]dichlorotin(IV). Bis(trimethylsilyl)methyl-lithium (0.53 g, 3.18 mmol) was added in portions during 1 h to a solution of tin(IV) chloride (0.18 cm^3, 1.59 mmol) in n-hexane (25 cm^3). The reaction mixture was stirred overnight. n-Pentane (25 cm^3) was added and the mixture was filtered through Celite. Volatiles were removed *in vacuo* to leave a free-flowing, white powder of the compound $SnCl_2R_2$ (1.36 g, 84%), m.p. 70—72 °C.

In another experiment, an ether solution of bis(trimethylsilyl)methyl-lithium (10.0 cm^3, 0.3 mol dm^{-3}) and *N,N,N′,N′*-tetramethylethylenediamine (0.23 cm^3, 1.5 mmol) was added dropwise to a cold (-78 °C) solution of tin(IV) chloride (0.17 cm^3, 1.5 mmol) in n-pentane (10 cm^3). A white solid was immediately precipitated. The reaction mixture was allowed to warm to room temperature and stirring was maintained overnight. Diethyl ether (*ca.* 30 cm^3) was added and the mixture was refluxed (2.5 h), filtered (Celite), and pumped to dryness. Methanol (*ca.* 1 cm^3) was added and again all volatiles were removed *in vacuo*. n-Pentane (*ca.* 30 cm^3) was added and the mixture was filtered through Celite; the filtrate was concentrated to dryness *in vacuo* leaving a sticky white oil, which gradually solidified after being kept at 20 °C (5×10^{-3} Torr) for 48 h. It was identified as $SnCl_2R_2$, with no reduction apparent or formation of bis[bis(trimethylsilyl)methyl]tin(II), and the yield was essentially quantitative.

In a third experiment, dropwise addition of an ether solution of bis(trimethylsilyl)methyl-lithium (30 cm^3, 0.54 mol dm^{-3}) to a solution of tin(IV) chloride (0.93 cm^3, 8.1 mmol) in n-pentane (50 cm^3) immediately yielded a heavy, white precipitate. Towards the end of the addition a persistent (*ca.* 10—20 s) pink-red colour was observed. Reflux was maintained overnight, whereafter the mixture was stirred for a further 24 h. *N,N,N′,N′*-Tetramethylethylenediamine (0.65 cm^3, 4.05 mmol) was added to the resultant pale yellow mixture. The solution was refluxed for a further 3 h, and was then filtered. The filtrate was concentrated *in vacuo* with heating, to leave an oil. This slowly solidified at 20 °C (5×10^{-3} Torr) to yield the *compound* $SnCl_2R_2$ (2.75 g, 67%) (Found: C, 34.5; H, 7.75. $C_{14}H_{38}Cl_2Si_4Sn$ requires C, 33.1; H, 7.55%).

Tetra-alkyldistannene Sn_2R_4 [$R = CH(SiMe_3)_2$] *by a reduction procedure.* Under an atmosphere of argon, an ether solution of dilithiocyclo-octatetraene (2.23 cm^3, 0.22 mol dm^{-3}) was added dropwise, during 1 min, to a cooled (-80 °C) ether (10 cm^3) solution of bis[bis(trimethylsilyl)methyl]dichlorotin(IV) (0.26 g, 0.51 mmol). The bath temperature was not allowed to exceed -25 °C during 5.5 h, whereafter the mixture was allowed to warm up to room temperature overnight. The orange-red mixture was filtered and cooled (-78 °C) for *ca.* 18 h. Red-orange crystals were isolated by filtration at this temperature. The precipitate of the compound Sn_2R_4 (0.13 g, 58%), m.p. 134—136 °C (lit.,[2] 135—137 °C), was freed from solvent *in vacuo.*

The germylene, GeR_2, *and stannylene,* SnR_2 [$R = CH(SiMe_3)_2$], *for gas-phase electron diffraction.* Each of the monomeric compounds GeR_2 or SnR_2 was introduced in turn into the Balzers Eldigraph KDG-2 instrument by vaporising the solid dimer at *ca.* 155 (GeR_2) or *ca.* 120 °C (SnR_2) at *ca.* 0.1 Torr. As noted previously,[2] mass spectrometry of each vapour indicated solely the monomer, and this was confirmed by the g.e.d. analyses.

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