Journal of Organometallic Chemistry, 212 (1981) C4—C6
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary Communication

OXIDATIVE ADDITION OF AN ALCOHOL TO THE ALKYLGERMANIUM-(II) COMPOUND $Ge[CH(SiMe_3)_2]_2$; MOLECULAR STRUCTURE OF $Ge[CH(SiMe_3)_2]_2(H)OEt$

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(Received February 10th, 1981)

Summary

The alkylgermanium(II) compound GeR_2 ($R = CH(SiMe_3)_2$) readily reacts with an alcohol R′OH (R′ = Me or Et) to yield the oxidative adduct $GeR_2 \cdot R'OH$, one of which (R′ = Et) has been characterised by single crystal X-ray diffraction as $Ge(H)R_2(OR')$: Ge—O 1.797(5) Å, Ge—C 1.969(6) and 1.953(7) Å, Ge—H 1.46(6) Å, angle HGeO 98(2)°, angle HGeC 108(2) and 120(2)°, angle CGeO 105.9(3) and 108.7(3)°.

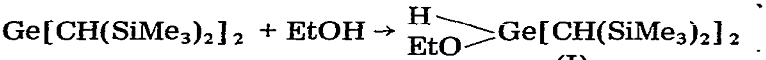
In 1976 we reported details of the synthesis of the yellow bivalent alkylgermanium(II) compound $Ge[CH(SiMe_3)_2]_2$ (abbreviated henceforth as GeR_2), which is a monomer in cyclohexane [1]. Subsequent publications on this compound relate to (i) the He(I) photoelectron spectrum [2], (ii) photolysis to yield the persistent Ge^{III} compound GeR_3 [3], and (iii) properties as a ligand, e.g. to afford $[Cr(CO)_5(GeR_2)]$ [4]. For a tin(II) analogue, SnR_2, we have also described oxidative addition reactions, e.g., with MeI to furnish $Sn(I)(Me)R_2$ [5].

Oxidative addition reactions are probably best known for low valent complexes of late transition metals, e.g., $Rh^I \rightarrow Rh^{III}$, $Pt^0 \rightarrow Pt^{II}$, or $Pt^{II} \rightarrow Pt^{IV}$ [6]; common addenda include H_2, HHal, Alk-Hal, Acyl-Hal, or O_2, but as far as we are aware the use, in this way, of an alcohol has no precedent; partly for this reason it was considered desirable to obtain crystallographic proof of the identity of the ethanol adduct (I) obtained in the present work.

Although the treatment of $GeEt_2 \cdot NEt_3$ with methanol yields $GeEt_2(H)OMe$ the same reaction involving another germylene GeR'_2, e.g., $GePh_2$, does not yield an adduct, because of the propensity of $GeR'_2(H)OMe$ to dissociation into its factors, a process which appears to be base catalysed, e.g., by MeOH [7]. Thus, hydrido-alkoxygermanium(IV) compounds are generally unstable, e.g., $GePh_2(H)OMe$ reductively eliminates methanol to yield $\frac{1}{n}(GePh_2)_n$ [8]. The unexpected robustness of $Ge[CH(SiMe_3)_2]_2(H)OEt$ now found is probably due to steric hindrance.

A further reason for our concern that the structure of the $GeR_2 \cdot EtOH$ adduct be established beyond doubt arises from our previous isolation from a sample of GeR_2 volatile white crystals, for which X-ray data showed the structure $Ge[CH(SiMe_3)_2]_2(Me)(OH)$ [9]. Full details of this will be published at a later date when we hope also to ascertain the nature of the reagent which had caused this transformation of GeR_2. Finally, there are very few X-ray data in the literature on Ge—O or Ge—H compounds.

We find that GeR_2 ($R = CH(SiMe_3)_2$) is extremely sensitive to moisture or an alcohol (MeOH or EtOH). Each reaction was carried out (on a ca. 0.3 mmolar scale) by mixing bis[bis(trimethylsilyl)methyl]germanium with a diethyl ethereal solution containing a stoicheiometric quantity of water or alcohol (total volume, ca. 5 ml) at 20°C with stirring until the yellow colour of GeR_2 was discharged. Solvent was removed at ca. 20°C/10^{-3} Torr. Purification of the product was by sublimation (20°C/10^{-3} Torr) on to a cooled (−78°C) probe. In this fashion, compound I (eq. 1) was obtained in ca. 50% yield, m.p. 35°C. Anal. found: C, 43.8; H, 9.1. $C_{16}H_{44}GeOSi_4$ calcd.: C, 44.0; H, 10.1%. Spectroscopic features include (a) IR ν(GeH) at 2020 (medium, broad) cm^{-1}, (b) ^1H NMR chemical shifts centred at τ 4.13 (Ge*H*, triplet), 6.07 (CH_2CH_3, quartet), and 8.60 ppm (CH_2CH_3, triplet), and (c) in the mass spectrum a weak parent molecular ion and a base peak corresponding to $[P - 15]^+$.



$$\mathrm{Ge[CH(SiMe_3)_2]_2 + EtOH \rightarrow \begin{matrix}H\\EtO\end{matrix}{>}Ge[CH(SiMe_3)_2]_2} \qquad (1)$$

