Reactivity of a 1-Germapropadiene

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α-Lithiofluorogermane **3** eliminated lithium fluoride to give 1-germapropadiene **1** even at −75 °C. The reactivity of 1-germapropadiene **1** was investigated. Compound **1** was not stable above 0 °C in solution or 90 °C in the solid state. Two C−H insertion cyclic compounds, **8** and **9**, were formed as a result of decomposition. Water, methanol, and ethanol added across the Ge═C double bond of **1** to give vinylalkoxy (hydroxy) germanes. Benzophenone did not react with **1** at 0 °C, but benzaldehyde gave oxagermetane **13** in good yield. When acetone was introduced to **1**, it gave the unexpected product **10**, the water adduct.

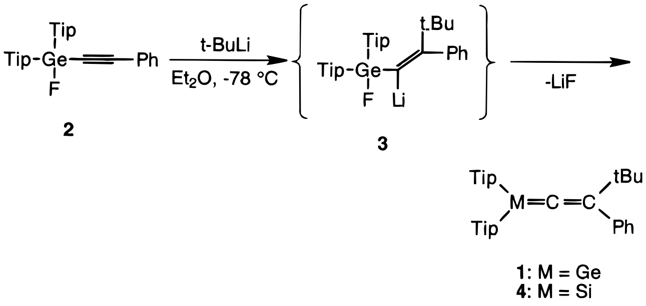
Introduction

In the last six years, much has been accomplished in the synthesis of stable group 14 heteronuclear allene analogues. A stannaketenimine[1] was synthesized by Grützmacher in 1992, but did not give trapping reaction characteristics of heavy alkenes. The following year we prepared a 1-silapropadiene,[2] but this molecule revealed very little in terms of reactivity because of the severe steric restraints put on it by large substituents. In 1997, other less sterically hindered 1-silapropadienes[3] were made that gave us insight into the reactivity of this moiety. With the recent synthesis of a stable 1-germaphosphaallene[4] and a trapping product of a 1-germapropadiene with chalcogens,[5] our focus shifted to the synthesis of a stable 1-germapropadiene.

Utilizing the salt-elimination method following a facile synthesis of a phenylethynylfluorogermane, **2**, we synthesized and characterized a stable 1-germapropadiene, **1** (Scheme 1).[6] An exactly analogous lithium fluoride elimination was employed earlier to synthesize the isostructural silicon analogue, **4**.[3] In the 1-silapropadiene synthesis, the intermediate lithium compound was stable in solution up to 0° C, but the corresponding germanium intermediate **3** eliminated LiF rapidly even at −75 °C. This contrasting behavior may reflect the difference in bond strengths, the Si−F bond being stronger than Ge−F. Recently the synthesis and crystal structure of a second example of a 1-germapropadiene have been reported.[7]

In this paper we report several chemical reactions of **1** and compare them with those of the silicon analogue **4**. Differences between these two molecules are revealed in reactions with alcohols, ketones, and aldehydes, as well as in their modes of decomposition.

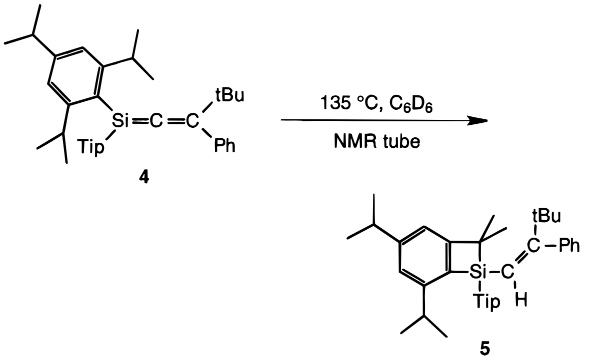
Scheme 1



Tip = 2,4,6-tri-isopropylphenyl

Results and Discussion

Decomposition. Thermolysis of 1-silapropadiene **4** at 130 °C in a C_6D_6 solution[3] led to a C−H insertion into an ortho isopropyl group to form silacyclobutane **5** (eq 1). 1-Silapropadiene **6**, which lacks a tertiary C−H bond, decomposed at 90 °C in Et_2O by Si═C insertion into one of the *tert*-butyl C−H bonds, forming five-membered ring **7** (eq 2). In both of these reactions, only one product was formed. Under much less vigorous conditions, above 0 °C in solution or above 90 °C in the solid state, **1** undergoes both reactions, giving compounds **8** and **9** in a ratio of 60:40. It has become evident that this type of C−H insertion cyclization reaction is a significant decomposition route for kinetically stablized group 14 multiple bonds[8] as well as for a germylene.[9] The formation of these rings emphasizes the



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[1] Grützmacher, H.; Freitag, S.; Herbst-Irmer, R.; Sheldrick, G. S. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 437.

[2] Miracle, G. E.; Ball, J. L.; Powell, D. R.; West, R. *J. Am. Chem. Soc.* **1993**, *115*, 11598.

