

Subvalent Group 4B Metal Alkyls and Amides. Part 9.¹ Germanium and Tin Alkene Analogues, the Dimetalenes M_2R_4 [$M = \text{Ge}$ or Sn , $R = \text{CH}(\text{SiMe}_3)_2$]: X-Ray Structures,[†] Molecular Orbital Calculations for M_2H_4 , and Trends in the Series $M_2R'_4$ [$M = \text{C}$, Si , Ge , or Sn ; $R' = \text{R}$, Ph , $\text{C}_6\text{H}_2\text{Me}_3$ -2,4,6, or $\text{C}_6\text{H}_3\text{Et}_2$ -2,6]

David E. Goldberg, Peter B. Hitchcock,* Michael F. Lappert,* K. Mark Thomas, and Andrew J. Thorne

School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ

Torgny Fjeldberg

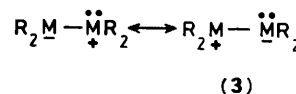
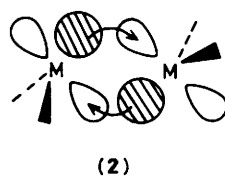
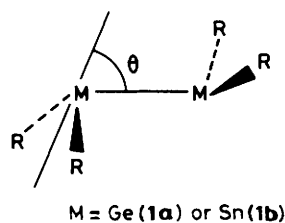
Department of Chemistry, University of Trondheim NLHT, Trondheim, Norway

Arne Haaland* and Birgitte E. R. Schilling

Department of Chemistry, University of Oslo, Blindern, Oslo 3, Norway

X-Ray structures of the isomorphous centrosymmetric crystalline Ge_2R_4 and Sn_2R_4 [$R = \text{CH}(\text{SiMe}_3)_2$] reveal a *trans*-folded C_{2h} M_2C_4 framework, with a fold angle θ of 32° for $M = \text{Ge}$ and 41° for $M = \text{Sn}$, but no twist of the MC_2 planes about the $M-M$ axis. The $M-M$ distance [$2.347(2)$ Å for Ge and $2.768(1)$ Å for Sn] is slightly shorter (4% for $M = \text{Ge}$, 1.5% for $M = \text{Sn}$) than in the tetrahedral element, M_∞ . The conformation of each MR_2 moiety in M_2R_4 approximates to planar *syn,anti* (cf. *ca. syn,syn* in gaseous MR_2), and the four ligands R^- are oriented in a 'paddle-wheel' fashion. There is consequently an asymmetry in the $M-C$ bonding in M_2R_4 as shown (data for $M = \text{Sn}$ in square brackets) by variations in $M-C$ and $M-C'$ (Å), 1.979(9) and 2.042(8) [2.207(5) and 2.225(6)]; $M'MC$ and $M'MC'$ ($^\circ$), 113.7(3) and 122.3(2) [112.0(1) and 119.4(1) $^\circ$]; individual MCSi angles ($^\circ$), 110.0(4) [110.2(3)], 113.9(4) [109.3(3)], 119.1(4) [119.1(2)], and 121.8(4) [118.9(2)]. The average $M-C$ bond lengths are comparable but the CMC angles are wider in M_2R_4 than those previously found for gaseous MR_2 . *Ab initio* molecular orbital calculations with better than double zeta basis on the model compounds M_2H_4 show that (i) *trans*-folded equilibrium structures are more stable than planar by 13 kJ mol^{-1} ($\theta = 40^\circ$) for $M = \text{Ge}$ and 26 kJ mol^{-1} ($\theta = 46^\circ$) for Sn ; (ii) the $M-M$ bond distance is 2.30 Å for Ge and 2.71 Å for Sn ; and (iii) the $M-M$ dissociation energy is 130 kJ mol^{-1} for Ge and 90 kJ mol^{-1} for Sn . These energies are about half the experimental $M-M$ single-bond dissociation energies of H_3GeGeH_3 or Me_3MMMe_3 . The decreasing strength of $M-M$ bonding in the series $M_2R'_4$ [$M = \text{C}$, Si , Ge , or Sn ; $R' = \text{R}$, Ph , $\text{C}_6\text{H}_2\text{Me}_3$ -2,4,6, or $\text{C}_6\text{H}_3\text{Et}_2$ -2,6] or, more generally, M_2X_4 ($X = R'$ or H) with increasing atomic number of M , as well as the increasing stability of the *trans*-folded relative to planar structures, is attributed to the increasing inertness of the electron lone pair in the MX_2 ($X = R'$ or H) monomer, which in turn is reflected in an increasing singlet \rightarrow triplet excitation energy.

In 1976 we described in preliminary form the crystal structure of the first heavy Main Group 4 metal analogue of an alkene, the diamagnetic, brick-red Sn_2R_4 [$R = \text{CH}(\text{SiMe}_3)_2$], having the centrosymmetric structure (1b), with each tin atom in a pyramidal environment (sum of angles at each $\text{Sn} = 342^\circ$).² The Sn-Sn bond length of 2.764(2) Å was similar to that found in Sn_2Ph_6 . Nevertheless, the Sn-Sn bond in Sn_2R_4 was weak, because in dilute solution, in benzene or cyclohexane, the cryoscopic molecular weight corresponded to that of the monomer, the carbene analogue SnR_2 .³ The Mössbauer spectrum of Sn_2R_4 at 77 K yielded an isomer shift of 2.16 mm s^{-1} (relative to BaSnO_3), a quadrupole splitting of 2.31 mm s^{-1} , and a negative quadrupole coupling constant eQV_{zz} (from magnetic Mössbauer measurements), consistent with structure (1).⁴ The bright yellow, solid, diamagnetic germanium(II) alkyl



$M = \text{Ge}$ or Sn , $R = \text{CH}(\text{SiMe}_3)_2$

† Tetrakis[bis(trimethylsilyl)methyl]di-germene and -stannene.

Supplementary data available (No. SUP 56580, 8 pp.): H-atom coordinates, torsional angles, thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii-xx. Structure factors are available from the editorial office.

Non-S.I. unit employed: Torr \approx 133 N m⁻².

showed a strong Raman band at 300 cm^{-1} , attributed to $\nu(\text{Ge-Ge})$ in Ge_2R_4 (1a); however, cryoscopy indicated dissociation into the monomeric germylene GeR_2 in C_6H_{12} .³

The original interpretation of these findings was in terms of a

double donor-acceptor bond (2) or, alternatively, the valence bond representation (3);^{2,3} the latter model was also advocated elsewhere.^{5,6} These descriptions appeared to account for the observed geometry and the weakness of the M-M bond with respect to dissociation.

