A New Synthesis of Divalent Group 4B Alkyls $M[CH(SiMe_3)_2]_2$ (M=Ge or Sn), and the Crystal and Molecular Structure of the Tin Compound†

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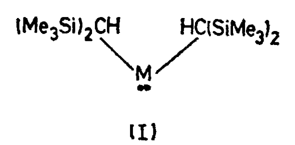
Summary Reaction of 2LiR [R = $(Me_3Si)_2CH$] and $M[N(SiMe_3)_2]_2$ affords a new route to SnR_2 and also the isolation of the yellow, crystalline, volatile, and diamagnetic GeR_2; *X*-ray single crystal analysis of the former shows a dimeric centrosymmetric structure with *l*(Sn-Sn) = 2·76 Å, ∠Sn–Sn–C (mean) = 115°, and ∠C–Sn–C = 112°.

THE recently prepared bulky alkyls (I) of tin(II) and lead(II) are unusual in being highly coloured and monomeric in benzene or cyclohexane solution,[1] and react as singlet carbene analogues in their co-ordination chemistry; for example *X*-ray analysis shows $[Cr(CO)_5SnR_2]$ [R = $(Me_3Si)_2CH$] to have the tin atom in a trigonal planar environment.[2] The synthesis of the alkyls (I) was from LiR and $SnCl_2$, or $PbCl_2$ in Et_2O. However, a similar method using $GeCl_2$.dioxan or GeI_2 afforded a green solution containing $\cdot GeR_3$.[3]



(I)

We now report (*i*) a new synthesis, using $M[N(SiMe_3)_2]_2$,[4] of the divalent group 4B alkyls [equation (1)], (ii) the isolation and characterisation of the first germanium(II) alkyl [(I), M = Ge], and (iii) the crystal and molecular structure of the diamagnetic $(SnR_2)_2$, which shows the presence of a tin–tin ('bent' double) bond.

$$\begin{array}{rl} M[N(SiMe_3)_2]_2 + 2LiR \xrightarrow[M\,=\,Ge\ \mathrm{or}\ Sn]{Et_2O} & MR_2 + 2LiN(SiMe_3)_2 \\ & \quad\downarrow SnCl_2 \qquad (1) \\ & Sn[N(SiMe_3)_2]_2 + 2LiCl \end{array}$$

The addition of $SnCl_2$ to the reaction mixture facilitated the separation of the products, because the amide $M[N(SiMe_3)_2]_2$ is extremely soluble in cyclohexane, whereas the dialkyl MR_2 is only sparingly soluble.

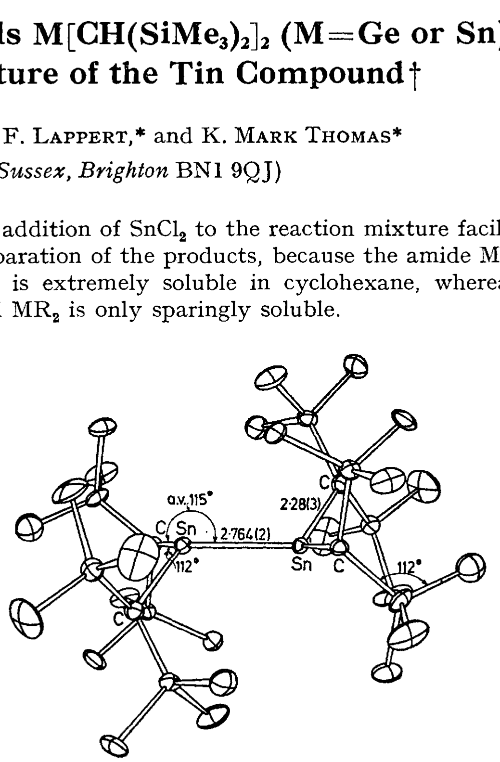


FIGURE. Structure of $\{Sn[CH(SiMe_3)_2]_2\}_2$. Important bond lengths (in Å) and angles (degrees) are given.

The bright-yellow volatile crystalline GeR_2 [R = $CH(SiMe_3)_2$: 40% yield; analytically pure; m.p. 179—181 °C; sublimes at 110 °C and 10^{-3} mmHg; *m/e* 392 (M^+) (monomer requires 392); τ 9·51 (Me) and 6·40 (CH); Raman 300 cm^{-1} (strong, polarized); photoelectron 7·75 (Ge:) and 8·87 (Ge–R) eV; λ_{max} (hexane) 414 (ε 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 GeR_2 upon cooling. Its solubility in non-polar solvents is quite low, and less than that of SnR_2. U.v.

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† No reprints available.

irradiation caused slow formation of $\cdot GeR_3$,[3] which was also obtained in a dark reaction by the addition of one or two drops of LiR in Et_2O to GeR_2.

Single crystals of the red $Sn[CH(SiMe_3)_2]_2$ were obtained from the product of reaction (1) (M = 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 $a = 9{\cdot}459(1)$, $b = 12{\cdot}083(1)$, $c = 12{\cdot}439(1)$ Å, $\alpha = 112{\cdot}11(1)^\circ$, $\beta = 108{\cdot}65(1)^\circ$, $\gamma = 65{\cdot}59(1)^\circ$, space group $P\bar{1}$ (structure solution and refinement), $Z = 2$ (SnR_2), $D_c = 1{\cdot}232$ g cm^{-3}. Intensity data for 2988 reflections having $I_{obs} \geqslant 3\sigma(I_{obs})$ and $4^\circ \leqslant 2\theta \leqslant 50^\circ$ were obtained on a Hilger and Watts Y290 four-circle diffractometer with Mo-K_α 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 $R = 0{\cdot}082$. 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.[5] However, the Sn–C bond (2·28 Å average) is significantly longer than that found[2] in $[Cr(CO)_5(SnR_2)]$ (2·185 Å average), the shorter bond length in the latter probably being a consequence of the π-electron-withdrawing effect of the $Cr(CO)_5$ group. The stereochemistry around the tin is non-planar and the ∠C–Sn–C angle has increased to 112°, compared with[2] 98° in $[Cr(CO)_5(SnR_2)]$. 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 $(SnR_2)_2$ 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 R_2 groups with respect to one another. There may be a tenuous relationship between the crystal structure of $(SnR_2)_2$ and that of the green form of chlorobis-[1,2-bis-(diphenylphosphine)ethane]cobalt(II) trichlorostannate(II) in which the $SnCl_3^-$ is near a centre of symmetry which results in l(Sn–Sn) = 3·597(4) Å with the 3 Cl atoms bonded to tin directed away from the Sn–Sn vector.[6]

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