[3] Trommer, M.; Miracle, G. E.; Eichler, B. E.; Powell, D. R.; West, R. *Organometallics* **1997**, *16*, 5737.

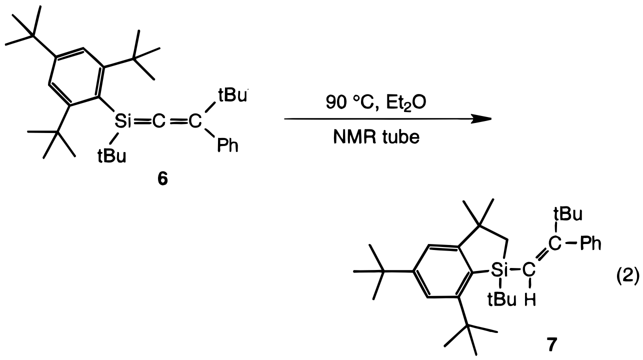
[4] Ramdane, H.; Ranaivonjatovo, H.; Escudié, J.; Mathieu, S.; Knouzi, N. *Organometallics* **1996**, *15*, 3070.

[5] Kishikawa, K.; Tokitoh, N.; Okazaki, R. *Organometallics* **1997**, *16*, 5127.

[6] Eichler, B. E.; Powell, D. R.; West, R. *Organometallics* **1998**, *17*, 2147.

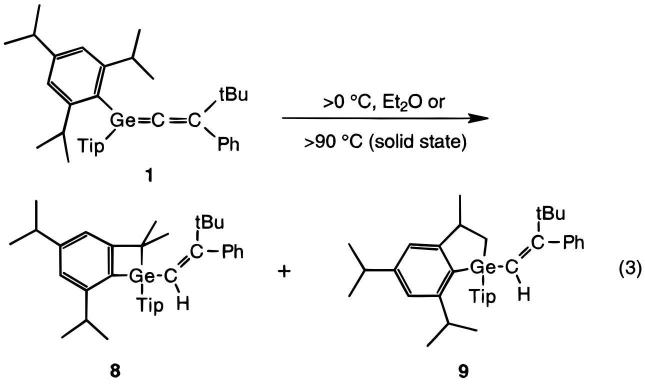
[7] Tokitoh, N.; Kishikawa, K.; Okazaki, R. *Chem. Lett.* **1998**, 811.

10.1021/om980555r CCC: $18.00



instability of heteronuclear multiple bonds. Under even mild conditions (as for **1**), the germanium−carbon double bond forms strained four- and five-membered rings rather than remaining as a double bond.

Compounds **8** and **9** were synthesized by simply warming **1** to room temperature overnight in diethyl ether or hexane (eq 3) and separating them by flash column chromatography. Compound **8** was characterized by single-crystal X-ray diffraction (Figure 1).



There are two slightly different molecules ($Z = 4$) in the unit cell of **8**. In the two molecules, the four-membered ring of **8** is folded to an angle of 7.3° and 9.6° between the planes of Ge−C(19)−C(14) and Ge−C(13)−C(14). The Ge−C(13) bond lengths are 1.993 and 1.979 Å, and the Ge−C(19) bond lengths are 2.015 and 2.035 Å. It is evident that the four-membered ring of **8** is very strained, since the C(13)−Ge−C(19) bond angle (73.2 °) is very small compared to the ideal value of 90°. A large residual peak in the final difference map was located about 1 Å from Ge(1A), which is believed due to a small amount of twinning in the crystal. One isopropyl group was disordered and modeled in two orientations. The occupancies of atoms C(22B)−C(24B) and C(22″)−C(24″) refined to 0.483(12) and 0.517(12).

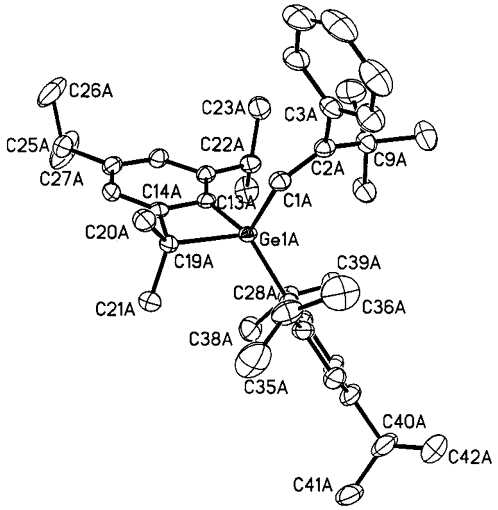


Figure 1. Molecular structure of germacyclobutane, **8**. Thermal ellipsoid (50% probability level) drawing with hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge−C(1) 1.951(3), Ge−C(13) 1.993(3), Ge−C(19) 2.015(3), Ge−C(28) 1.983(3), C(13)−C(14) 1.403(4), C(14)−C(19) 1.516(4), C(1)−C(2) 1.339(4); Ge−C(1)−C(2) 138.0(3), C(1)−Ge−C(28) 113.68(12), C(1)−Ge−C(19) 107.92(13), C(1)−Ge−C(13) 113.37(12), C(19)−Ge−C(28) 114.45(12), C(13)−Ge−C(28) 126.13(12), C(13)−Ge−C(19) 73.17(12), Ge−C(13)−C(14) 90.2(2), Ge−C(19)−C(14) 86.3.