In Part 8 we described (as well as synthetic procedures) the structures of these two compounds by gas electron diffraction (g.e.d.).¹ In the gas phase (120–155 °C, 1 Torr), they exist as the monomeric V-shaped dialkyl-germylene or -stannylene MR₂ [M = Ge or Sn]. The detailed structural parameters agreed reasonably with *ab initio* molecular orbital (m.o.) calculations on the model compounds MH₂ and MMe₂.

In preliminary publications we have given a brief account of (i) the X-ray structure of Ge₂R₄⁷ and (ii) m.o. calculations on the model compounds Ge₂H₄⁸ and Sn₂H₄.⁹ We have also correlated our Ge₂R₄ X-ray data with those for Sn₂R₄^{2,3} and those published by others on C₂Ph₄¹⁰ and Si₂(C₆H₂Me₃-2,4,6)₄.¹¹ Recent reviews have included discussions of the Main Group 4 dimetallanes.¹²

We now provide full accounts of the results of the X-ray structure determination of Ge₂R₄ and of m.o. calculations on Ge₂H₄ and Sn₂H₄. The X-ray structure of Sn₂R₄ has been redetermined, using a better quality crystal; a discussion is provided of structural trends for a wider range of dimetallanes, including M₂(C₆H₃Et₂-2,6)₄ (M = Si¹³ or Ge¹⁴), and *trans*-[Si(Bu¹)(C₆H₂Me₃-2,4,6)]₂.¹⁵

Results and Discussion

The samples of Ge₂R₄ and Sn₂R₄ were obtained as described in Part 8.¹ X-Ray quality crystals were grown by low-temperature recrystallisation from concentrated toluene solutions.

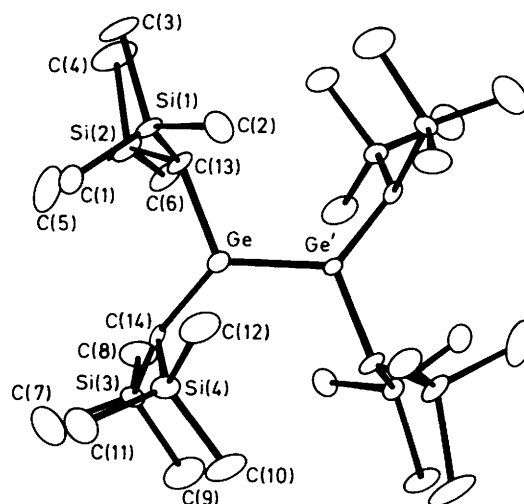


Figure 1. Molecular structure and atom numbering scheme for {Ge[CH(SiMe₃)₂]₂}₂ (**1a**)

*Molecular Structures of the Crystalline Tetra-alkyldimetalenes, M₂R₄ [R = CH(SiMe₃)₂, M = Ge (**1a**) or Sn (**1b**)]*.—The crystal structures of Ge₂R₄ (**1a**) and Sn₂R₄ (**1b**) have nearly identical cell dimensions and contain discrete dimers lying across inversion centres with no significantly short inter-dimer contacts. The molecular structures and atom numbering scheme are shown in Figures 1 and 2, which are views from different directions of what are very similar molecules. Intramolecular distances and angles are listed in Table 1, least-squares plane calculations in Table 2, and fractional atomic co-ordinates for non-hydrogen atoms in Table 3.

Table 1. Intramolecular distances (Å) and angles (°) for M₂R₄ [R = CH(SiMe₃)₂ and M = Ge, (**1a**), or Sn, (**1b**)]; estimated standard deviations are given in parentheses*

(a) Bonds	(1a)	(1b)	Bonds	(1a)	(1b)
M-M'	2.347(2)	2.768(1)	M-C(13)	2.042(8)	2.225(6)
M-C(14)	1.979(9)	2.207(5)	Si(1)-C(1)	1.858(11)	1.857(7)
Si(1)-C(2)	1.857(10)	1.870(7)	Si(1)-C(3)	1.901(10)	1.880(9)
Si(1)-C(13)	1.850(9)	1.877(7)	Si(2)-C(4)	1.885(12)	1.865(10)
Si(2)-C(5)	1.863(14)	1.876(9)	Si(2)-C(6)	1.866(10)	1.862(10)
Si(2)-C(13)	1.911(9)	1.864(5)	Si(3)-C(7)	1.829(13)	1.848(10)
Si(3)-C(8)	1.836(11)	1.830(9)	Si(3)-C(9)	1.860(12)	1.831(15)
Si(3)-C(14)	1.905(8)	1.882(6)	Si(4)-C(10)	1.851(10)	1.858(11)
Si(4)-C(11)	1.812(13)	1.843(10)	Si(4)-C(12)	1.826(11)	1.883(9)
Si(4)-C(14)	1.927(9)	1.883(5)			
(b) Angles	(1a)	(1b)	Angles	(1a)	(1b)
M'-M-C(13)	113.7(3)	112.0(1)	M'-M-C(14)	122.3(2)	119.4(1)
C(13)-M-C(14)	112.5(3)	109.2(2)	C(1)-Si(1)-C(2)	110.3(5)	110.5(3)
C(1)-Si(1)-C(3)	105.7(5)	105.0(4)	C(1)-Si(1)-C(13)	112.4(4)	113.7(3)
C(2)-Si(1)-C(3)	106.1(5)	106.0(4)	C(2)-Si(1)-C(13)	110.6(4)	110.4(4)
C(3)-Si(1)-C(13)	111.5(4)	110.9(3)	C(4)-Si(2)-C(5)	107.5(6)	109.9(7)
C(4)-Si(2)-C(6)	105.2(5)	104.5(5)	C(4)-Si(2)-C(13)	110.8(5)	110.6(4)
C(5)-Si(2)-C(6)	109.2(5)	107.9(5)	C(5)-Si(2)-C(13)	111.0(5)	110.4(3)
C(6)-Si(2)-C(13)	112.9(4)	113.4(4)	C(7)-Si(3)-C(8)	108.5(6)	107.7(6)
C(7)-Si(3)-C(9)	106.9(6)	105.9(6)	C(7)-Si(3)-C(14)	110.2(5)	111.3(5)
C(8)-Si(3)-C(9)	103.8(6)	104.9(7)	C(8)-Si(3)-C(14)	113.0(4)	112.7(4)
C(9)-Si(3)-C(14)	114.1(5)	113.9(4)	C(10)-Si(4)-C(11)	105.8(6)	109.2(5)
C(10)-Si(4)-C(12)	105.4(5)	104.8(4)	C(10)-Si(4)-C(14)	113.6(4)	112.7(4)
C(11)-Si(4)-C(12)	107.8(6)	106.6(5)	C(11)-Si(4)-C(14)	109.9(5)	110.0(4)
C(12)-Si(4)-C(14)	113.7(4)	113.3(3)	M-C(13)-Si(1)	119.1(4)	119.1(2)
M-C(13)-Si(2)	110.0(4)	110.2(3)	Si(1)-C(13)-Si(2)	116.8(5)	117.4(4)
M-C(14)-Si(3)	113.9(4)	109.3(3)	M-C(14)-Si(4)	121.8(4)	118.9(2)
Si(3)-C(14)-Si(4)	112.9(5)	116.1(3)			

* M' indicates M atom at \bar{x} , \bar{y} , \bar{z} .

