

## A New Method for the Preparation of Bis(bistrimethylsilylmethyl)tin(II) $\text{Sn}[\text{CH}(\text{SiMe}_3)_2]_2$ and Its Molecular Structure has been Determined by Gas Electron Diffraction. Prediction of Non-planar, *trans*-Folded Ground State Structures for Digermene ( $\text{Ge}_2\text{H}_4$ ) and Distannene ( $\text{Sn}_2\text{H}_4$ )

Torgny Fjeldberg,<sup>a</sup> Arne Haaland,<sup>\*b</sup> Michael F. Lappert,<sup>\*c</sup> Birgitte E. R. Schilling,<sup>b</sup> Ragnhild Seip,<sup>b</sup> and Andrew J. Thorne<sup>c</sup>

<sup>a</sup> Department of Chemistry, University of Trondheim NLHT, Trondheim, Norway

<sup>b</sup> Department of Chemistry, University of Oslo, Blindern, Oslo 3, Norway

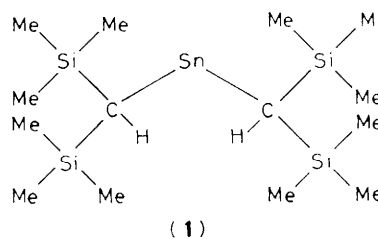
<sup>c</sup> School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ, U.K.

Reduction of  $\text{SnCl}_2\text{R}_2$  [ $\text{R} = \text{CH}(\text{SiMe}_3)_2$ ] ( $\text{Li}_2\text{C}_8\text{H}_8$ ) provides  $\text{SnR}_2$ , which in the gas phase (electron diffraction) is a V-shaped monomer with  $\angle \text{CSnC } 96(1)^\circ$  and  $\text{Sn}-\text{C } 224(1)$  pm; *ab initio* M.O. calculations predict non-planar *trans*-folded equilibrium structures for the ethene analogues  $\text{Ge}_2\text{H}_4$  and  $\text{Sn}_2\text{H}_4$ .

Bis(bistrimethylsilylmethyl)tin(II)  $\text{SnR}_2$  [ $\text{R} = \text{CH}(\text{SiMe}_3)_2$ ] (**1**) is monomeric in cyclohexane or benzene solution (by cryoscopy) and in the gas phase (by mass spectroscopy).<sup>1,2</sup> In the crystalline phase  $\text{SnR}_2$  forms dimers,  $\text{Sn}_2\text{R}_4$ , which may be regarded as ethene analogues. The synthesis of the disilene  $\text{Si}_2(\text{mesityl})_4$  has recently been reported by West and co-workers.<sup>3</sup>

$\text{SnR}_2$  has previously been made only from  $\text{Sn}^{\text{II}}$  precursors:  $(\text{SnCl}_2)_n$  or  $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$ . We now show that it is available from a  $\text{Sn}^{\text{IV}}$  starting material. Treatment of  $\text{SnCl}_2\text{R}_2$  with  $\text{Li}_2(\text{cot})$  ( $\text{cot} = \text{C}_8\text{H}_8$ ) (1 mmol) as a saturated solution (0.24 mol  $\text{dm}^{-3}$ ) in diethyl ether readily yields  $\text{SnR}_2$ .  $\text{SnCl}_2\text{R}_2$  is prepared from  $\text{SnCl}_4$ , 2LiR, and tetramethylethylenediamine in diethyl ether.

We have recorded the electron diffraction pattern of monomeric  $\text{SnR}_2$  with reservoir and nozzle temperatures of about 120 °C and determined the molecular structure. Structure refinements were based on a model of  $C_2$  symmetry defined by three bond distances (Sn-C, Si-C, and C-H), five valence angles, and three torsional angles, see (**1**). Least-squares refinements gave Sn-C 224(1) and Si-C 189(1) pm (mean

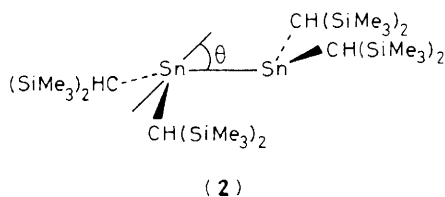


(1)

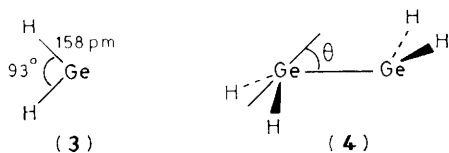
Sn-C 224(1) pm,  $\angle \text{CSnC } 96(1)^\circ$ .

value);  $\angle \text{CSnC } 96(1)$ ,  $\angle \text{SnCSi } 109(1)$ , and  $\angle \text{SiCSi } 113(1)^\circ$ . The other structure parameters were unexceptional.

