THE SYNTHESIS AND CHARACTERIZATION OF THE CYCLOTRIGERMOXANE: $(Ph_4C_4GeO)_3$

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Abstract

The cyclotrigermoxane, $(Ph_4C_4GeO)_3$, first isolated adventitiously, was synthesized in good yield by the hydrolysis of 1,1-dichlorotetraphenylgermole. The cyclotrigermoxane crystallized as small yellow rectanglar blocks, which were analyzed by X-ray crystallography. The Ge-O ring is planar with a Ge-O bond length of 1.7680(11) Å and endocyclic bond angles of 132.45(17)° (Ge-O-Ge) and 107.55(17)° (O-Ge-O). The cyclotrigermoxane was fully characterized by ^1H, ^{13}C NMR, ir and mass spectrometry.

Introduction

Recent interest in the chemistry of germole derivatives [1] has focussed on the synthesis of and the extent of delocalization in anionic germole derivatives [2] as well as on the incorporation of the germole moiety into conjugated polymeric materials [3]. The facile and high yield synthesis of the stable, bulky dilithiogermole, 1,1-dilithiotetraphenylgermole, was of particular interest to us since the dilithiogermole appeared to be well suited as a reagent for the synthesis of doubly-bonded germanium derivatives, such as digermenes and germasilenes [4]. We envisioned a new synthetic route to a stable germasilene by the reaction between the stable dilithiogermole and a dihalosilane such as dichloro- or difluorobis(2,4,6-triisopropylphenyl)silane in THF. However, all attempts to synthesize a stable germasilene failed [5]. During the course of these studies, we did observe the formation of the cyclotrigermoxane **1**, in low yield. Given the current interest in germole derivatives and the limited number of structurally characterized cyclotrigermoxanes [6], we synthesized the cyclotrigermoxane in good yield by a cyclocondensation reaction and fully characterized this compound, including the determination of its molecular structure. We report herein on the results of those studies.

Results and Discussion

Many attempts were made to synthesize a germasilene by the reaction between 1,1-dilithiotetraphenylgermole and a dihalosilane. In a typical experiment, a solution of the dilithiogermole in THF was added to an equivalent of either dichloro- or difluorobis(2,4,6-triisopropylphenyl)silane dissolved in THF. No evidence for the formation of a germasilene was obtained. The use of toluene as a solvent, the addition of 12-crown-4, or the use of a less bulky silane (dichlorodimesitylsilane) all failed to provide any proof for the formation of a germasilene. During the course of these experiments, a small amount of a crystalline solid was often isolated. The solid was identified as the cyclotrigermoxane **1** (Figure 1) by X-ray crystallography.

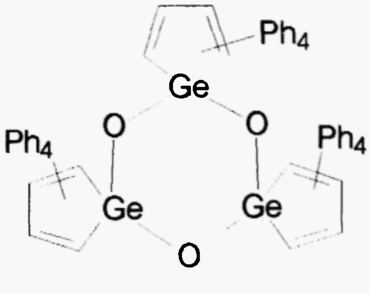

Figure 1. Cyclotrigermoxane **1**

To obtain enough material for complete characterization, the cyclotrigermoxane was prepared, in 76 % yield, by the hydrolysis of 1,1-dichlorotetraphenylgermole with an excess of distilled water and triethylamine. The product crystallized as small, rectangular, yellow blocks from a saturated hexanes solution or as small yellow plates from a CH_2Cl_2/hexanes mixture.

Assignment of the ^{1}H and ^{13}C NMR Chemical Shifts of the Cyclotrigermoxane 1

The assignment of the signals in the ^{1}H and ^{13}C NMR spectra of tetraphenylgermole derivatives has proven to be a non-trivial task [7]. These compounds are expected to have at least ten different carbon signals, all of which resonate between 120 and 160 ppm, arising from the two chemically distinct carbon atoms of the heterocycle and the two different sets of two phenyl groups. The ^{1}H NMR spectra of neutral, substituted tetraphenylgermoles, in general, are also complex. All of the protons are extensively coupled. In addition, these signals resonate over a narrow chemical shift range (6.8 – 7.2 ppm) which leads to overlap of at least some of the multiplets [7]. The chemically distinct proton and carbon atoms of tetraphenylgermole compounds are shown below (Figure 2). An accurate assignment of each signal in the spectra could only be made after analysis of the 2-D correlation spectra of **1**.