For both the molecules M_2R_4 there is an M_2C_4 framework with approximate C_{2h} symmetry which, however, does not extend to the substituents on the C atoms. The $CH(SiMe_3)_2$ groups are arranged with the H substituents in the rough plane of the M_2C_4 atoms and pointing cyclically around the molecule

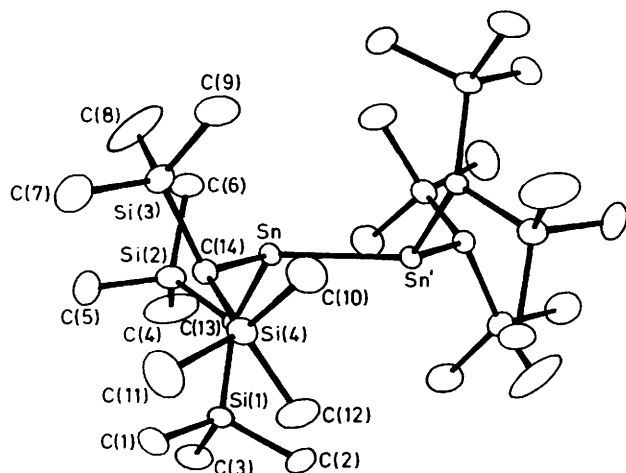


Figure 2. Molecular structure and atom numbering scheme for $\{Sn[CH(SiMe_3)_2]_2\}_2$ (**1b**)

Table 2. Deviations (\AA) of atoms from various mean planes for M_2R_4 [$R = CH(SiMe_3)_2$ and $M = Ge$, (**1a**), or Sn , (**1b**); atoms marked * were not used in the calculation of the plane

Compound (**1a**)

- (a) Ge , $C(13)$, $C(14)$; Ge^* 1.25
 (b) $C(13)$, $Si(1)$, $Si(2)$; Ge^* -1.25
 (c) $C(14)$, $Si(3)$, $Si(4)$; Ge^* 1.06

Angles between planes ($^\circ$): a-b 83, a-c 81, b-c 72

Compound (**1b**)

- (d) Sn , $C(13)$, $C(14)$; Sn^* 1.83
 (e) $C(13)$, $Si(1)$, $Si(2)$; Sn^* -1.32
 (f) $C(14)$, $Si(3)$, $Si(4)$; Sn^* 1.40

Angles between planes ($^\circ$): a-b 78, a-c 80, b-c 67

in a manner presumably decided by intramolecular steric constraints.

The redetermination of the Sn_2R_4 structure provides molecular parameters which are more accurate than those obtained previously.^{2,3} The small differences between the two sets of dimensions are only marginally significant on the basis of the e.s.d.s of the earlier results. However, the Sn-C bond length, which previously averaged 2.28(3) \AA , was noted as being significantly longer than that in $[Cr(CO)_5(SnR_2)]$ (2.185 \AA average);¹⁶ this was ascribed to the π -electron-withdrawing effect of the $Cr(CO)_5$ moiety. The present data now lead to an average Sn-C bond length of 2.216(9) \AA , which is essentially the same as in the Cr complex.

In each M_2R_4 molecule ($M = Ge$ or Sn) the bonding at the M atoms is not planar but shows distortion towards pyramidity. There is a *trans*-folding (θ) of the MC_2 moieties which is greater for Sn ($\theta = 41^\circ$) than for Ge ($\theta = 32^\circ$). [The fold angle θ , see (1), is defined as the angle between the M-M vector and the MC_2 plane of each monomer.] There is no twist (τ) of the MC_2 planes about the M-M axis. There is an asymmetry in the M-C bonding since in both structures the M-C(14) (see Figures 1 and 2) bond is significantly shorter than the M-C(13) bond, whilst the M'-M-C(13) angle is smaller than the M'-M-C(14) angle, by *ca.* 7° , probably for steric reasons. The C(13) and C(14) atoms bonded to M have three bulky substituents and the average angle between them is $116(4)^\circ$ for Ge and $115(4)^\circ$ for Sn; however, there are wide variations in the individual angles with M-C(13)-Si(1) and M-C(14)-Si(4), average $120.4(4)^\circ$ for Ge and $119.0(1)^\circ$ for Sn, considerably larger than the others. This latter effect may also have a steric origin; presumably it counteracts the otherwise close approach of the Si(1)Me₃ and Si(4)Me₃ groups caused by the out-of-plane folding at the M atoms. The Si-C(H) distances average 1.90(3) \AA for Ge and 1.88(1) \AA for Sn, which are only marginally longer than the average Si-CH₃ bond lengths of 1.85(2) for Ge and 1.86(2) for Sn. The CH-Si-CH₃ angles average $112(1)^\circ$ whilst the CH₃-Si-CH₃ angles average $107(2)^\circ$ in both structures.

In (**1a**), the Ge-Ge bond length of 2.347(2) \AA is longer than that found in tetrakis(2,6-diethylphenyl)digermene [2.213(2) \AA]¹⁴ but is still significantly shorter than Ge-Ge single bonds, *e.g.* 2.445 \AA in tetrahedral Ge_4 ,¹⁷ 2.465 \AA in $(GePh_2)_4$,¹⁸ or 2.463 and 2.457 \AA in $(GePh_2)_6$.¹⁹ In (**1b**), the Sn-Sn bond length of 2.768(1) \AA is slightly shorter than Sn-Sn single bonds, *e.g.*

Table 3. Fractional atomic co-ordinates ($\times 10^4$) for the non-hydrogen atoms of M_2R_4 (**1a**) and (**1b**); estimated standard deviations in parentheses

