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Preliminary communication

PENTACOORDINATE SILICON AND GERMANIUM DERIVATIVES: MOLECULAR STRUCTURE

C. BRELIERE, F. CARRE, R.J.P. CORRIU*, A. DE SAXCE, M. POIRIER and G. ROYO
Laboratoire des Organométalliques, Equipe de recherche associée au CNRS No. 554,
Université des Sciences et Techniques du Languedoc, Place Eugène Bataillon,
34060 Montpellier-Cedex (France)

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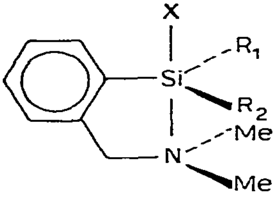
Summary

The crystal structure of *o*-$(Me_2NCH_2)C_6H_4GeMePhCl$ has been determined by single crystal X-ray diffraction study. The germanium atom has a distorted trigonal-bipyramidal (T.B.P.) geometry. The low temperature ^{19}F NMR spectra of *o*-$(Me_2NCH_2)C_6H_4SiMeF_2$ and *o*-$(Me_2NCH_2)C_6H_4SiF_3$ are also consistent with a T.B.P. geometry. The stability of the T.B.P. structure is not determined by the apicophilicity of the fluorine atoms.

Recently, we have reported that an internal coordination previously observed with Sn derivatives was also possible for monofunctional silanes, as in **1** [1].



(1, X = functional group)

The extent of intramolecular Si—N coordination is determined by the ease with which the Si—X bond can be stretched and replaced with inversion of configuration.

Pentacoordination ability

X: H, OR < F, SR < OAc, Cl, Br

$\longrightarrow$

Stereochemistry

Retention inversion

$\longrightarrow$

The order observed is not related to the electronegativity of X, and is very different from the order of apicophilicity of X in pentacoordinated phosphorus compounds [2]. Thus it was important to know whether the geometry of pentacoordinated silicon compounds was close to the trigonal bipyramid (T.B.P commonly observed for pentacoordinated phosphorus compounds.

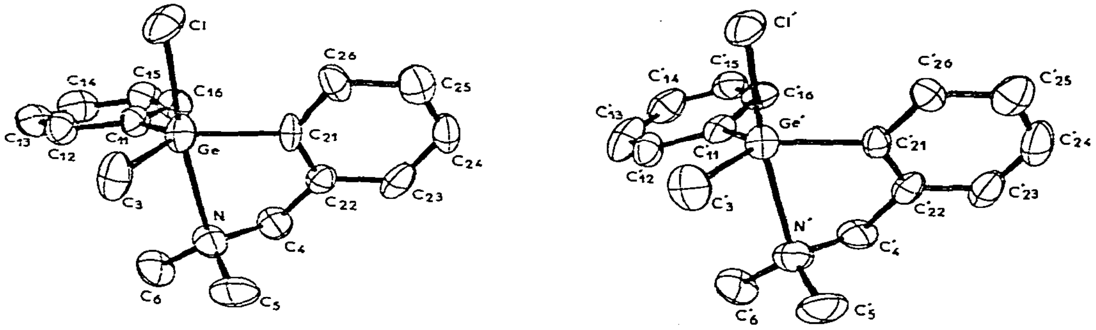
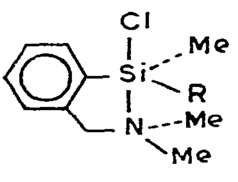


Fig. 1. A view of the structure of chlorogermane 2 with the two slightly different conformations. Main bond lengths are: Ge—Cl 2.327(5), Ge′—Cl′ 2.301(4), Ge—N 2.479(11), Ge′—N′ 2.508(11) Å. Selected bond angles are: Cl—Ge—N 174.0(2), Cl′—Ge′—N′ 173.8(3), N—Ge—C_{21} 77.3(4), N′—Ge′—C'_{21} 76.6(4)°.

An X-ray investigation of chlorogermane 2 shows that the germanium atom has a distorted trigonal bipyramidal geometry (Fig. 1) similar to that in the pentacoordinated tin compound 3a studied by Van Koten [3].

Crystal data. $C_{16}H_{20}ClNGe$, M 334.4, monoclinic, a = 7.540(2), b = 33.461(4), c = 12.876(1) Å, β = 96.56(1)°, U = 3227.2 Å^3, Z = 8, D_c = 1.376 g cm^{-3}, D_m = 1.371(8) g cm^{-3}; graphite monochromated Cu-K_α radiation, λ = 1.5418 Å, $\mu(\text{Cu}-K_\alpha)$ = 39.9 cm^{-1}; space group $P2_1/n$. The Cl and Ge atoms were located by direct methods and the remaining non-hydrogen atoms from a subsequent electron density-difference synthesis. The structure was refined by full matrix least-squares using 2546 observed [$I > 4\sigma(I)$] intensities out of a total 5231 measured, to a current R value of 0.10.