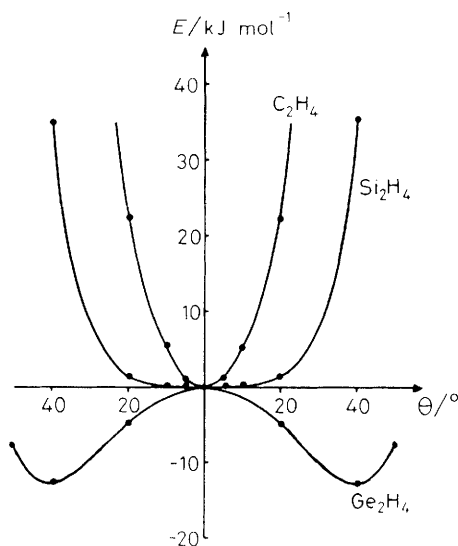
The Sn-C bond distance is about 10 pm longer than in  $\text{SnMe}_4$ , 214.4(2) pm.<sup>4</sup> A somewhat smaller difference is found between Sn-N bond distances in  $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$  and  $\text{Sn}(\text{NMe}_2)_4$ , 209(1)<sup>5</sup> and 204.5(7) pm,<sup>6</sup> respectively. In the  $\text{Sn}^{\text{II}}$  diamide the  $\angle \text{NSiN}$  angle is  $96^\circ$ . The longer Sn-X bonds and smaller  $\angle \text{XSnX}$  angles in the  $\text{Sn}^{\text{II}}$  compounds may be rationalized by assuming that the electron lone pair



Sn-C 228(3) pm.  $\angle$ CSnC 112°. Sn-Sn 276.4(2) pm.  $\theta = 41^\circ$ .



For (4): Ge-H 158 pm.  $\angle$ HGeH 107°. Ge-Ge 230 pm.  $\theta = 40^\circ$ .



**Figure 1.** Variation in SCF energy for  $C_2H_4$ ,  $Si_2H_4$ , and  $Ge_2H_4$  with fold angle  $\theta$ , where  $\theta$  is the angle between the metal-metal bond and the  $MH_2$  plane of each monomer unit.

orbital has predominantly s-character, while the Sn-X bonding orbitals have mainly p-character.

An X-ray crystallographic study has shown  $SnR_2[R=CH-(SiMe_3)_2]$  to be dimeric in the solid phase (2).<sup>1</sup> The structure is non-planar, *trans*-folded, the angle  $\theta$  between the Sn-Sn bond and the  $SnC_2$  plane of each monomer unit being about  $41^\circ$ . The Sn-Sn bond distance in the dimer is indistinguishable from the single Sn-Sn bond distance in hexaphenylditin, 277(1) pm.<sup>7</sup> This is in contrast with the short C=C bonds in ethene derivatives and the Si-Si bond reported for  $Si_2$ -(mesityl)<sub>4</sub>.<sup>3</sup> It is further noteworthy that the Sn-C bond distance in  $Sn_2R_4$  is indistinguishable from that in the monomer and significantly longer than in  $SnMe_4$ , while the C-C single bond in  $C_2Me_4$  is shorter than in  $CMe_4$ , 150.5(2)<sup>8</sup> and 153.7(3) pm, respectively.<sup>9</sup>

We plan to carry out structure determinations on  $GeR_2$  and  $Ge_2R_4$ . In the meantime we are exploring the structure and bonding in  $GeH_2$ ,  $Ge_2H_4$ ,  $SnH_2$ , and  $Sn_2H_4$  by means of *ab initio* M.O. calculations<sup>10</sup> with better than double zeta basis.<sup>11</sup> The calculated equilibrium structures of  $GeH_2$  and

$Ge_2H_4$  are shown in (3) and (4). The experimental value for the Ge-H bond distance in  $GeH_4$  is 152.5(1) pm<sup>12</sup> and for the Ge-Ge single bond in  $Ge_2H_6$  240.3(3) pm.<sup>13</sup> The structures are clearly related to those of  $SnR_2$  and  $Sn_2R_4$ , though the Ge-Ge single bond in  $Ge_2H_4$  appears to be somewhat shortened through  $\pi$ -bonding. If the molecule is constrained to a planar conformation the Ge-Ge bond distance decreases to 220 pm which seems reasonable for a Ge-Ge double bond, and the energy is about 12 kJ above that of the equilibrium conformation. Exploratory calculations on  $GeMe_2$  and  $Ge_2Me_4$  give similar results.