Atom	$\{Ge[CH(SiMe_3)_2]_2\}_2$ (1a)			$\{Sn[CH(SiMe_3)_2]_2\}_2$ (1b)		
	x	y	z	x	y	z
M	-593(2)	109(1)	1 000(2)	-805.6(4)	177.6(3)	1 097.8(3)
Si(1)	1 035(4)	1 718(3)	1 655(4)	1 003(2)	1 827(1)	1 754(1)
Si(2)	-2 690(5)	2 562(4)	2 056(4)	-2 745(2)	2 810(2)	1 997(2)
Si(3)	-1 980(5)	-2 002(4)	3 237(4)	-2 006(2)	-1 998(2)	3 410(2)
Si(4)	1 734(5)	-2 689(4)	2 598(4)	1 739(2)	-2 652(2)	2 656(2)
C(1)	1 272(16)	645(13)	3 227(13)	1 272(8)	743(7)	3 252(6)
C(2)	2 866(15)	1 259(14)	502(14)	2 840(8)	1 381(7)	636(7)
C(3)	783(16)	3 365(12)	1 690(16)	788(8)	3 418(6)	1 821(8)
C(4)	-2 978(20)	4 284(15)	1 828(19)	-3 005(11)	4 528(8)	1 551(13)
C(5)	-2 986(20)	1 764(18)	3 749(16)	-3 033(11)	2 162(12)	3 649(8)
C(6)	-4 288(16)	2 623(13)	1 459(15)	-4 391(8)	2 761(7)	1 527(7)
C(7)	-2 155(20)	-2 623(18)	4 911(18)	-1 993(12)	-2 870(11)	4 988(9)
C(8)	-3 857(17)	-788(14)	2 919(17)	-3 911(11)	-721(10)	3 316(15)
C(9)	-1 808(18)	-3 319(15)	2 685(18)	-2 041(11)	-3 092(9)	2 735(10)
C(10)	2 055(17)	-3 988(13)	1 968(16)	1 948(10)	-3 858(7)	1 982(8)
C(11)	1 887(22)	-3 446(18)	4 200(18)	2 164(13)	-3 448(11)	4 159(8)
C(12)	3 398(18)	-2 118(14)	1 777(17)	3 376(8)	-1 992(7)	1 746(9)
C(13)	-649(15)	1 738(11)	1 218(12)	-752(6)	1 913(4)	1 295(4)
C(14)	-270(13)	-1 361(10)	2 493(11)	-280(6)	-1 403(5)	2 706(5)

Table 4. Comparison of some key molecular structural parameters for M_2R_4 and MR_2 (from ref. 1) [$M = Ge$ or Sn , $R = CH(SiMe_3)_2$]

M in $(MR_2)_n$	M-C/Å		C-M-C/°		Conformation of the HC ⁱ MC ⁱ H moiety ^c	
	Crystal ^a		Gas ^b		Crystal ^a	Gas ^b
	Crystal ^a		Gas ^b		Crystal ^a	Gas ^b
Ge	1.979(9), 2.042(8)	2.038(15)	112.5(3)	107(2)	<i>syn, anti</i>	<i>syn, syn</i>
Sn	2.207(5), 2.225(6)	2.22(2)	109.2(2)	97(2)	<i>syn, anti</i>	<i>ca. syn, syn</i> ^d

^a $n = 2$, i.e., M_2R_4 . ^b $n = 1$, i.e., MR_2 . ^c Cⁱ refers to the inner, or methine, carbon atom. ^d In GeR_2 the HCⁱMCⁱH moiety has a nearly planar *syn, syn* conformation, whereas in SnR_2 there is a twist of $15(2)^\circ$.

Table 5. Selected equilibrium structural parameters for the tetrahydridodimetalenes M_2H_4 , and energy difference between D_{2h} and C_{2h} structures, obtained by *ab initio* m.o. calculations

M_2H_4	M-M/Å	Fold angle, $\theta/^\circ$	M-H/Å	H-M-H/°	$\Delta E/kJ mol^{-1}$ ^a	Ref.
H_2GeGeH_2	2.302	34.4	1.550	111.1	7.7	22
H_2GeGeH_2	2.272	36.2	1.536	109.5	6.7	23
H_2GeGeH_2	2.30	40	(1.58) ^b	107	13	c
H_2SnSnH_2	2.71	46	(1.77) ^b	105	26	c

^a Energy difference between optimal planar and *trans*-folded M_2H_4 structures. ^b Not optimised. ^c This work.

Table 6. Comparison of some structural parameters for the quasi-isoleptic series of Main Group dimetalenes $M_2R'_4$ ($M = C, Si, Ge, or Sn$)

M, R' in $M_2R'_4$	Sum of angles at M, $\Sigma/^\circ$	Fold angle, $\theta/^\circ$	Twist angle, $\tau/^\circ$	M-C(sp^2 or sp^3)/Å	MM/Å	M-M in M_∞ ^a /Å	Percentage shortening	Ref.
(8) C, Ph	360	0	8.4	1.494	1.356	1.545	12	10
(4) Si, $C_6H_2Me_3-2,4,6$	356.3	18	6.5	1.871	2.160	2.352	8	11, 15
(5) Si, $C_6H_3Et_2-2,6$	360.0	0	10	1.882	2.140	2.352	9	13
(6) Si, $(Bu^i, C_6H_2Me_3-2,4,6)_1$	359.9	0	0	1.884	2.143	2.352	9	15
(7) Ge, $C_6H_3Et_2-2,6$	358.4	15	11	1.962	2.213	2.445	9	14
(1a) Ge, $CH(SiMe_3)_2$	348.5	32	0	2.010	2.347	2.445	4	b
(1b) Sn, $CH(SiMe_3)_2$	340.6	41	0	2.216	2.768	2.810	1.5	b

^a From ref. 17. ^b This work.

2.810 Å in tetrahedral Sn_∞ ,¹⁷ but essentially the same as the 2.780(4) and 2.759(4) Å in Sn_2Ph_6 ,²⁰ or 2.77, 2.78, and 2.77 Å in $(SnPh_2)_6$.²¹ Further pertinent structural comparisons relate to those between the tetra-alkyldimetalenes M_2R_4 (1) and their corresponding dialkylcarbene analogues MR_2 ,¹ as summarised in Table 4. The averaged M-C bond lengths in compounds (1) are similar to those in their monomer equivalents, whilst the CMC bond angles are significantly greater, and there is a difference in conformation of the geminal R^- ligands.

Molecular Orbital Calculations on the Tetrahydridodimetalenes, M_2H_4 ($M = Ge$ or Sn).—The *ab initio* m.o. calculations on M_2H_4 ($M = Ge$ or Sn) were carried out with the program DISCO,¹ employing the following Gaussian type basis functions [for atom Y an (x, y, z) basis contracted to $\langle x', y', z' \rangle$]: Y = Sn (15,11,6) to $\langle 10,8,4 \rangle$; Y = Ge (14,11,15) to $\langle 8,7,3 \rangle$; Y = Si (10,6,1) to $\langle 6,2,1 \rangle$; Y = C (7,3) to $\langle 4,2 \rangle$; and Y = H (4) to $\langle 2 \rangle$.