(I)

Crystal data. $C_{16}H_{44}GeOSi_4$, triclinic, space group $P\bar{1}$, M 437.5, $a = 9.356(5)$, $b = 11.369(6)$, $c = 14.845(8)$ Å, $\alpha = 68.49(4)$, $\beta = 68.04(4)$, $\gamma = 71.19(4)°$, $U = 1331$ Å^3, $D_c = 1.09$ g cm^{-3}, $Z = 2$ and μ(Mo-K_α) 13.9 cm^{-1}. 3702 independent observed reflections $I > 3\sigma(I)$ were collected with graphite crystal monochromated radiation ($2\theta \leqslant 50°$) on an Enraf-Nonius Cad-4 diffractometer, Inspection of a Patterson map led to the coordinates of the germanium atom. Full matrix, least-squares refinement of the model obtained from the resulting difference Fourier phased on the germanium atom led to an R value of 0.071. Location and refinement of the hydrogens attached to the germanium atom and the secondary carbon of the bis(trimethylsilyl)methyl ligands, along with location and fixing of all other hydrogens led to a final R value of 0.061. The molecule is shown in Fig. 1.

The germanium atom inhabits an approximately tetrahedral environment, with distortions as expected from steric considerations. The Ge—O distance

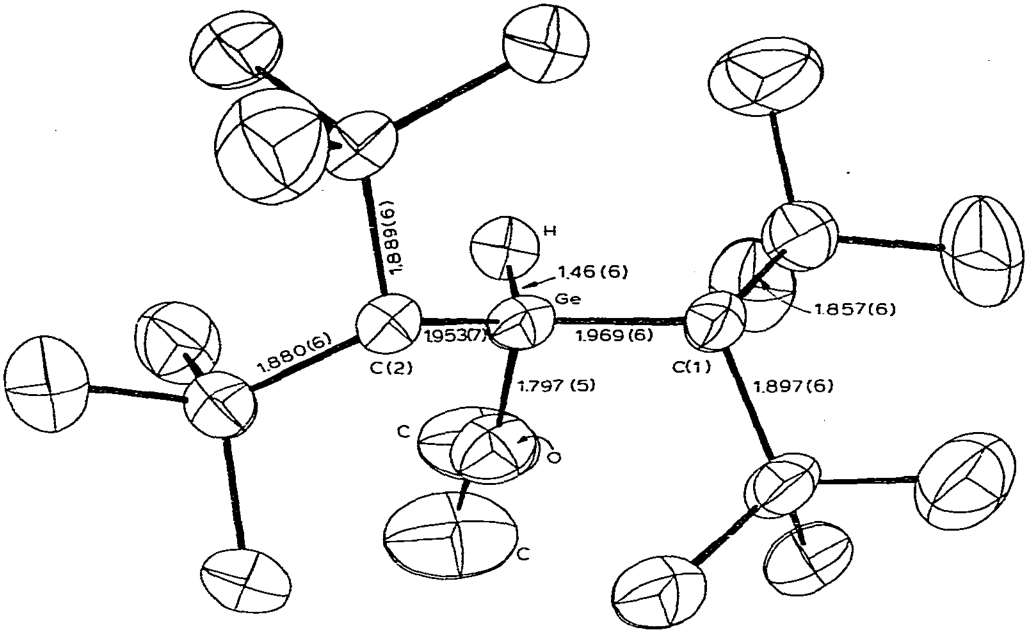


Fig. 1. Molecular structure of Ge[CH(SiMe$_3$)$_2$]$_2$(H)OEt showing some important bond lengths (Å); significant bond angles (°) include H—Ge—O 98(2), H—Ge—(2) 120(2), H—Ge—C(1), 108(2), C(1)—Ge—O 105.9(3), C(1)—Ge—C(2) 114.5(3), C(2)—Ge—O 108.7(3).

of 1.797(5) Å and the Ge—O—C(15) angle of 124.4(6)° may be compared with 1.730(1) Å and 136.2° (ave) in [Ge(CH$_2$Ph)$_3$]$_2$O [10] and 1.80(7) Å and 128.6° in the bivalent Ge(OC$_6$H$_2$-Me-4-Bu$^t{}_2$-2,6)$_2$ [11]. The Ge—C distances, 1.969(6) and 1.953(7) Å, are similar to those found in [Cr(CO)$_5$(GeR$_2$)], 1.98(7) Å [4], and within the range of known related distances: 1.89(3) Å in GeBr$_3$Me [12] to 2.08(3) Å in [Fe$_2$(CO)$_6$(μ-GeMe$_2$)$_3$] [13]. The difference in the H—Ge—C(1) and H—Ge—C(2) angles is attributed to the different H···CH$_3$ non-bonding contacts from the SiMe$_3$ groups attached to C(1) and C(2) (see Fig. 1).

We are grateful to Dr. P. Rivière for comments and access to his unpublished data; we thank S.R.C. (studentship for S.J.M.), N.A.T.O. (M.F.L. and A.J.C.) and the U.S. National Science Foundation (to J.L.A.) for support.

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