Neutral Ethers of Germanium and Tin, Linear at Oxygen: *X*-Ray Crystal and Molecular Structures of $[(PhCH_2)_3M]_2O$ (M = Ge or Sn)

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Summary The compounds $[(PhCH_2)_3M]_2O$ (M = Ge or Sn) have been found by *X*-ray analysis to contain linear Ge–O–Ge and Sn–O–Sn fragments.

WE recently reported[1] the first example of a linear Si–O–Si fragment in a neutral ether $(Ph_3Si)_2O$. Although such linear Si–O–Si bridges have been observed in a number of disilicates,[2] only a single example has been reported[3] of a linear Ge–O–Ge fragment, in a digermanate, $K_2Pb_3Ge_2O_7$, while tin analogues appear to be quite unknown. We now report that linear Ge–O–Ge and Sn–O–Sn fragments occur in $[(PhCH_2)_3M]_2O$, (M = Ge or Sn).

Crystal data: $C_{42}H_{42}Ge_2O$, rhombohedral, $R\bar{3}$, $a = 9{\cdot}621(2)$ Å, $\alpha = 85{\cdot}48(3)°$; $M_r = 707{\cdot}94$; $U = 882{\cdot}7$ Å^3, $F(000) = 366$, $D_c = 1{\cdot}332$ kg dm^{-3}, $Z = 1$, μ(Mo-K_α) = 16·65 cm^{-1}. $C_{42}H_{42}OSn_2$, $R\bar{3}$, $a = 9{\cdot}667(2)$ Å, $\alpha = 84{\cdot}05(3)°$; $M_r = 800{\cdot}14$; $U = 889{\cdot}7$ Å^3, $F(000) = 402$, $D_c = 1{\cdot}493$ kg dm^{-3}, $Z = 1$, μ(Mo-K_α) = 13·11 cm^{-1}.

The structures (Figure) were solved by Patterson and difference Fourier methods using diffractometer data (Philips PW 1100) and refined with C, O, and Ge or Sn anisotropic, H isotropic; the present conventional *R* indices are 0·0197 for 1569 data (M = Sn) and 0·0876 for 1025 data (M = Ge): the corresponding values of the generalised index[4] R_G are 0·0248 and 0·0455. The two compounds are isostructural, and in each the M–O–M fragment lies along the 3-fold axis of the rhombohedral cell, and hence is strictly linear. The possibility that the oxygen positions are disordered is eliminated by the difference maps and by the dimensions of the thermal ellipsoids of the oxygen atoms.†

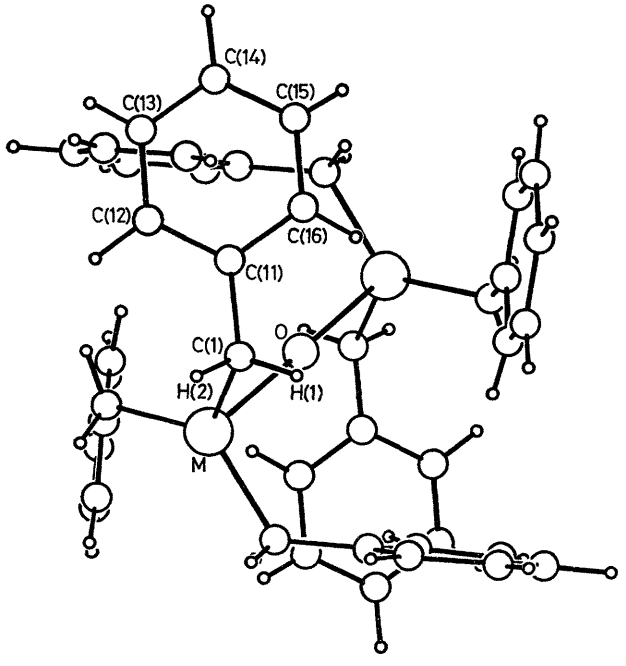

FIGURE. The molecule of $[(PhCH_2)_3M]_2O$. Mean bond distances are: (M = Ge), Ge–O, 1·730(1); Ge–C(1), 1·980(5); C(1)–C(11), 1·492(6); C(11)–C(12), 1·399(6); C(12)–C(13), 1·379(6); and C(13)–C(14), 1·371(6) Å; (M = Sn), Sn–O, 1·919(1); Sn–C(1), 2·167(2); C(1)–C(11), 1·490(3); C(11)–C(12), 1·393(3); C(12)–C(13), 1·384(3); and C(13)–C(14), 1·375(5) Å.

† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

In the analogous phenyl derivatives $(Ph_3M)_2O$, the bond angles at oxygen are 135·2(2)° for M = Ge[5] and 137·3(1)° for M = Sn;[6] these large values were ascribed primarily to the non-bonded M · · · M contacts.[7] It has been suggested[8] that in molecules of general type $(MX_n)_2O$ in which M is a *p*-block element, the tendency of a linear M–O–M fragment to bend is small when MX_n is of low electronegativity; the effect of the low electronegativity of M, here Ge or Sn, is reinforced when X is an electron donor group. The structures observed when M = Ge or Sn, X = Ph or CH_2Ph are consistent with this suggestion.

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