Addition of Chloroform to Tetramesityldigermene

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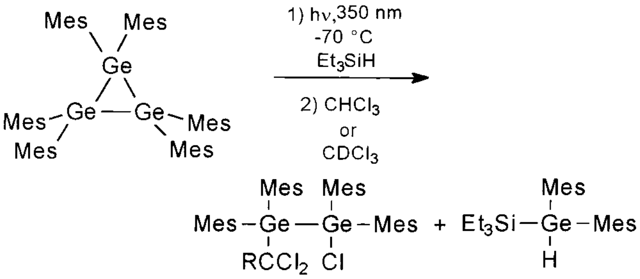
Summary: The addition of chloroform to tetramesityldigermene yields 1,1,2,2-tetramesityl-1-chloro-2-(dichloromethyl)digermane in 25% isolated yield.

Introduction

Since the discovery, in 1982, by Masamune and coworkers that stable digermenes are readily produced by the photolysis of cyclotrigermanes, there have been many reports of the reactivity of these novel compounds.[1] However, the reaction between stable digermenes and chlorinated methanes is notably absent. In view of the report by Kira and co-workers on the addition of halogenated methanes to tetrasilyl-substituted disilenes[2] and a recent report by Mochida and coworkers on the reaction between transient tetramethyldigermene and carbon tetrachloride,[3] we are prompted to report on our recent research concerning the reaction between tetramesityldigermene and chloroform.



1a R=H **2**
1b R=D

Results and Discussion

Chloroform was added to a solution of tetramesityldigermene, generated by photolysis of hexamesitylcyclotrigermane at −70 °C in toluene in the presence of triethylsilane.[4] The yellow color of the solution immediately disappeared. Removal of the solvent gave approximately a 1:1 mixture of 1,1,2,2-tetramesityl-1-chloro-2-(dichloromethyl)digermane, **1a**, and the silylgermane[5] **2**. The ^{1}H NMR spectrum of **1a** revealed the presence of an equal amount of two unique mesityl substituents in addition to a singlet at 6.33 ppm which integrated for one hydrogen. There was no band observed in the IR spectrum of **1a** in the region of 2000−2100 cm^{-1}, which would have indicated the presence of a Ge−H bond. In addition to the signals attributable to the two unique mesityl substituents, a signal at 67.97 ppm was observed in the ^{13}C NMR spectrum of **1a**. The gHSQC spectrum (*J* set at 180 Hz) revealed a cross-peak between the signal observed at 6.33 ppm in the ^{1}H dimension and the signal observed at 67.97 ppm in the ^{13}C dimension. The EI and CI mass spectra of **1a** did not contain a signal that could be attributed to the molecular ion of an adduct between chloroform and the digermene. However, using potassium (K^+) ionization of desorbed species (K^+IDS) as a mild ionization technique,[6] a signal attributable to the molecular ion of **1a** (+ K^+) was clearly evident. From these data, it was clear that an adduct between chloroform and the digermene had been obtained, and furthermore, a C−Cl bond of $HCCl_3$ had regioselectively added to the Ge═Ge bond to give the chloro(dichloromethyl)digermane, **1a**. The addition of deuterated chloroform to tetramesityldigermene resulted in the formation of **1b**. As expected, the ^{1}H (6.33 ppm) and the ^{13}C (67.97 ppm) signals attributed to the dichloromethyl group in **1a** were absent from the ^{1}H and ^{13}C NMR spectra, respectively, of **1b**.

The identity of the product was confirmed by X-ray crystallography. The molecular structure of **1b** is shown in Figure 1. The crystal data and selected structure refinement parameters are given in Table 1. All bond lengths, including the lengths of the Ge−Ge (2.5090(9) Å) and the Ge−Cl (2.209(2) Å) bonds, and angles fall within normal ranges (see Table 2).[7] The torsion angle ClGe(2)Ge(1)C(1) is 169.1°.