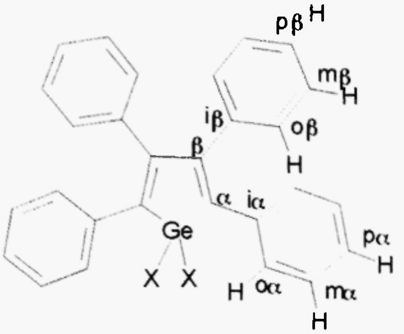

Figure 2. The Chemically Distinct ^{1}H and ^{13}C Atoms of Tetraphenylgermole Derivatives

A unique feature of this class of compounds is that the resonance for the β-C atom is typically found downfield of the signal attributed to the α-C atom [7]. Furthermore, the chemical shift of the β-C has been found to be almost constant (151.9 +/- 2 ppm) over a range of substituted tetraphenylgermoles [7]. The chemical shifts of the α-C and the β-C for several tetraphenylgermoles are listed in Table 1.

Table 1. ^{13}C NMR Chemical Shifts for Various Tetraphenylgermoles (Ph$_4$C$_4$GeX$_2$)

X	C_α	C_β	Ref.
H	139.18	153.79	7a
Cl	132.68	149.92	7a
Me	143.88	151.20	7a
SiMe$_3$	149.31	151.57	7a

Because the β-C is invariably the lowest field signal in the ^{13}C NMR spectrum of tetraphenylgermoles, it provides a useful starting point for assigning the ^{13}C and ^{1}H NMR spectra of the cyclotrigermoxane. The lowest field signal in the ^{13}C NMR spectrum of the cyclotrigermoxane, (Ph$_4$C$_4$GeO)$_3$, occurs at 152.65 ppm. The Attached Proton Test (APT) spectrum revealed that the signal was either due to a quaternary or a methylene carbon atom, and thus, was assigned as the β-C resonance.

To distinguish between the α and β rings, gradient-Heteronuclear Multiple Bond Correlation (g-HMBC) spectroscopy was utilized. The experiment was optimized to reveal the three-bond ^{1}H-^{13}C correlations [8]. A correlation was observed between the signal at 152.65 ppm in the ^{13}C dimension, which has been assigned to C_β, and a doublet at 6.55 ppm (7.6 Hz) in the ^{1}H dimension. Thus, this doublet was assigned to $H_{o\beta}$. Since only the ortho hydrogen atoms are expected to be a doublet with J ~ 7-8 Hz, the remaining doublet at 6.73 ppm (8.0 Hz) in the ^{1}H NMR spectrum of the cyclotrigermoxane was assigned to $H_{o\alpha}$. A crosspeak was observed between this doublet and the signal at 131.12 ppm in the carbon domain. According to the APT spectrum of the cyclotrigermoxane, the carbon signal at 131.12 ppm was either a quaternary or a methylene carbon atom, and therefore, was assigned to the C_α atom.

Establishing the assignment of the $H_{o\alpha}$ and $H_{o\beta}$ resonances allowed for the assignment of $H_{m\alpha}$ and $H_{m\beta}$ by gradient-Correlation Spectroscopy (g-COSY). In the g-COSY spectrum, the doublet assigned to $H_{o\alpha}$

at 6.73 ppm was correlated to a triplet at 6.47 ppm (7.8 Hz). Thus, the signal at 6.47 ppm was assigned to $H_{m\alpha}$. The doublet at 6.55 ppm, assigned to $H_{o\beta}$, was correlated with a resonance in the broad multiplet centred at 6.9 ppm. According to the integrated areas, this multiplet accounted for twice the number of protons as any of the other multiplets. Therefore, this multiplet must contain signals from $H_{p\alpha}$, $H_{p\beta}$, and $H_{m\beta}$.

