

Note

A new heptacoordinated organogermanium compound; trichlorogermyl[tris(2-methoxyphenyl)]methane

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Received 11 June 2004; accepted 13 July 2004

Available online 12 August 2004

Abstract

A new hypercoordinated organogermanium compound, trichlorogermyl[tris(2-methoxyphenyl)]methane (**4**) was prepared, and its tricapped tetrahedral structure was confirmed by X-ray crystallographic analysis. All interatomic oxygen–germanium distances are shorter than the sum of van der Waals radii of O and Ge (3.62 Å).

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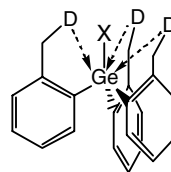
Keywords: Hypercoordination; X-ray crystallography; Organogermanium compounds; Tricapped tetrahedron

1. Introduction

Recently, hypercoordinated or hypervalent group 14 element compounds have attracted considerable attention [1]. In particular, Corriu and coworkers [2] described a variety of penta-, hexa- or heptacoordinate silicon compounds. We were interested in tris[(2-dimethylaminomethyl)phenyl]germane (**1a**) reported by Corriu et al. [3] which had a unique tricapped tetrahedron structure.

We found that tris[(2-*t*-butoxymethyl)phenyl]germane (**1b**) and tris[2-(2-methylthiomethyl)phenyl]germane (**1c**) displayed dicapped and tricapped tetrahedral structures, respectively [4]. We further reported tris[(2-dimethylaminomethyl)phenyl]germanes (**1d–1h**) with a substituent on germanium would be either tetrahedral or trigonal bipyramidal (TBP) depending on the nature of the substituent [5]. In all

these compounds, the coordination site (i.e., $-\text{C}_6\text{H}_4\text{CH}_2\text{D}$; D = a donor) is directly bonded to the central atom Ge.

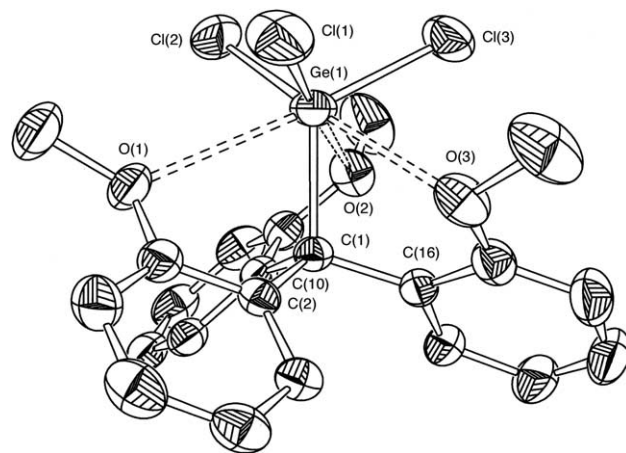
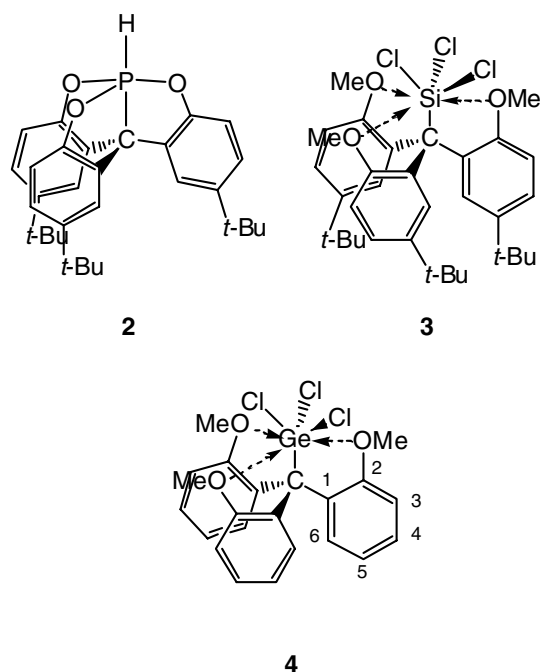