The regiochemistry of the addition of chloroform to tetramesityldigermene as well as the ease of reaction parallels that observed in the addition of chloroform to tetrasilyl-substituted disilenes.[2] However, the apparently facile reaction between tetramesityldigermene and chloroform is in contrast with the fact that tetramethyldigermene does not react with chloroform, at least at a rate greater than 10^4 M^{-1} s^{-1}.[3] The addition of the C−Cl bond of $HCCl_3$ to tetramesityldigermene is also in marked contrast with the addition of the C−H bond of $HCCl_3$ to the Ge═C bond of two transient germenes[8] or addition of the C−H bond of $HCCl_3$ to the Ge═N bond

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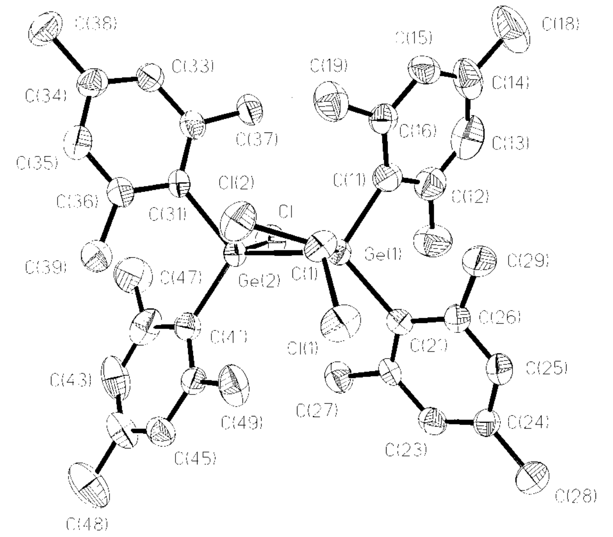

Figure 1. Molecular structure of **1b**.

Table 1. Crystal Data and Structure Refinement Parameters for $Mes_2Ge(Cl)Ge(CDCl_2)Mes_2$ (1b)

empirical formula	$C_{37}H_{44}DCl_3Ge_2$
fw	741.26
temp	150(2) K
wavelength	0.71073 Å
cryst syst	monoclinic
space group	*Cc*
unit cell dimensions	
a	12.722(3) Å
b	17.339(4) Å
c	16.538(3) Å
α	90°
β	101.85(3)°
γ	90°
volume	3570.1(12) $Å^3$
Z	4
density (calcd)	1.379 Mg/m^3
abs coeff	1.932 mm^{-1}
F(000)	1528
cryst size	0.20 × 0.15 × 0.10 mm^3
θ range for data collection	4.19−26.34°
index ranges	$0 \le h \le 15$, $0 \le k \le 21$, $-20 \le l \le 20$
no. of rflns collected	17 665
no. of indep rflns	3621 [R(int) = 0.0570]
abs corr	integration
refinement method	full-matrix least-squares on F^2
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0342, wR2 = 0.0848
R indices (all data)	R1 = 0.0404, wR2 = 0.0968

of two stable germanimines.[9] Differences in the reactivity between digermenes, germenes, and germanimines and other reagents have been noted previously. For example, phenylacetylene reacts with $Dep_2Ge{=}GeDep_2$ (Dep = 2,6-diethylphenyl) to give a digermetene,[10] whereas the C−H bond of phenylacetylene adds across the Ge═N bond of two stable germanimines to give (alkynylgermyl)amines.[11] The formal [2 + 2] cycloadduct is obtained from the reaction between acetone and $Dep_2Ge{=}GeDep_2$,[10] whereas the formal ene product is obtained from the reaction between acetone and a stable germene.[12] These differences in reactivity can be attributed to the differences in the polarity of the double bonds of digermenes, germenes, and germanimines. We continue to study the scope of the addition of halogenated methanes to group 14 dimetallenes as well as the mechanism of these additions.

Table 2. Selected Bond Distances (Å) and Angles (deg) for $Mes_2Ge(Cl)Ge(CDCl_2)Mes_2$ (1b)

Distance		Angle	
Ge(1)−C(1)	2.050(6)	C(21)−Ge(1)−C(11)	104.2(2)
Ge(1)−Ge(2)	2.5090(9)	C(1)−Ge(1)−Ge(2)	105.0(2)
Ge(2)−Cl	2.209(2)	C(21)−Ge(1)−Ge(2)	122.8(2)
C(1)−Cl(2)	1.746(7)	C(41)−Ge(2)−Cl	101.3(2)
C(1)−Cl(1)	1.800(7)	Cl−Ge(2)−Ge(1)	96.87(6)
		Cl(2)−C(1)−Cl(1)	108.8(4)
		C(31)−Ge(2)−Cl	110.1(2)
		C(21)−Ge(1)−C(1)	104.3(3)
		C(11)−Ge(1)−C(1)	110.9(3)
		C(11)−Ge(1)−Ge(2)	109.4(2)
		C(41)−Ge(2)−C(31)	110.1(2)
		C(41)−Ge(2)−Ge(1)	121.9(2)
		C(31)−Ge(2)−Ge(1)	114.1(2)
		Cl(2)−C(1)−Ge(1)	115.7(3)
		Cl(1)−C(1)−Ge(1)	112.5(3)