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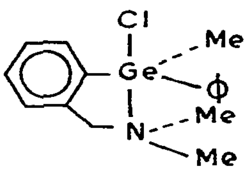

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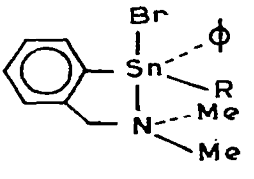

3

a, R = 1-Np; T_c = −35°C; ΔG^* = −12.3 T_c = −28°C
b, R = H; T_c = −40°C; ΔG^* = −12.3 G^* = −13
T_c = temperature of coalescence, ΔG^* in kcal mol^{-1}

a, R = ϕ(Ph) [3]
b, R = Me; T_c = 30°C [4]

The asymmetric unit consists of two crystallographically non-equivalent molecules, with closely related conformations.

An X-ray investigation of halogenosilanes 1 was not possible because they are liquids at room temperature. However, we can assume a T.B.P. geometry for the silicon compounds 1 since the ^1H NMR spectra of 1, 2 and 3 are very similar. The formation of an intramolecular metal—N bond induces diastereotopy of the two Me groups. The values of $\Delta G^\star$ are very similar for compounds 1 and 2.

In order to confirm these results the ^{19}F NMR spectra of fluorosilanes 4 and 5 have been examined and the data are summarized in Fig. 2.

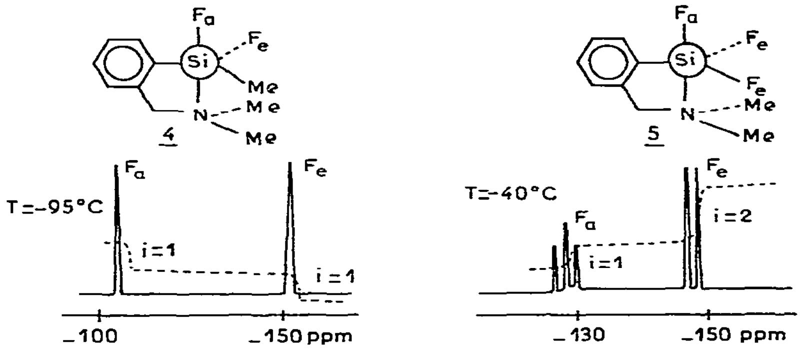

Fig. 2. The ^{19}F NMR spectrum of 4 and 5 in CD_2Cl_2 (recorded on a Varian EM 390 spectrometer at 84.67 MHz). Chemical shifts were measured relative to internal $CFCl_3$. Negative values are to high fields.

The low temperature spectra of 4 in non-polar media display two lines of relative intensities 1 and 1 ($F_a,\delta = -111$ ppm; $F_e,\delta = -154$ ppm). Under the same conditions the ^{19}F NMR spectrum of 5 consists of a triplet and a doublet of relative intensities 1 and 2 ($F_a,\delta = -128$ ppm; $F_e = -148$ ppm) in good agreement with T.B.P. geometry, involving two equatorial and none apical F atoms.

As for pentacoordinated phosphorus compounds, the apical fluorine signal is downfield and the equatorial one at high field [5].

These results confirm the generality of the trigonal bipyramid as the geometry of pentacoordinated compounds of Si, Ge, and Sn. Furthermore the ^{19}F NMR spectra of 4 and 5 show that the stability of the T.B.P. structure is not determined by the electronegativity of the F atoms, since in 4 and 5 one and two F atoms, respectively, are in equatorial positions.

References

1 R. Corriu, G. Royo and A. De Saxcé, J. Chem. Soc. Chem. Commun., (1980) 892.
2 S.A. Bone, S. Trippett and P.J. Whittle, J. Chem. Soc. Perkin I, (1974) 2125; J. Brierly, S. Trippett and M.W. White, J. Chem. Soc. Perkin I, (1977) 273; S. Trippett, Pure Appl. Chem., 40 (1974) 595.
3 G. van Koten, J.G. Noltes and A.L. Spek, J. Organometal. Chem., 118 (1976) 183.
4 G. van Koten and J.G. Noltes, J. Amer. Chem. Soc., 98 (1976) 5393.
5 F. Klanberg and E.L. Muetterties, Inorg. Chem., 7 (1968) 155.