Synthesis and Structure of a 1-Germapropadiene

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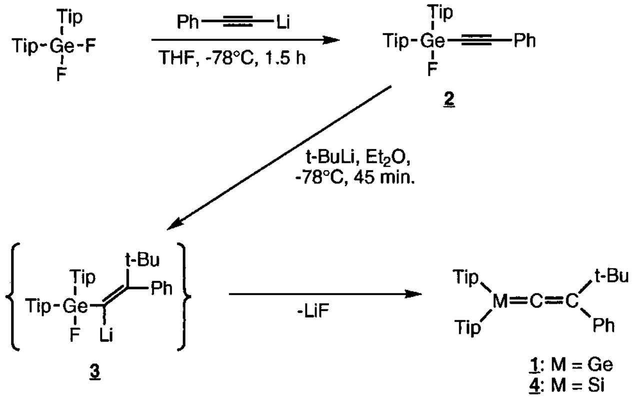
Summary: The reaction of t-BuLi with a fluoroalkynylgermane produces the title compound, ***1****. Single-crystal X-ray analysis shows the Ge═C bond length to be 1.783(2) Å. The Ge atom is somewhat pyramidalized, and the Ge═C═C bond angle (159.2°) reveals a bent structure at the central carbon atom.*

Compounds with cumulated double bonds to metalloid atoms have been of considerable interest during the past few years. The first 1-silapropadiene[1] was reported in 1993, and the synthesis of three additional examples of 1-silaallenes[2] has recently been published. A germaphosphaallene[3] has been characterized, and evidence has been presented for the existence of a 1-germapropadiene[4] as a transient reaction intermediate. We now report the synthesis and characterization by single-crystal X-ray diffraction of a stable 1-germapropadiene, **1**.

Compound **1** was synthesized[5] by the route shown in Scheme 1. In the final step, fluoroalkynylgermane **2**[6] was treated with 1 equiv of *tert*-butyllithium in diethyl ether at −78 °C. The presumed intermediate **3** rapidly eliminated lithium fluoride to give the 1-germapropadiene **1** in approximately 85% conversion. The latter is stable in ether solution only up to 0 °C, so it was isolated by crystallization at −20 °C as colorless plates.

Scheme 1[a]



[a] Tip = 2,4,6-triisopropylphenyl.

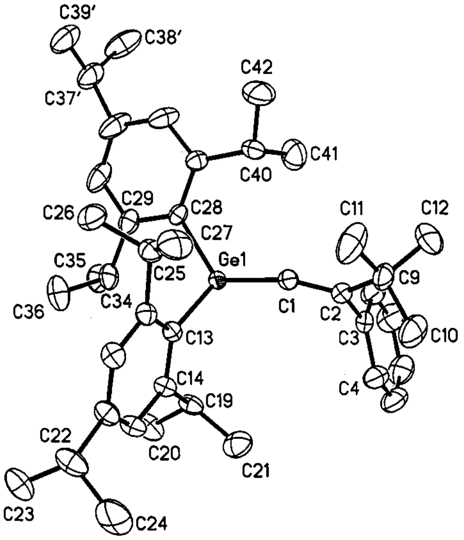


Figure 1. Molecular structure of 1-germapropadiene, **1**. Thermal ellipsoid (50% probability level) drawing with hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge−C(1) 1.783(2), Ge−C(13) 1.950(2), Ge−C(28) 1.951(2), C(1)−C(2) 1.314(2), C(2)−C(3) 1.498(3), C(2)−C(9) 1.537(3); Ge−C(1)−C(2) 159.2(2), C(1)−Ge−C(28) 123.15(8), C(1)−Ge−C(13) 111.24(8), C(13)−Ge−C(28) 114.04(7), C(1)−C(2)−C(3) 119.9(2), C(1)−C(2)−C(9) 121.6(2), C(3)−C(2)−C(9) 118.4(2).

The synthetic protocol for **1** is analogous to that used for preparation of the isostructural silicon compound **4**. In the silicon case, however, the intermediate lithium compound analogous to **3** is stable up to 0 °C, and so could be isolated and studied by crystallography. Com-

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(5) **1**: A 1.7 M solution of t-BuLi in pentane (1.00 mL, 1.70 mmol, 1.02 equiv) was syringed into a solution of **2** (1.0033 g, 1.6737 mmol) in diethyl ether at −78 °C. The light yellow solution was stirred at −78 °C for 1 h. The solution was warmed to 0 °C for 5 min, turning it deep red. This was cooled for 3 days at −20 °C to produce crystals of **1**. Mp: 125 °C. ^{1}H NMR (500 MHz, toluene-d_8, 253 K): δ 1.16−1.19 (m, 36H, i-Pr CH_3), 1.34 (s, 9H, t-Bu), 2.71 (sept, 2H, $^3J_{HH} = 6.8$ Hz), 3.62 (sept, 4H, $^3J_{HH} = 6.8$ Hz), 7.01 (1H, obscured by solvent), 7.05 (2H, obscured by solvent), 7.06 (s, 4H, Tip aryl H), 7.27 (d, 2H, $^3J_{HH} = 8.1$ Hz). ^{13}C NMR (126 MHz, toluene-d_8, 253 K): δ 24.2, 24.7, 24.9, 30.2, 34.7, 37.6, 38.1, 121.8, 126.1, 127.5, 128.9, 136.5, 144.0, 149.8, 150.7, 153.4, 235.1 (Ge═C).