Experimental Section

General Information. All experiments were carried out in flame-dried glassware under an atmosphere of argon. Toluene was freshly distilled from sodium/benzophenone. Chloroform was distilled from phosphorus pentoxide prior to use. Hexamesitylcyclotrigermane was synthesized according to the published procedure.[13] Photolyses were carried out at 350 nm using a Rayonet photochemical reactor. Low-temperature photolyses were carried out by cooling the sample using an Endocal model ULT-70 low-temperature external bath circulator to force cold (−70 °C) methanol through a vacuum-jacketed Pyrex (350 nm) immersion well.

NMR spectra were recorded on a Varian Gemini 300 or Inova 400 or 600 spectrometer using benzene-d_6 as a solvent, unless noted otherwise. IR spectra were recorded (cm^{-1}) as thin films of the compound deposited on NaCl plates from CH_2Cl_2 on a Perkin-Elmer System 2000 FT IR spectrometer. A Finnegan MAT model 8200 mass spectrometer, with an ionizing voltage of 70 eV, was used to obtain electron impact or chemical ionization mass spectra (reported in mass-to-charge units, *m*/*z*, with ion identity and peak intensities relative to the base peak in parentheses). The detailed experimental procedure to perform K^+IDS has been described elsewhere.[6]

Reaction of Tetramesityldigermene with Chloroform. Cyclo-Ge_3Mes_6 (50 mg, 0.054 mmol) and Et_3SiH (0.1 mL, excess) were dissolved in toluene (4 mL) and photolyzed (350 nm) at −70 °C for 16 h. After irradiation for 16 h, the reaction mixture appeared clear and bright yellow in color. Upon the addition of chloroform (2 mL, 0.026 mmol) to the cold solution, the yellow color of the solution faded to clear and colorless. The solvent was removed in vacuo to yield an oily white residue. The product mixture (containing **1a**, **2**, and oxidation byproducts[14]) was separated by preparative thin-layer chromatography (silica gel; 50/50 CH_2Cl_2/hexanes) to yield a 1:2 mixture of **1a** and **2**[5] as determined by ^1H NMR spectroscopy. This mixture was also separated by preparative thin-layer chromatography (silica gel; 50/50 CH_2Cl_2/hexanes) to give 1,1,2,2-tetramesityl-1-chloro-2-(dichloromethyl)digermane, **1a** (10.2 mg, 25%), as a white solid. Mp: 198−199 °C. IR (cm^{-1}):

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3365 (m), 2974 (m), 2921 (m), 1602 (s), 1554 (w), 1449 (s), 1405 (m), 1379 (m), 1289 (w), 1261 (m), 1092 (s), 1049 (s), 951 (w), 880 (w), 847 (s), 802 (s), 701 (w). ^{1}H NMR (ppm): 6.68 (s, 4H, Mes CH), 6.65 (s, 4H, Mes CH), 6.33 (s, 1H, CCl$_2$H), 2.46, 2.32 (each bs, 21H total, Mes *o*CH$_3$), 2.05, 2.03 (each s, 12H total, Mes *p*CH$_3$). ^{13}C NMR (ppm): 144.21 (bs), 143.92 (bs), 139.73, 139.32, 138.61 (Mes C), 130.54, 130.28 (Mes CH), 67.97 (CHCl$_2$) 26.52 (bs), 26.03 (bs), 21.19 (Mes CH$_3$). MS (*m*/*z*), CI:isobutane: 705 [M$^+$(^{72}Ge^{74}Ge) − Cl, 23], 583 [Mes^{72}Ge^{72}Ge(CCl$_2$)Mes$_2$, 9], 479 [Mes$_3$^{74}GeCHCl, 49], 395 [Mes$_2$^{74}GeCHCl$_2$, 21], 361 (Mes$_2$^{74}GeCHCl +H, 100), 347 (Mes$_2$^{74}GeCl, 62), 311 (Mes$_2$^{72}Ge +H, 65), 277 (24), 237 (Mes^{72}GeCCl −H, 64), 133 (48), 120 (MesH, 18). MS (*m*/*z*): 847(7), 727 (13), 623 [M$^+$(^{72}Ge^{74}Ge) − CCl$_3$, 18], 465 (Mes$_2$^{72}Ge(Cl)^{72}GeCHCl, 9), 431 (Mes$_3$^{74}Ge, 100), 345 (Mes$_2$^{72}GeCl, 14), 311 (Mes$_2$^{72}Ge +H, 76), 235 (62), 221 (63), 191 (Mes^{72}Ge, 45), 119 (Mes, 55). K$^+$IDS MS (*m*/*z*): 779 (M$^+$ + 39, 100).