The signals assigned to the meta protons in the ^1H dimension also exhibit a crosspeak in the g-HMBC spectrum. A crosspeak was found between the $H_{m\alpha}$ resonance at 6.47 ppm in the ^1H dimension and the signal at 137.01 ppm in the ^{13}C domain. According to the APT spectrum this resonance can be assigned to a quaternary or a methylene carbon atom. This crosspeak was assigned to vicinal coupling between $H_{m\alpha}$ and $C_{i\alpha}$. The remaining carbon resonance at 137.57 ppm, which is a quaternary or a methylene according to the APT spectrum, was assigned to $C_{i\beta}$. This resonance exhibited a correlation with the multiplet at 6.9 ppm in the ^1H dimension.

The ortho protons show additional vicinal coupling with the para carbon atoms. The doublet assigned to $H_{o\alpha}$ (6.73 ppm) in the ^1H dimension exhibited a correlation with the resonance at 125.97 ppm in the ^{13}C dimension. This signal was assigned to $C_{p\alpha}$. A crosspeak was observed between the doublet at 6.55 ppm in the ^1H dimension, assigned to $H_{o\beta}$, and the signal at 126.41 ppm in the ^{13}C dimension. Thus, the signal at 126.41 ppm in the ^{13}C dimension was assigned to $C_{p\beta}$.

The remaining signals were assigned using a gradient-Heteronuclear Spin Quantum Coherence (g-HSQC) spectrum of the cyclotrigermoxane. Crosspeaks were located for $H_{o\alpha}$ and $H_{o\beta}$. The correlated carbon signals are located at 128.82 and 129.73 ppm, respectively. A correlation was found between the signal assigned to $H_{m\alpha}$ at 6.47 ppm and the resonance at 128.24 ppm in the ^{13}C dimension. Thus, the signal at 128.24 ppm was assigned to $C_{m\alpha}$. The remaining unidentified carbon signal at 127.35 ppm was assigned to $C_{m\beta}$, and accordingly this signal exhibited a crosspeak with the multiplet at 6.9 ppm in the ^1H dimension.

Extraction of the $H_{m\beta}$ $H_{p\alpha}$ and $H_{p\beta}$ chemical shifts was possible using the g-HSQC spectrum. The centre of the $C_{m\beta}$-$H_{m\beta}$ crosspeak was located at (127.35, 6.85 ppm). The chemical shift of $H_{p\alpha}$ is 6.87 ppm based on the correlation with $C_{p\alpha}$, and likewise, the chemical shift of $H_{p\beta}$ is 6.91 ppm based on the correlation with $C_{p\beta}$. The chemical shift assignments for both the ^1H and ^{13}C NMR spectra of the cyclotrigermoxane are listed in Table 2.

Table 2. ^1H and ^{13}C NMR Chemical Shifts (in $CDCl_3$) for $(Ph_4C_4GeO)_3$.

Atom	Position	Chem. Shift (ppm)	Atom	Position	Chem. Shift (ppm)	J (Hz)
C_α		131.12	C_p	α/β	125.97/126.41	
C_β		152.65	H_o	α/β	6.73/6.55	8.0/7.6
C_{ipso}	α/β	137.01/137.57	H_m	α/β	6.47/6.85	7.8/-
C_o	α/β	128.82/129.73	H_p	α/β	6.87/6.91	
C_m	α/β	128.24/127.35				

Molecular Structure of $(Ph_4C_4GeO)_3$

The molecular structure of **1** is shown in Figure 3. The Ge-O ring system forms a plane; the C_4Ge unit was found to lie in a perpendicular plane. Selected bond lengths and angles observed for this cyclotrigermoxane are listed in Table 3 along with those observed for other known cyclotrigermoxanes. The bond lengths and angles of **1** are comparable to those of the known cyclotrigermoxanes. The molecular symmetry of **1** is D_3