In Figure 1 we show how the calculated SCF energy of  $C_2H_4$ ,  $Si_2H_4$ , and  $Ge_2H_4$  varies with the fold angle  $\theta$ . The potential energy (PE) surface of  $C_2H_4$  shows a clearly defined minimum at the planar ( $\theta = 0^\circ$ ) conformation. The potential well for  $Si_2H_4$  is, however, very wide; only when  $\theta > 20^\circ$  is  $PE > kT$  at room temperature.<sup>14</sup> For  $Ge_2H_4$  the curve develops distinct minima corresponding to a *trans*-folded  $C_{2h}$  conformation. Calculations on  $Sn_2H_4$  which are still in progress have yielded similar results; the energy of a *trans*-folded model is at least 18 kJ mol<sup>-1</sup> below that of a planar model. It seems therefore that the stability of the non-planar form of the ethene analogues  $Si_2H_4$ ,  $Ge_2H_4$ , and  $Sn_2H_4$  increases with increasing atomic number of the metal.

We thank the S.E.R.C. and Dow Corning (Barry) for a C.A.S.E. grant to A.J.T. and the N.T.N.F. for a grant to B.E.R.S.

Received, 23rd August 1982; Com. 1022

## References

- D. E. Goldberg, D. H. Harris, M. F. Lappert, and K. M. Thomas, *J. Chem. Soc., Chem. Commun.*, 1976, 256.
- P. J. Davidson, D. H. Harris, and M. F. Lappert, *J. Chem. Soc., Dalton Trans.*, 1976, 2268.
- R. West, M. J. Fink, and J. Michl, *Science*, 1981, **214**, 1342; American Chemical Society Regional Meeting, June 1982, Midland, Michigan, U.S.A.
- M. Nagashima, H. Fujii, and M. Kimura, *Bull. Chem. Soc. Jpn.*, 1973, **46**, 3708.
- M. F. Lappert, P. P. Power, M. J. Slade, L. Hedberg, K. Hedberg, and V. Schomaker, *J. Chem. Soc., Chem. Commun.*, 1979, 369.
- L. V. Vilkov, N. A. Tarasendo, and A. K. Prokofev, *Zh. Strukt. Khim.*, 1970, **11**, 129.
- H. Preut, H. J. Haupt, and F. Huber, *Z. Anorg. Allg. Chem.*, 1973, **396**, 81.
- I. Tokue, T. Fukuyama, and K. Kuchitsu, *J. Mol. Struct.*, 1974, **23**, 33.
- B. Beagley, D. P. Brown, and J. J. Monaghan, *J. Mol. Struct.*, 1969, **4**, 233.
- J. Almlöf, K. Faegri, Jr., and K. Korsell, *J. Comput. Chem.*, 1982, **3**, 385.
- S. Huzinaga, personal communication; T. H. Dunning, *J. Chem. Phys.*, 1970, **53**, 2823; A. Strömberg, O. Gropen, and U. Wahlgren, personal communication.
- H. W. Kattenberg, W. Gabes, and A. Oskam, *J. Mol. Spectrosc.*, 1972, **44**, 425.
- B. Beagley and J. J. Monaghan, *Trans. Faraday Soc.*, 1970, **66**, 2745.
- Similar results on  $Si_2H_4$  have already been reported by others: K. Krogh-Jespersen, *J. Phys. Chem.*, 1982, **86**, 1492; H. Lischka and H.-J. Köhler, *Chem. Phys. Lett.*, 1982, **85**, 467; R. A. Poirier and J. D. Goddard, *ibid.*, 1981, **80**, 37; L. C. Snyder and Z. R. Wasserman, *J. Am. Chem. Soc.*, 1979, **101**, 5222; F. F. Roelandt, D. F. van de Vondel, and G. P. van der Kelen, *J. Organomet. Chem.*, 1979, **165**, 151; R. Daudel, R. E. Kari, R. A. Poirier, J. D. Goddard, and I. G. Csizmadia, *J. Mol. Struct.*, 1978, **50**, 115.