The structures of the tetrahydridodimetalenes were partially optimised under D_{2h} and under C_{2h} symmetry. The M-H bond distances were fixed at the optimal values for the monomers.¹ For the planar D_{2h} model, the M-M distance and HMH angle were optimised; for the non-planar *trans*-folded C_{2h} structure, the distance M-M, angle HMH, and the fold angle θ were optimised. (The angle θ is defined as the angle between the M-M vector and the MH_2 plane).

While this work was in progress,^{8,9} others published *ab initio* calculations on H_2GeGeH_2 ,^{22,23} H_3GeGeH_3 ,²² and $HGeGeH_3$.^{22,23} Our conclusions, together with these published data, on the equilibrium structures of H_2MMH_2 ($M = Ge$ or Sn) are summarised in Table 5. Charge iterative relativistic extended-

Hückel calculations for H_2MMH_2 ($M = Ge, Sn, or Pb$) have been performed,²⁴ as well as MNDO calculations for $H_2-SnSnH_2$.²⁵

The Nature of the M-M Bond in Main Group 4 Dimetalenes.—For a comparison of the M-M bond in a series of Main Group 4 dimetalenes M_2X_4 ($M = C, Si, Ge, Sn, or Pb$; X is a unidentate ligand) it would be ideal if data on an isoleptic series were available (i.e. the same X^- for each M, e.g. M_2R_4). However, experimentally the only dimetalenes so far known to be stable are a selected number of hydrocarbyls: X-ray data are accessible not only on various alkenes, but also on M_2R_4 (1), $Si_2R^1_4$ ($R^1 = C_6H_2Me_3-2,4,6$ throughout) (4),¹¹ or $Si_2R^2_4$ ($R^2 = C_6H_3Et_2-2,6$ throughout) (5),¹³ *trans*-($SiBu^iR^1$)₂ (6),¹⁵ and $Ge_2R^2_4$ (7),¹⁴ which, except for compounds (5) and (6), are *trans*-folded. It is evident that in each of (1a), (1b), and (4)–(7), the hydrocarbyl ligand is bulky, and this must be a factor in determining their kinetic stability with respect to oligomerisation. Nevertheless, the crystal structures of these tetrahydrocarbyldimetalenes reveal that the steric compression is not so excessive as to give rise to dissociation into the monomers [e.g. the M-M bond lengths are of the same magnitude or shorter than found in tetravalent compounds, including the diamond form of the elements (M_∞),¹⁷ see Table 6].

The following experimental findings relating to the quasi-isoleptic series $M_2R'_4$ [C_2Ph_4 (8), (1a), (1b), or (4)–(7)] require accommodation: variations in (i) the geometry at M, (ii) the symmetry of the M_2C_4 skeleton, (iii) the M-M bond length relative to a standard (e.g. M-M in tetrahedral, or diamond-like, M_∞), and (iv) the propensity for dissociation into $2MR'_2$. Additionally, we note that Main Group 4 dimetalenes are at

present not found for other than hydrocarbyls or their derivatives (*e.g.* R). Thus, a number of crystalline $(MX_2)_n$ molecules having bulky X^- ligands, which are N-, O-, or S-centred, are monomers (*i.e.* $n = 1$; for bibliography, see ref. 1). The reasons are probably not steric, *cf.* the isoelectronic ligands $N(SiMe_3)_2^-$ and (the sterically slightly more demanding) $CH(SiMe_3)_2^-$. As for items (i)—(iii), comparative quantitative data are in Table 6. With regard to (iv), qualitative observations show that the Ge and Sn compounds M_2R_4 (1) dissociate readily (see Introduction section), and almost certainly are more labile than the Si or Ge compounds (4)—(7); whereas alkenes, of course, have a very high C=C bond dissociation energy. The *ab initio* m.o. calculations focus, *inter alia*, onto each of the

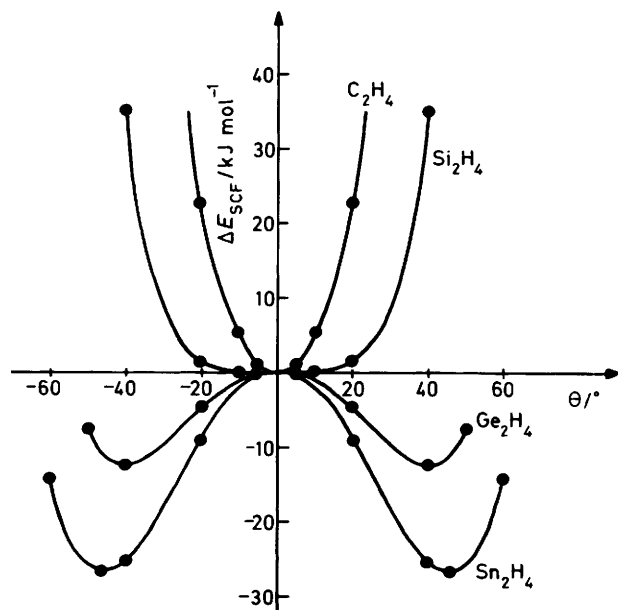


Figure 3. Variation of SCF energies for M_2H_4 with the *trans*-fold angle θ . The curves for C_2H_4 and Si_2H_4 were calculated for non-adiabatic folding (*i.e.*, with constant values for M–M and M–H bond lengths and H–M–H bond angles). The curves for Ge_2H_4 and Sn_2H_4 were calculated for adiabatic folding (*i.e.*, with reoptimised values for the M–M bond lengths and H–M–H angles)

problems (i)—(iv), as far as they relate to the tetrahydridodigermenes and -stannenes, M_2H_4 .

The geometry at M in $M_2R'_4$ at one extreme might be expected to be trigonal planar, with the sum of bond angles at M (Σ) equal to 360° ; while with increasing pyramidity at M, Σ will tend to the limit of *ca.* 330° . From Table 6 it is evident that for the series of crystalline molecules $M_2R'_4$, there is an increasing tendency for pyramidity with increasing atomic number of M, and the percentage shortening of the M–M bond length in $M_2R'_4$ compared to that in the diamond form, M_∞ , of the element decreases in the sequence $C > Si > Ge > Sn$. It can also be seen that for each of the pairs of disilenes (4) and (5) or the two digermenes (1a) and (7), the one with the lower fold angle (θ) has a shorter M–M bond. Whilst these differences in bond length might be due to different partial double-bond character, it should also be remembered that in the molecule with the larger fold angle the bonds to the M atom are formed using hybrid orbitals on M that have a higher *p* component and hence a larger effective covalent radius.