Addition of *d*-chloroform (0.05 mL, 0.62 mmol), instead of chloroform, gave 1,1,2,2-tetramesityl-1-chloro-2-[dichloro(deuterio)methyl]digermane, **1b** (21 mg, 52%), as a white solid after purification by chromatography (30/70 CH$_2$Cl$_2$/hexanes). Compound **1b** was recrystallized from hexanes to afford clear, colorless crystals. Mp: 201−202 °C. IR (cm^{-1}): 2922 (s), 1601 (s), 1554 (m), 1448 (s), 1404 (m), 1378 (m), 1289 (m), 1260 (w), 1120 (w), 1026 (w), 846 (s), 805 (m), 719 (m), 706 (m). ^{1}H NMR (ppm): 6.68 (s, 4H, Mes CH), 6.65 (s, 4H, Mes CH), 2.46 (bs, 12H, Mes *o*CH$_3$), 2.31 (bs, 12H, Mes *o*CH$_3$), 2.05 (s, 6H, Mes *p*CH$_3$), 2.03 (s, 6H, Mes *p*CH$_3$). ^{13}C NMR (ppm): 143.89, 143.63 (bs), 139.41, 139.01, 138.27 (bs), 137.59 (Mes C), 130.07 (bs), 129.85 (bs) (Mes CH), 26.11 (bs), 25.72 (bs), 20.98, 20.75 (Mes CH$_3$). ^{2}H NMR (CHCl$_3$, ppm): 6.29. MS (*m*/*z*), CI:isobutane: 706 [M$^+$(^{72}Ge^{74}Ge) − Cl, 50], 672 [M$^+$(^{72}Ge^{74}Ge) − Cl$_2$ +H, 15], 636 [M$^+$(^{72}Ge^{74}Ge) − Cl$_3$, 9], 622 [M$^+$(^{72}Ge^{74}Ge) − CDCl$_3$, 14], 480 (Mes$_3$^{74}GeCDCl, 41), 362 (Mes$_2$^{74}GeCDCl +H, 100), 347 (Mes$_2$^{74}GeCl, 30), 328 (32), 311 (Mes$_2$^{72}Ge +H, 85), 239 (Mes^{72}GeCCl +H, 50), 121 (MesH +H, 51). MS (*m*/*z*): 623 [M$^+$(^{72}Ge^{74}Ge) − CDCl$_3$ +H, 4], 465 (Mes$_3$^{74}GeCl −H, 11), 362 (Mes$_2$^{74}GeCDCl +H, 15), 347 (Mes$_2$^{74}GeCl, 100), 311 (Mes$_2$^{72}Ge +H, 53), 237 (Mes^{72}GeCCl −H, 80), 221 (54), 207 (35), 191 (Mes^{72}Ge, 25), 120 (MesH, 56). K$^+$IDS MS (*m*/*z*): 780 (M$^+$ + 39, 39). High-resolution MS: M$^+$ − Cl, calcd for C$_{37}$H$_{44}$D^{72}Ge^{74}GeCl$_2$ 706.1393, found 706.1395.

Crystals of **1b** were grown from a saturated solution of hexanes. A crystal suitable for X-ray analysis was selected and mounted on a glass fiber. Data were collected on a Nonius Kappa CCD diffractometer using COLLECT software at 150 K. Crystal cell refinement and data reduction was carried out using the Nonius DENZO package. The crystal data and selected refinement parameters for **1b** are listed in Table 1. The unit cell parameters were calculated and refined from the full data set. Selected interatomic distances and angles are listed in Table 2. Complete details are given in the Supporting Information.

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Supporting Information Available: Full crystallographic data, bond lengths, and bond angles for **1b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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