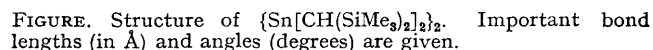
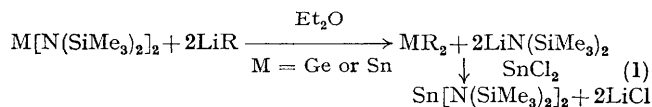


(School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ)

The addition of  $\text{SnCl}_2$  to the reaction mixture facilitated the separation of the products, because the amide  $\text{M}[\text{N}(\text{Si-Me}_3)_2]_2$  is extremely soluble in cyclohexane, whereas the dialkyl  $\text{MR}_2$  is only sparingly soluble.



The bright-yellow volatile crystalline  $\text{GeR}_2$  [ $\text{R} = \text{CH}-(\text{SiMe}_3)_2$ : 40% yield; analytically pure; m.p. 179–181 °C; sublimes at 110 °C and  $10^{-3}$  mmHg;  $m/e$  392 ( $M^+$ ) (monomer requires 392);  $\tau$  9.51 (Me) and 6.40 (CH); Raman  $300\text{ cm}^{-1}$  (strong, polarized); photoelectron 7.75 (Ge:) and 8.87 (Ge-R) eV;  $\lambda_{\text{max}}$  (hexane) 414 ( $\epsilon$  970), 312 (1450), and 227 (19,600 nm)] is air-stable for quite long periods (ca. 1 h), but solutions were decomposed almost immediately in air. The crystals are thermochromic, becoming orange upon heating, melting to a red liquid, and resolidifying to the yellow  $\text{GeR}_2$  upon cooling. Its solubility in non-polar solvents is quite low, and less than that of  $\text{SnR}_2$ . U.v.



† No reprints available.

irradiation caused slow formation of  $\cdot\text{GeR}_3$ ,<sup>3</sup> which was also obtained in a dark reaction by the addition of one or two drops of LiR in  $\text{Et}_2\text{O}$  to  $\text{GeR}_2$ .

Single crystals of the red  $\text{Sn}[\text{CH}(\text{SiMe}_3)_2]_2$  were obtained from the product of reaction (1) ( $\text{M} = \text{Sn}$ ), by evaporation, and manual separation facilitated by its colour. One red crystal was sealed in a capillary and was found to be triclinic with  $a = 9.459(1)$ ,  $b = 12.083(1)$ ,  $c = 12.439(1)$  Å,  $\alpha = 112.11(1)^\circ$ ,  $\beta = 108.65(1)^\circ$ ,  $\gamma = 65.59(1)^\circ$ , space group  $P\bar{1}$  (structure solution and refinement),  $Z = 2$  ( $\text{SnR}_2$ ),  $D_c = 1.232 \text{ g cm}^{-3}$ . Intensity data for 2988 reflections having  $I_{\text{obs}} \geq 3\sigma(I_{\text{obs}})$  and  $4^\circ \leq 2\theta \leq 50^\circ$  were obtained on a Hilger and Watts Y290 four-circle diffractometer with  $\text{Mo-K}\alpha$  radiation (graphite monochromator). The structure was solved by conventional heavy-atom techniques. The least-squares refinement of the positional parameters and anisotropic temperature factors for all non-hydrogen atoms converged with  $R = 0.082$ . The e.s.d.s for the Sn–Sn and Sn–C bond lengths are 0.002 and 0.03 respectively. The overall stereochemistry and important bond lengths are shown in the Figure.

The structure consists of a centrosymmetric dimer. The Sn–Sn bond length is not significantly different from that found in hexaphenylditin,  $2.764(2)$  Å.<sup>5</sup> However, the Sn–C bond ( $2.28$  Å average) is significantly longer than that found<sup>2</sup> in  $[\text{Cr}(\text{CO})_5(\text{SnR}_2)]$  ( $2.185$  Å average), the shorter bond length in the latter probably being a consequence of the  $\pi$ -electron-withdrawing effect of the  $\text{Cr}(\text{CO})_5$  group. The stereochemistry around the tin is non-planar

and the  $\angle \text{C–Sn–C}$  angle has increased to  $112^\circ$ , compared with<sup>2</sup>  $98^\circ$  in  $[\text{Cr}(\text{CO})_5(\text{SnR}_2)]$ . No metal–hydrogen bond could be detected by either i.r. or n.m.r. spectroscopy and the final difference electron density synthesis revealed only peaks consistent with anisotropic motion around the tin atom.

As solid  $(\text{SnR}_2)_2$  is diamagnetic, we regard the dimerisation as caused by the aggregation of two singlet bent monomers, whereby the approximately  $sp_xp_y$  lone-pair hybrid filled orbital on the tin atom of one of the partners overlaps with the vacant  $p_z$  orbital of the other. The molecule is thus considered as having a 'bent' and weak SnSn double bond, which also accounts for the relative disposition of the two sets of  $\text{R}_2$  groups with respect to one another. There may be a tenuous relationship between the crystal structure of  $(\text{SnR}_2)_2$  and that of the green form of chlorobis-[1,2-bis-(diphenylphosphine)ethane]cobalt(II) trichlorostannate(II) in which the  $\text{SnCl}_3^-$  is near a centre of symmetry which results in  $l(\text{Sn–Sn}) = 3.597(4)$  Å with the 3 Cl atoms bonded to tin directed away from the Sn–Sn vector.<sup>6</sup>

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