(6) **2**: To 25.7 g (1.32 equiv) of ethynylbenzene in 150 mL of dry THF at −78 °C was added 0.21 mol of n-BuLi (1.1 equiv). The resulting solution was slowly added to a solution of bis(2,4,6-triisopropylphenyl)-difluorogermane[8] (98.64 g, 0.1907 mol) in dry THF (350 mL) at −78 °C. The solution was stirred at −78 °C for 1.5 h. Water (100 mL) was poured into the flask, and the solution was warmed to room temperature overnight. The solvents were removed by rotary evaporation, and the residue was taken up in diethyl ether and washed with water. The organic layer was dried with $MgSO_4$ and gravity filtered, and the ether was removed by rotary evaporation. Bulb-to-bulb distillation (195−200 °C/0.02 Torr) gave **2** as a colorless oil. The oil was recrystallized from hot 2-methoxyethanol, giving colorless crystals of **2** (96.28 g, 0.1606 mol, 84.2%). Mp: 123 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.14 (d, $^3J_{HH} = 6.4$ Hz, 12H), 1.16 (d, $^3J_{HH} = 6.4$ Hz, 12H), 1.23 (d, $^3J_{HH} = 6.8$ Hz, 12H), 2.87 (sept, $^3J_{HH} = 6.8$ Hz, 2H), 3.58 (sept, $^3J_{HH} = 6.6$ Hz, 4H), 7.03 (s, 4H), 7.29−7.31 (m, 3H), 7.46−7.49 (m, 2H). ^{13}C NMR (75.6 MHz, $CDCl_3$, ^{1}H decoupled): δ 23.9, 24.6, 24.8, 33.7, 33.8, 34.4, 93.6 (d, $^2J_{CF} = 24.2$ Hz), 106.2 (d, $^3J_{CF} = 5.1$ Hz), 122.1, 122.8, 128.4, 129.0, 131.8 (d, $^2J_{CF} = 12.7$ Hz), 132.0, 151.3, 153.9. ^{19}F NMR (282.2 MHz, $CDCl_3$, ^{1}H decoupled): δ −6.32. Anal. Calcd for $C_{38}H_{51}GeF$: C, 76.14; H, 8.58. Found: C, 75.81; H, 8.80. MS[EI] [m/z (I_{rel})]: 600 [0.5, M^+], 580 [1.1, −HF], 498 [10.2, − H−CC−Ph], 478 [14.5, −F, − H−CC−Ph, −H], 202 [100, Tip-H].

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Table 1. Crystallographic Data for 1

formula	$C_{42}H_{60}Ge$
fw	637.49
cryst size (mm^3)	0.52 × 0.34 × 0.26
a (Å)	31.6357(11)
b (Å)	12.0309(5)
c (Å)	21.9950(10)
α (deg)	90
β (deg)	114.2900(10)
γ (deg)	90
cryst syst	monoclinic
space group	$C2/c$
vol. (Å^3)	7630.3(5)
D_{calcd} (g cm^{-3})	1.110
Z	8
wavelength (Å)	0.710 73
temp (K)	133(2)
abs coeff (mm^{-1})	0.828
abs corr	semiempirical
min/max trans	0.753/0.928
no. of reflns collected	18 608
no. of indep reflns	8989
no. of obsd reflns	6938
no. of params	404
restraints	65(disorder)
θ range (deg)	2.51−29.34
goof on F^2	1.026
largst diff peak (eÅ^{-3})	0.418
largst diff hole (eÅ^{-3})	−0.383
R1 (%)	0.0362
wR2 (%)	0.0874
largst and mean D/esd	0.005/0.000

pound **3** was never detected in the reaction mixture; the weaker Ge−F bond evidently favors rapid LiF elimination from **3**. Low-temperature elimination of LiF from α-lithiofluorogermanes has also been observed in the preparation of the germaphosphaallene[3] and in the synthesis of a germene.[7]

The structure of **1**, determined by single-crystal X-ray crystallography at −140 °C, is shown in Figure 1 (Table 1). The Ge=C bond length is 1.783(2) Å. It is of interest to compare the structure of **1** with that of the exactly isostructural silicon compound **4**. In both compounds the M=C=C skeleton is nonlinear, but the bending at the central C atom is much greater in **1** (159.2°) than in **4** (172.0°). The germanium atom in **1** is also much more strongly pyramidalized than the silicon atom in **4**; the sum of the bond angles at Ge is 348.4° and at Si is 357.2°. Also, the angle between the plane defined by C(13)−Ge−C(28) and the vector made by the Ge−C(1) bond is 147.4°, which is much more bent than the corresponding angle in **4** (163.8°). The isopropyl group C(37)−C(39) is disordered and modeled in two orientations with refined occupancies of 0.420(6) for one set of atoms and 0.580(6) for the others.

The ^{13}C NMR spectra of 1-silapropadienes and allenes, in general, show characteristically deshielded central carbon atoms. For **4**, the central C atom resonance lies at +223.6 ppm; in **1**,[5] the analogous carbon resonance is found at +235.1 ppm.

An important difference between **1** and **4** is in their thermal stability in solution. In diethyl ether or hexane solution, **1** is stable indefinitely at 0 °C but is completely decomposed after 15 h at 25 °C, whereas **4** is unchanged in toluene up to 135 °C. Crystalline **1** is more stable, decomposing only above 90 °C.

Compound **4**, the silicon analogue of **1**, was found to undergo various addition reactions at the Si=C bond[2]. The reaction chemistry of **1** is currently under investigation.

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Supporting Information Available: Tables giving atomic coordinates, hydrogen coordinates, anisotropic displacement parameters, bond lengths, bond angles, and torsion angles and a figure of the unit cell diagram of **1** (8 pages). Ordering information is given on any current masthead page.

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