A New Synthesis of Divalent Group 4B Alkyls M[CH(SiMe₃)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 = (Me₃Si)₂CH] and M-[N(SiMe₃)₂]₂ affords a new route to SnR₂ and also the isolation of the yellow, crystalline, volatile, and diamagnetic GeR₂; 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, and react as singlet carbene analogues in their co-ordination chemistry; for example X-ray analysis shows [Cr(CO)₅SnR₂] [R = (Me₃-Si)₂CH] to have the tin atom in a trigonal planar environment. The synthesis of the alkyls (I) was from LiR and SnCl₂, or PbCl₂ in Et₂O. However, a similar method using GeCl₂ dioxan or GeI₂ afforded a green solution containing ·GeR₃.

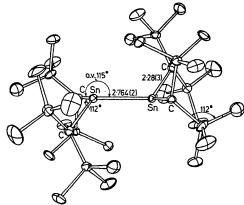
We now report (i) a new synthesis, using $M[N(SiMe_3)_2]_2$, of the divalent group 4B alkyls [equation (1)], (ii) the isolation and characterisation of the first germanium(II) alkyl [(I), M = Ge], and (iii) the crystal and molecular structure of the diamagnetic $(SnR_2)_2$, which shows the presence of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

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

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-(SiMe₃)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; $\lambda_{\rm max}$ (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 GeR₂ upon cooling. Its solubility in non-polar solvents is quite low, and less than that of SnR₂. U.v.

The addition of $SnCl_2$ to the reaction mixture facilitated the separation of the products, because the amide $M[N(Si-Me_3)_2]_2$ is extremely soluble in cyclohexane, whereas the dialkyl MR_2 is only sparingly soluble.



† No reprints available.

irradiation caused slow formation of ·GeR₃,3 which was also obtained in a dark reaction by the addition of one or two drops of LiR in Et₂O to GeR₂.

Single crystals of the red Sn[CH(SiMe₃)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 = 9.459(1), b = 12.083(1), c = 12.439(1) Å, $\alpha = 112 \cdot 11(1)^{\circ}$, $\beta = 108 \cdot 65(1)^{\circ}$, $\gamma = 65 \cdot 59(1)^{\circ}$, space group P1 (structure solution and refinement), Z = 2 (SnR₂), $D_c =$ $1.232~{\rm g~cm^{-3}}$. Intensity data for 2988 reflections having $I_{\rm obs} \geqslant 3\sigma(I_{\rm obs})$ and $4^{\circ} \leqslant 2\theta \leqslant 50^{\circ}$ were obtained on a Hilger and Watts Y290 four-circle diffractometer with $Mo-K_{\alpha}$ 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. 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 found2 in [Cr(CO)5(SnR2)] (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 98° in [Cr(CO)₅(SnR₂)]. 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 (SnR₂)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 R₂ groups with respect to one another. There may be a tenuous relationship between the crystal structure of (SnR₂)₂ and that of the green form of chlorobis-[1,2-bis-(diphenylphosphine)ethane]cobalt(II) trichlorostannate(II) in which the SnCl₃⁻ 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

We thank Professor R. Mason for provision of X-ray facilities, the S.R.C. (K.M.T.) and the U.S. Army (D.H.H.) for support, Mr. S. J. Miles (u.v.), Drs. M. J. S. Gynane (Raman and u.v.), and G. J. Sharp (photoelectron), for spectroscopic data, and the Brooklyn College of the City University of New York for study leave to D.E.G.

(Received, 5th February 1976; Com. 120.)

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