	D	X
1a :	Me ₂ N	H
1b :	<i>t</i> -BuO	H
1c :	MeS	H
1d :	MeO	F
1e :	MeO	Cl
1f :	MeO	Br
1g :	MeO	Me
1h :	MeO	Ph

Meanwhile Kawashima and coworkers [6] reported a phosphorus compound, 1-hydro-5-carbaphosphatrane (**2**). It occurred to us that if the phosphorus atom were to be replaced with germanium, an interesting skeleton for hypercoordinated organogermanium compounds might be formed. Indeed, Kawashima and coworkers [7] further reported the synthesis and tricapped tetrahedral structure of trichlorosilyltris(4-*t*-butyl-2-methoxyphenyl)methane (**3**).

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Fig. 1. ORTEP drawing of **4**.

In this paper, we report the synthesis and structure of a germanium analog of **3**, trichlorogermyl[tris(2-methoxyphenyl)methane (**4**).

2. Results and discussion

The synthesis of **4** was carried out as depicted in Scheme 1. The method is essential that reported for the synthesis of **2** [6]. The Grignard reagent of 2-bromoanisoole (**5**) was converted to tris(2-methoxyphenyl)methanol (**6**), which was reduced to tris(2-methoxyphenyl)methane (**7**) with the aid of Et_3SiH . The trichlorogermyl group was introduced into **7** via its lithio derivative **8**.

Compound **4** was fully characterized by NMR spectroscopy and elemental analysis. The ^1H and ^{13}C chemical shifts of methoxy group are close to those of anisole, suggesting the possible $\text{MeO}\cdots\text{Ge}$ interaction will be weak if presents at all.

The X-ray crystallographic analysis of **4** was carried out. The ORTEP drawing is shown in Fig. 1.

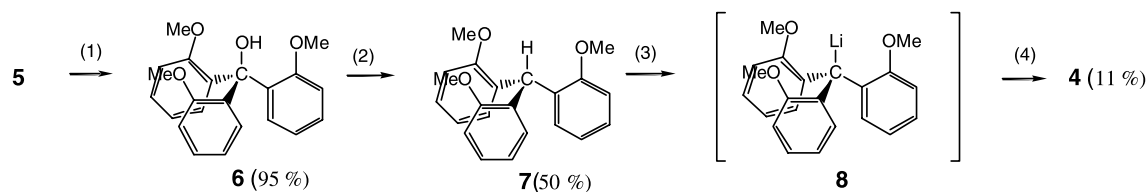
All the Cl–Ge–C and Cl–Ge–Cl angles are in the range of $100\text{--}117^\circ$, indicating that the central carbon and three Cl atoms form a tetrahedron with the germanium atom in the center.

The interatomic Ge \cdots O lengths are 2.736(2), 2.806(2), 2.808(2) Å, all of which are shorter than the sum of the van der Waals radii of germanium and oxygen, 3.62 Å. Furthermore, one of the lone pairs of each oxygen atom is directed towards the germanium atom. It is certain that there exist donor–acceptor interaction between the oxygen atoms and germanium. Thus, **4** has a tricapped tetrahedral structure as does its silicon counterpart, **3**. The germanium atom is in the center and the three oxygen atoms approach the germanium to form caps outside the faces of the tetrahedron. It must be added that all Ge–Cl bond lengths are 2.16–2.17 Å, which is slightly longer than the standard Ge–Cl length of 2.113 Å. This slight elongation may be due to the hypercoordination (see Table 1).

3. Experimental

3.1. General

^1H NMR spectra were determined on a JEOL ECP 500 spectrometer operating at 500 MHz, and the



(1) Mg, diethyl carbonate in THF, reflux 14 h (2) Et_3SiH in AcOH, stirring 12 h at 80°C (3) $n\text{-BuLi}$ in C_6H_6 , stirring 24 h at 50°C
 (4) $\text{GeCl}_4\cdot\text{HMPA}$ in THF, reflux 40 h.

Scheme 1. Synthesis of **4**.