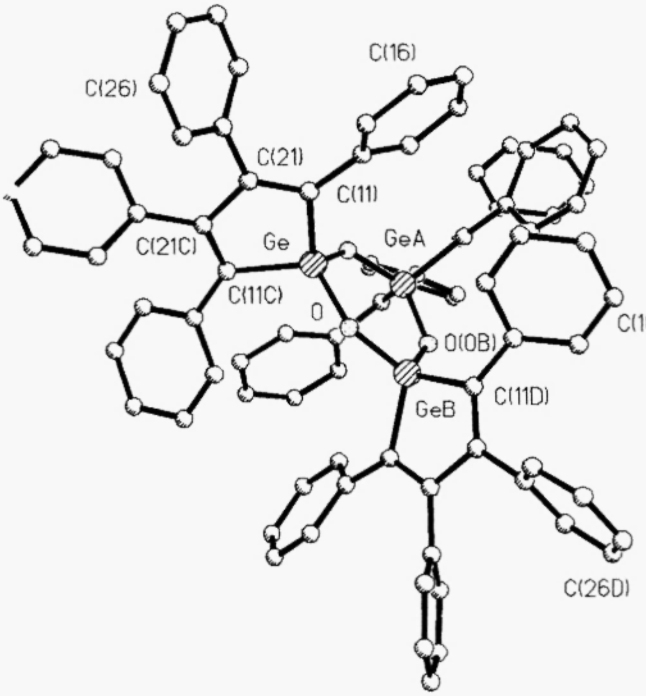

Figure 3. Molecular Structure of Cyclotrigermoxane **1**

Table 3. Bond Lengths and Angles for Cyclotrigermoxanes

Bond	(Ph$_2$GeO)$_3$ [6b]	(^{t}Bu$_2$GeO)$_3$ [6c]	(Ph$_4$C$_4$GeO)$_3$
Ge-O (Å)	1.76-1.77	1.781(1)	1.7680(11)
Ge-O-Ge(°)	128-130	133.0(1)	132.45(17)
O-Ge-O (°)	107-108	107.0(1)	107.55(17)

Conclusions

The reaction between 1,1-dilithiotetraphenylgermole and bulky dihalosilanes does not appear to be a viable route to a stable germasilene. The cyclotrigermoxane (Ph$_4$C$_4$GeO)$_3$ can be prepared in good yield by the hydrolysis of 1,1-dichlorotetraphenylgermole. The ^{1}H and ^{13}C NMR spectroscopic data, with complete assignments, has been reported. The structure of the cyclotrigermoxane was determined by X-ray crystallography and was found to be very similar to other reported cyclotrigermoxanes.

Experimental Section

All experiments were carried out in flame-dried glassware under an argon atmosphere using dry solvents unless otherwise noted. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl. Literature methods were used to prepare 1,1-dichlorotetraphenylgermole [2f,h]. A Gallenkamp metal block apparatus was used to determined all melting points. NMR spectra were recorded on a Mercury 400 spectrometer using chloroform-D as a solvent, unless otherwise noted. The standards used were residual CHCl$_3$ (7.24 ppm) for ^{1}H NMR spectra and CDCl$_3$ central transition (77.0 ppm) for ^{13}C NMR spectra. Infrared spectra were recorded (cm^{-1}) as thin films on a Perkin Elmer System 2000 FT IR spectrometer. A Finnegan MAT model 8200 instrument was used with an ionizing voltage of 70 eV to obtain electron impact mass spectra (reported in mass-to-charge units, m/z, with ion identity and intensities of peaks relative to the base peak in parentheses).

Synthesis and Characterization of the Cyclotrigermoxane

1,1-Dichlorotetraphenylgermole (504 mg, 1.01 mmol) was dissolved in a solution of THF (25 mL), distilled water (1.0 mL, 56 mmol) and triethylamine (0.83 mL, 6.0 mmol). The clear yellow solution was stirred at room temperature overnight. The volatiles were removed under vacuum to give a yellow oil. The oil was dissolved in CH_2Cl_2 and the solution was extracted with H_2O (3 x 20 mL). The organic phase was dried over $MgSO_4$, filtered and the CH_2Cl_2 evaporated under vacuum to give a yellow foam. The foam was dissolved in a minimum of hot CH_2Cl_2 and hexanes was layered over the yellow solution. Initially, small yellow plates formed and later small yellow cubes crystallized.