Comparison of the calculated equilibrium structures of M_2H_4 (Table 5) with those of M_2R_4 [$M = Ge$ (1a) or Sn (1b); Table 1] shows that the *trans*-folded symmetry of the M_2X_4 ($X = H$ or C) skeleton is not an artefact arising from the bulky ligands R or crystal packing forces, but rather is an inherent electronic property of digermenes or distannenes.

The experimental M–M bond distances in M_2R_4 ($M = Ge$ or Sn) are 0.04–0.05 Å longer than the calculated equilibrium bond distances in the appropriate molecule M_2H_4 . Comparison with the (single) M–M bond distances in the diamond-like modifications of the elements (Table 6) indicates a relative shortening of *ca.* 4% for Ge_2R_4 and *ca.* 1.5% for Sn_2R_4 . Calculations on H_2MMH_2 , when the molecules are constrained to a planar configuration, yield optimal M–M bond distances of 2.20 (Ge) and 2.55 (Sn) Å, *ca.* 10% shorter than the single M–M bond distances and consistent with the presence of double bonds.

The SCF energies of the planar forms of digermene and distannene are 13 kJ mol⁻¹ (Ge) and 26 kJ mol⁻¹ (Sn) above the energies of the optimal *trans*-folded structures. In Figure 3 are plotted the variations of the SCF energies ('potential energies') of H_2MMH_2 ($M = C, Si, Ge, \text{ or } Sn$) as a function of the fold angle θ . It is clear that stability of the *trans*-folded form increases with increasing atomic number of M. Ethene, C_2H_4 , has a rigid,

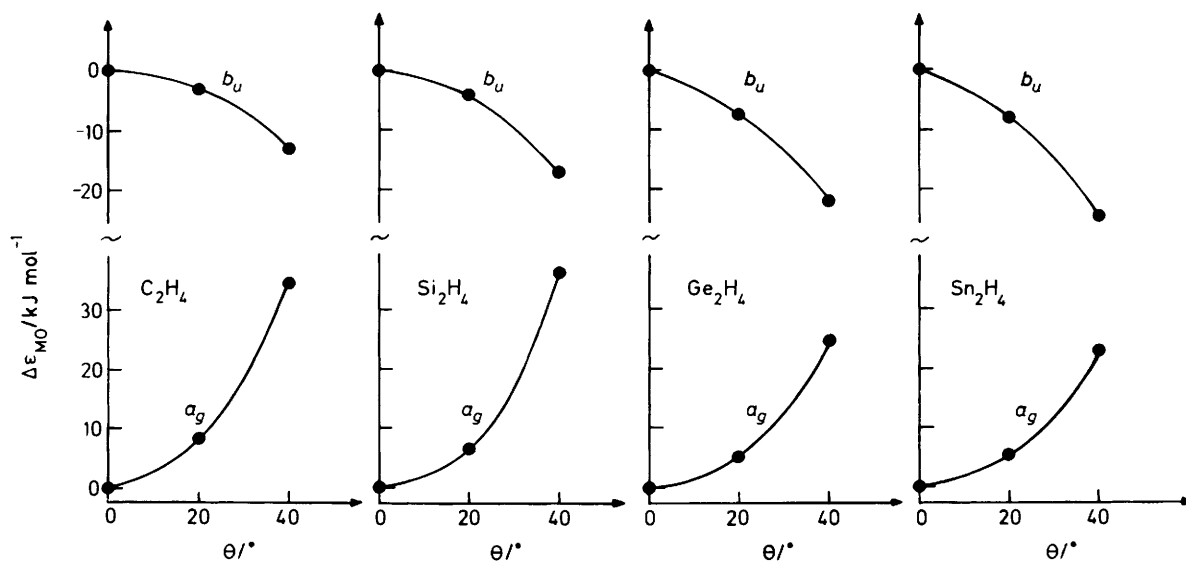
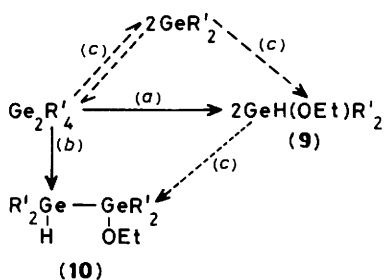


Figure 4. Variation of energies of the two h.o.m.o.s of M_2H_4 with the *trans*-fold angle θ . All curves were calculated for non-adiabatic folding



Scheme. Reaction pathways in the $\text{Ge}_2\text{R}'_4$ -EtOH system

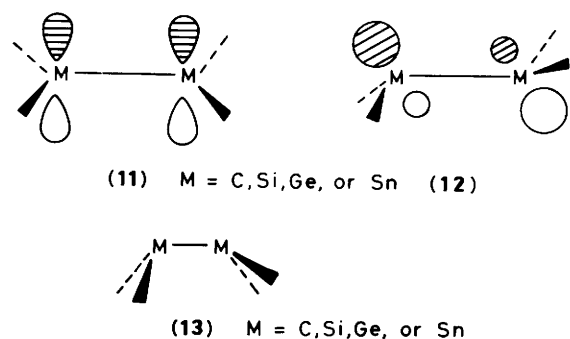
planar equilibrium structure. Disilene is non-rigid, the SCF energy increases very slowly with θ ; only when $\theta = 20^\circ$ is the potential energy equal to kT at ambient temperature. For Ge and Sn, the potential energy curves have distinct minima at $\theta = 40^\circ$ and $\Delta E = -13 \text{ kJ mol}^{-1}$ (Ge) and 46° and -26 kJ mol^{-1} (Sn).

The spread of fold angles θ for the disilenes, 0° in $\text{Si}_2\text{R}'_4$ and *trans*- $\text{Si}_2\text{Bu}^1\text{R}'_2$ and 18° in $\text{Si}_2\text{R}'_4$ agrees with the non-rigid nature indicated by the m.o. calculations. Comparison of the structures of $\text{Si}_2\text{R}'_4$ and Si_2R^2_4 , or $\text{Ge}_2\text{R}'_4$ and Ge_2R_4 , indicates that the R^2 ligand favours low values for θ and concomitant short M-M bonds, see Table 6.