Table 1
Selected bond lengths (Å) and bond angles (°) for **4**

Bond lengths		Bond angles	
Ge(1)–O(1)	2.736(2)	Cl(1)–Ge(1)–Cl(2)	102.11(3)
Ge(1)–O(2)	2.806(2)	Cl(1)–Ge(1)–Cl(3)	100.19(3)
Ge(1)–O(3)	2.808(2)	Cl(1)–Ge(1)–C(1)	117.37(6)
Ge(1)–Cl(1)	2.1589(8)	Cl(2)–Ge(1)–Cl(3)	101.10(3)
Ge(1)–Cl(2)	2.1684(6)	Cl(2)–Ge(1)–C(1)	116.83(6)
Ge(1)–Cl(3)	2.1651(6)	Cl(3)–Ge(1)–C(1)	116.45(6)
Ge(1)–C(1)	2.052(2)		

chemical shifts were reported in δ (ppm) with respect to Me₄Si. ¹³C NMR spectra were determined on the same instrument operating at 125 MHz and the chemical shifts were reported in δ (ppm) with respect to Me₄Si. Elemental analysis was carried out by the Microanalytical Laboratory, Department of Chemistry, School of Science, the University of Tokyo.

3.2. Trichlorogermyl{tris[(2-methoxy)phenyl]}methane (**4**)

The syntheses of **6** and **7** were performed with the method in the literature [6]. With the aid of Shlenk apparatus, tris-(2-methoxyphenyl)methane (**7**) (681 mg, 2.04 mmol) in benzene (20 ml) was reacted with *n*-BuLi (10.4 mmol). After the solvent was exchanged to THF, HMPA (1.5 ml) was added. To this mixture was added GeCl₄ (3.93 g, 18.4 mmol), and the mixture was refluxed for 40 h. After removal of the solvent, the residue was separated and purified by column chromatography (SiO₂/CHCl₃:hexane) and GPC. After removal of the

solvent, the residue was recrystallized from CHCl₃ + hexane (1:2) to obtain colorless plates **4**, (115 mg, 0.225 mmol); m.p. 267–269 °C. Anal. Calc. for C₂₂H₂₁Cl₃GeO₃: C, 51.57; H, 4.13. Found: C, 51.65; H, 4.17%. ¹H NMR (CDCl₃, 500 MHz); δ 3.69, (–OMe), 6.41 (dd, H₆), 6.83 (t, H₅), 6.93 (d, H₃), 7.37(m, H₄); ¹³C NMR (CDCl₃, 125 MHz); δ 58.9 (–OMe), 68.3 (C), 110.1 (C₃), 120.7 (C₅), 126.9 (C₁), 129.4 (C₄), 130.0 (C₆), 156.6 (C₂).

3.3. X-ray crystallography

Crystal data for **4** were collected on a Rigaku MSC Mercury CCD diffractometer with graphite monochromated Mo K α ($\lambda = 0.7107$ Å). The structure was solved by direct methods using the programs SIR 92 and were refined by full-matrix least-squares procedures using Crystal Structure. Final atomic parameters of **4** were deposited at the Cambridge Crystallographic Data Centre [8]. The crystallographic data are summarized in Table 2. Perspective views of the molecules (Fig. 1) were made by the use of ORTEP for –3 [9].

Acknowledgments

Y.T. thanks the financial support (The High-tech Research Center Project) from The Ministry of Education, Culture, Sports, Science and Technology. We thank Prof. T. Kawashima, the University of Tokyo, for valuable discussion.

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Table 2
Crystallographic data for **4**

Formula	C ₂₂ H ₂₁ Cl ₃ GeO ₃
Formula weight	512.36
Crystal color, habit	Colorless, platelet
Crystal dimensions (mm)	0.20 × 0.20 × 0.20
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	11.423(7)
<i>b</i> (Å)	10.975(5)
<i>c</i> (Å)	18.73(2)
β (°)	103.415(7)
<i>V</i> (Å ³)	2283.9(30)
<i>Z</i>	4
Calculated density (g/cm ³)	1.490
Reflection collected	48384
Unique	5457
<i>R</i> _{int}	0.038
<i>F</i> ₀₀₀	1040.00
<i>R</i> ₁ (all data)	0.033
<i>wR</i> ₂ (all data)	0.081
Goodness-of-fit	0.997