The X-ray diffraction pattern of the cubes was analyzed and the size of the unit cell was found to match the cell dimensions found for the crystals of $(Ph_4C_4GeO)_3$, isolated from the attempted reactions of 1,1-dilithiotetraphenylgermole with dihalosilanes. A mixture of the plates and cubes was crushed and the melting point of the mixture was found to be 312.3-313.7 °C. The yield of the cyclotrigermoxane, $(Ph_4C_4GeO)_3$, was 344 mg (76.4 %). The ^1H and ^{13}C NMR data are given in Table 2.
MS (m/z) : 1334 (M^+, $[Ph_4C_4]_3{}^{72}Ge_2{}^{74}GeO_3$, 4). 964 ($[Ph_4C_4{}^{72}GeO]_2{}^{74}Ge$, 8), 785 ($[Ph_4C_4]_2{}^{74}Ge$ - H, 100)
High Res. MS (m/z) : Calc. For $[Ph_4C_4]_3{}^{72}Ge_2{}^{74}GeO_3$: 1334.22; found : 1334.24.
IR (thin film, cm^{-1}) : 3055 (w), 1598 (w), 1487 (m), 1441(m), 1299 (w), 1264 (w), 1073 (w), 1025 (w), 923 (m) 859 (s), 785 (m), 780 (w), 735 (w), 697 (s)

Structure of the Cyclotrigermoxane

Crystals of $(Ph_4C_4GeO)_3$ were grown from a saturated hexanes solution. A small yellow rectangular block suitable for X-ray analysis was selected and mounted on a glass fibre. Data were collected at 200 K on a Nonius Kappa-CCD diffractometer using COLLECT (Nonius, 1998) software. The unit cell parameters were calculated and refined from the full data set. Crystal cell refinement and data reduction were carried out using the Nonius DENZO package. The data were processed using SCALEPACK (Nonius, 1998). The crystal data and refinement parameters for $(Ph_4C_4GeO)_3$ are listed in Table 4. Systematic absences implied either R-3c or R3c. E-statistics and successful solution confirmed R-3c (the centrosymmetric choice). Attempted solution in R3c led to a final R value larger by 0.007.

The SHELXTL 5.101 (Sheldrick, G.M., Madison, WI) program package was used to solve the structure by direct methods and successive difference Fouriers. The refinement was straightforward. Only one-sixth of $(Ph_4C_4GeO)_3$ had to be located as the rest of the molecule was generated by symmetry. The germanium and oxygen atoms were on special positions and had half occupancies assigned to them. Two C-Ph groups were located and all non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were calculated geometrically and were riding on their respective carbon atoms. The largest residual electron density peak (0.53 e/$Å^3$) was associated with one of the phenyl rings.

Table 4. Crystal Data and Refinement Parameters for $(Ph_4C_4GeO)_3$

Formula	$C_{84}H_{60}Ge_3O_3$	Formula Weight	1335.09
Crystal System	Hexagonal	Space Group	R-3c
a, Å	18.8439(7)	c, Å	31.2930(15)
Volume, $Å^3$	9623.2(7)	Z	6
Crystal Size, mm	0.16 x 0.07 x 0.07	Temperature	200(2) K
X-Ray Wavelength	0.71073 Å	Density (calc.)	1.382 mg/m^3
F(000)	4104 electrons	Theta Range for Data Collection	2.82 to 30.04°
Reflections Collected	9653	Independent Reflections	3109 [R(int) = 0.094]
Abs. Coeff.	1.449 mm^{-1}	Completeness to theta = 30.04°	99.2 %
Index Ranges	$0 <= h <= 26$, $-22 <= k <= 0$, $-42 <= l <= 42$	Refinement Method	Full-matrix least squares on F^2
Absorption Correction	Integration	Data / Restraints	3109 / 0
Goodness-of-Fit	1.01	Parameters	137
R indices (all data)	R1 = 0.168, wR2 = 0.113	Final R [I>2sigma(I)]	R1 = 0.067, wR2 = 0.093
Largest diff. Peak and Hole e.$Å^3$	0.53 and –0.39		
Weighting Scheme	$W=1/[\Phi^2(F_o^2)+(aP)^2+bP]$, a=.0335, b=.3222 . $P=[max(F_o^2,N)+2F_c^2]/3$		
Deposition no.	168370		

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