The chemical behaviour of the dimetallenes $\text{M}_2\text{R}'_4$ becomes increasingly that of the carbene analogues MR'_2 with decrease in the percentage of M-M bond shortening compared with M-M in M_x . Thus, the compounds (1a) and (1b) react essentially as the monomers,^{7,26} whereas the disilenes and digermenes show a limited number of addition reactions, as exemplified for EtOH addition by pathway (b) in the Scheme. Thus, the oxidative mononuclear Ge^{IV} adduct (9) was isolated, for the case of $\text{R}' = \text{R} = \text{CH}(\text{SiMe}_3)_2$ when the stoichiometry was $\text{Ge}_2\text{R}_4 + 2\text{EtOH}$ [reaction (a)];²⁷ whereas the 1:1 adduct (10) was obtained for the case of $\text{R}' = \text{R}^2 = \text{C}_6\text{H}_3\text{Et}_{2,6}$ when the stoichiometry was $\text{Ge}_2\text{R}'_4 + \text{EtOH}$ [reaction (b) in the Scheme].¹⁴ However, isolation of an addition product, such as (10), does not necessarily imply that the integrity of the Ge-Ge bond is maintained during the course of the reaction. On the present evidence, pathway (c) cannot be ruled out; this involves successive $\text{Ge}_2\text{R}'_4$ predissociation, formation of the Ge^{IV} compound (9), and final insertion of GeR'_2 into the Ge-H bond of (9). Similarly, although $(\text{SiClR}'_2)_2$ is formed from $\text{Si}_2\text{R}'_4$ and Cl_2 ,¹¹ an analogue $(\text{SnClR}_2)_2$ has been structurally authenticated²⁸ (although not, at this time, prepared from $\text{Sn}_2\text{R}_4 + \text{Cl}_2$); but Sn_2R_4 is known readily to undergo predissociation.²⁶ For chlorination, a possible pathway to $(\text{SiClR}'_2)_2$, analogous to (c) in the Scheme, would involve $\text{SiCl}_2\text{R}'_2$ as an intermediate which could be responsive to insertion of SiR'_2 into an Si-Cl bond.

Not only is much of the chemistry of the dimetallenes $\text{M}_2\text{R}'_4$ essentially that of the monomer units, so the geometry for (1a) and (1b) is closely related to that of the monomers (Table 4). It was pointed out by Trinquier *et al.*²² that the description of the M-M bond in M_2R_4 (M = Ge or Sn) as a double donor-acceptor bond, (2),^{2,3} is consistent with *ab initio* calculations on Ge_2H_4 and Sn_2H_4 . The stability of the *trans*-folded form relative to the planar, double-bonded form in M_2H_4 (M = C, Si, Ge, or Sn) increases with increasing atomic number of M, and this correlates with the increasing energy difference between the singlet and triplet states of the monomers. Only for CH_2 is the triplet of 3B_1 symmetry the ground state; SiH_2 , GeH_2 , and SnH_2 all have singlet ground states of 1A_1 symmetry, with a progressively increasing 1A_1 to 3B_1 energy gap.²³

We now approach the *trans*-folding problem from another standpoint: if the planar double-bonded species $\text{H}_2\text{M}=\text{MH}_2$



(M = C, Si, Ge, or Sn) have been formed, why do they distort? In Figure 4 are shown variations of the two highest occupied molecular orbitals (h.o.m.o.s) as a function of the fold angle θ . (The m.o. energies represented are calculated for non-adiabatic folding, *i.e.*, with all other structure parameters constant. The m.o. energies for the adiabatic folding of digermene and distannene have already been published⁹ and are qualitatively similar to those in Figure 4.) In all species M_2H_4 the h.o.m.o. is the b_u orbital. When the molecule is planar, this is the π -bonding orbital, (11); when the molecule is distorted, it is transformed into a delocalised lone-pair *sp*-hybrid orbital on the metal atoms, (12). The effect is achieved through mixing the b_u with the M-M σ^* orbital.²⁹ For each of the four species M_2H_4 , the h.o.m.o. b_u orbital energy decreases with increasing fold angle. The degree of mixing, and hence the degree of energy lowering, depends on the energy gap between the orbitals involved, the h.o.m.o. π orbital and the antibonding σ^* orbital. This energy difference decreases with decreasing electronegativity of the metal, and the energy lowering thus becomes more pronounced as the group is descended. This trend is apparent in Figure 4.

The second highest occupied orbital is the M-M σ -bonding orbital of A_g symmetry; the energy of this a_g orbital increases upon *trans*-folding, mainly due to the loss of M-M σ -bonding.

For C_2H_4 , the rise of the a_g orbital energy more than cancels the drop in the b_u orbital energy; the equilibrium structure is planar. For disilene, the two effects cancel when $\theta < 20^\circ$; the molecule is non-rigid. For digermene and distannene, the energy drop of the b_u orbital predominates. The non-planar equilibrium structures of these molecules may therefore be rationalised as due to the 'inertness' of the b_u electrons: the stabilisation through π -bonding in the planar form does not appear to compensate to a sufficient degree for the energy required to promote these electrons to pure *p* orbitals.

When calculations are performed on *cis*-folded forms, (13), mixing of the b_u h.o.m.o. with the antibonding σ^* is forbidden by symmetry and the SCF energy *increases* with θ . The barrier to rigid rotation about the M-M bond is therefore *ca.* 20 kJ mol^{-1} for M = Ge and *ca.* 40 kJ mol^{-1} for M = Sn.

The calculated dissociation energy for the gas-phase process $\text{H}_2\text{MMH}_2 \longrightarrow 2\text{MH}_2$ (M = Ge or Sn) is *ca.* 130 kJ mol^{-1} for M = Ge and *ca.* 90 kJ mol^{-1} for M = Sn. Inclusion of correlation energies is expected to increase dissociation energies. Experimentally determined energies for $\text{M}_2\text{R}_4 \longrightarrow 2\text{MR}_2$ (M = Ge or Sn) are not available, but the fact that these compounds exist predominantly as monomers in dilute freezing cyclohexane solution³ suggests that the enthalpy of dissociation is $< 20 \text{ kJ mol}^{-1}$. It is interesting that experimentally determined single M-M bond dissociation energies in molecules such as H_3GeGeH_3 and Me_3MMMe_3 (M = Ge or Sn) are in the range 200 – 300 kJ mol^{-1} ,³⁰ and hence very much higher than our calculated bond energies in M_2H_4 ; this is quite consistent with their observed chemistry.

The discrepancy in bond dissociation energies for M_2H_4 and M_2R_4 ($M = Ge$ or Sn) is probably due to destabilisation of the tetra-alkyldimetalenes through repulsion between the bulky ligands R^- . The structures of R_2GeGeR_2 and R_2SnSnR_2 do indeed offer indications of significant ligand–ligand repulsions. As seen in Figures 1 and 2, the ligands are oriented in a ‘paddle-wheel’ fashion which minimises interaction between the four alkyl ligands. This means that one alkyl group in each monomer unit is rotated about 180° around the $M-C$ bond from its position in the free monomer. We have already pointed out that such a rearrangement must lead to a significant increase of ligand–ligand repulsion within the monomer.¹ Further evidence of strain is provided by the difference between the angles: $Ge'GeC(13)$ [$113.7(3)^\circ$] and $Ge'GeC(14)$ [$122.3(2)^\circ$]; $GeC(13)Si(1)$ [$119.1(4)^\circ$] and $GeC(13)Si(2)$ [$110.0(4)^\circ$]; $GeC(14)Si(4)$ [$121.8(4)^\circ$] and $GeC(14)Si(3)$ [$113.9(4)^\circ$]. In the monomers MR_2 , the $MCiSi$ angles were assumed equal [C^i represents the methine carbon of $CH(SiMe_3)_2$];¹ the magnitudes obtained for the vibrational amplitudes, $l(Ge \cdots Si) = 10(1)$ and $l(Sn \cdots Si) = 12(1)$ pm, confirmed that the assumption was justified.

Finally, the lack of tendency for dimerisation in bulky germanium(II) and tin(II) amides, alkoxides, aryloxides, or arenethiolates, such as $M[N(SiMe_3)_2]_2$,³¹ may be due to $M-X$ π -overlap for these N-, O-, or S-centred (X^-) ligands in the monomeric MX_2 molecules competing for MM π -overlap in the putative dimers M_2X_4 . A more important factor, however, may involve the greater electronegativity of these X^- ligands compared with R^- . In that connection, we refer to calculations by Krogh-Jespersen³² on SiF_2 and Si_2F_4 , which show that, although for the D_{2h} form for the latter, this represents an energy minimum, with *trans*-folding there is no energy barrier to dissociation into $2SiF_2$; broadly similar deductions are implicit in an earlier discussion of GeF_2 and Ge_2F_4 .²²

We conclude that substitution for H^- or R^- in M_2H_4 or M_2R_4 by an electronegative ligand such as NR_2^- , OR^- , or F^- is expected to lead to increased positive charge on M and hence to a contraction and stabilisation of the *ns* lone-pair M -centred orbital of MX_2 and consequently to an increased singlet \rightarrow triplet energy difference. This is probably the principal reason why the solid-state structures of compounds such as $M[N(SiMe_3)_2]_2$ ($M = Ge$ or Sn) are those of the monomers rather than dimers. Incidentally, we note that tetrakis(dialkylamino)-alkenes have readily cleavable C–C bonds; for example, often undergoing scission by transition metal reagents.³³

Finally we wish to make a comment on the structures and bonding in dimetalenes of the Main Group 5 elements, As and Sb. The crystal structure of $RAs=AsR^3$ [$R = CH(SiMe_3)_2$, $R^3 = C_6H_2Bu^1_{3-2,4,6}$] reveals a planar *trans* structure with the As–As bond distance of $2.224(2)$ Å³⁴ consistent with the presence of an As=As double bond.

We note that the above experimental As=As distance is very similar to the Ge=Ge double-bond distance obtained by optimisation of planar Ge_2H_4 (2.20 Å). The single-bond radii of Ge and As are both 1.20 Å.

Even though the ligands R^- and R^{3-} are bulky, the AsAsC valence angles in *trans*- $RAs=AsR^3$ are both small, $AsAsC(R) = 99.9(3)$ and $AsAsC(R^3) = 93.6(3)^\circ$,³⁴ indicating that the non-bonding lone pairs occupy atomic orbitals of predominant *s* character. Since the valence-shell *s* orbitals are fully occupied in the diarsene, they do not provide a driving force for elongation or deformation, and we expect diarsenes and distibenes to possess *rigid* double-bonded structures.

Experimental

Crystal Data for $\{Ge[CH(SiMe_3)_2]_2\}_2$ (**1a**).— $C_{28}H_{76}Ge_2Si_8$, $M = 782.8$, triclinic, space group $P\bar{1}$, $a = 9.612(2)$, $b =$

$11.982(4)$, $c = 11.983(3)$ Å, $\alpha = 67.62(2)$, $\beta = 70.35(2)$, $\gamma = 65.40(2)^\circ$, $U = 1134.1$ Å³, $Z = 1$, $D_c = 1.15$ g cm⁻³. Graphite-monochromated Mo- K_α radiation, $\lambda = 0.71069$ Å, $\mu = 16.2$ cm⁻¹.

A yellow crystal, *ca.* $0.3 \times 0.2 \times 0.2$ mm, sealed in a Lindemann glass capillary under argon, was mounted on an Enraf-Nonius CAD4 diffractometer. Diffraction peaks were relatively broad and weak and did not extend to high angle. Unique data with $2 < \theta < 20^\circ$ were measured by an ω - 2θ scan with a maximum scan time of 1 min. No correction was made for absorption. 1497 Reflections with $|F^2| > \sigma(F^2)$ were used in the structure refinement, where $\sigma(F^2) = \{\sigma^2(I) + (0.02I)^2\}^{1/2}/Lp$.

The structure was solved by routine heavy-atom methods and non-H atoms refined anisotropically by full-matrix least-squares methods. Hydrogen atoms were placed at calculated positions (C–H 1.08 Å) and held fixed with a common B_{iso} of 8.0 Å². Refinement converged at $R = 0.083$, $R' = 0.087$ with a weighting scheme of $w = 1/\sigma^2(F)$. A final difference map had peaks of up to 1.5 e Å⁻³ near the Ge atoms but was elsewhere featureless.

Crystal Data for $\{Sn[CH(SiMe_3)_2]_2\}_2$ (**1b**).— $C_{28}H_{76}Si_8Sn_2$, $M = 875.0$, triclinic, space group $P\bar{1}$, $a = 9.749(1)$, $b = 12.091(1)$, $c = 12.456(2)$ Å, $\alpha = 67.81(1)$, $\beta = 71.31(1)$, $\gamma = 65.55(1)^\circ$, $U = 1180.2$ Å³, $Z = 1$, $D_c = 1.23$ g cm⁻³. Graphite-monochromated Mo- K_α radiation, $\mu = 12.8$ cm⁻¹.

The structure was originally determined using diffraction data from a Hilger and Watts Y290 diffractometer,² but has now been redetermined using a better quality crystal on an Enraf-Nonius CAD4 diffractometer. The reduced unit-cell setting was used allowing a direct comparison with the Ge compound. A red crystal, *ca.* $0.35 \times 0.35 \times 0.25$ mm, was used and details of data collection and structure determination were mainly as for the Ge compound. Data collection limits were $2 < \theta < 22^\circ$. An empirical absorption correction based on ψ scans was applied. 3267 Reflections were used in the refinement which converged at $R = 0.048$, $R' = 0.057$. A difference map had peaks of up to 1.5 e Å⁻³ near the Sn atoms.

All calculations were performed on a PDP11/34 computer using the Enraf-Nonius SDP-Plus program package.

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