Compound **9** did not provide crystals of sufficient quality for X-ray analysis. The structure of **9** is tentatively assigned on the basis of similarities of the ^{1}H and ^{13}C NMR spectra and mass spectra of **8** and **9**. The mass spectrum of **9** is almost identical to that of **8**. Both compounds show M$^+$ at $m/z = 638$, loss of a *tert*-butyl group as the 100% peak ($m/z = 581$), and loss of a triisopropylphenyl group in the 70−80% intensity range. In the ^{1}H NMR of **9** the vinyl proton is evident at +6.36 ppm. The resonance at 1.59 ppm in **9** is assigned to the methyl group on the five-membered ring, by analogy with the 1.49 ppm resonance in **8**. The 1.59 ppm resonance appears as a singlet; for some reason, the coupling with the adjacent C−H proton must be very small.

Reactions with Water and Alcohols. In the synthesis of **4**, the α-lithiofluorosilane was stable up to 0 °C, so we initially assumed the same would be true for **3**. In an endeavor to trap the α-lithiofluorogermane **3**, we added methanol as a mild protic reagent. This would replace the lithium with a hydrogen, giving an air- and moisture-stable product that was still a fluorogermane. Methanol was syringed into a solution of **2** and *tert*-butyllithium in ether at −78 °C, and the reaction product was purified by bulb-to-bulb distillation. The resulting oil was washed with hot methanol, yielding a white solid, **11**, the formal methanol trapping product of the 1-germapropadiene **1**. Compound **11** was characterized by ^{1}H and ^{13}C NMR, mass spectroscopy, and single-crystal X-ray crystallography (Figure 2). There were two slightly different molecules in the unit cell of **11**, but the differences were not extraordinary. The Ge−O bonds were similar in both molecules [Ge(1A)−O(1A) = 1.812(3) Å and Ge(1B)−O(1B) = 1.822(4) Å], but the Ge−C(1) bonds were different by over 0.03 Å [Ge(1A)−C(1A) = 1.970(5) Å and Ge(1B)−C(1B) = 1.936(5) Å]. The O−Ge−C(1) bond angles were also slightly different [O−Ge−C(1A) = 111.2(2)° and O−Ge−C(1B) = 109.1(2)°]. A large residual peak in the final difference map was located about 1 Å from Ge(1B). This peak is believed to be due to a small amount of twinning in the crystal. Two isopropyl groups were disordered and both modeled in two orientations. The occupancies of atoms C(37A)−C(39A) and C(37′)−C(39′) refined to 0.43-

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(8) (a) Baines, K. M.; Groh, R. J.; Babu, J.; Parshotam, U. R. *Organometallics* **1998**, *11*, 2176. (b) Weidenbruch, M.; Schafers, K.; Schlaefke, J.; Peters, K.; von Schnering, H. G. *J. Organomet. Chem.* **1991**, *415*, 343.

(9) Jutzi, P.; Schmidt, H.; Neumann, B.; Stammler, H.-G. *Organometallics* **1996**, *15*, 741.

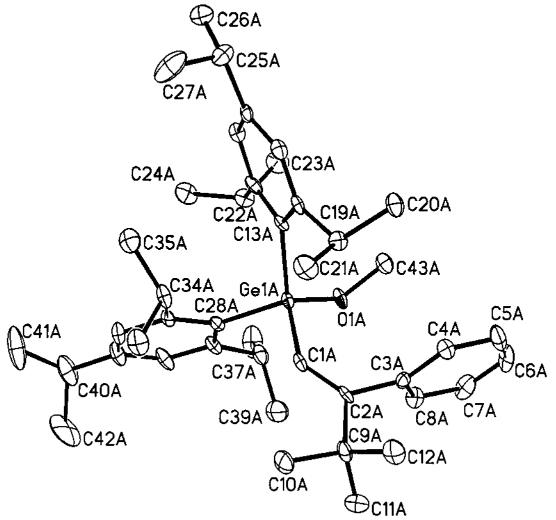
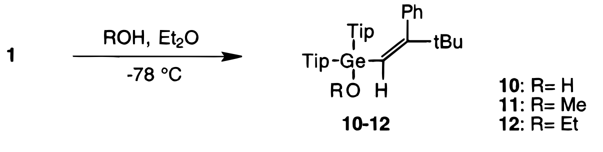


Figure 2. Molecular structure of hydroxygermane, **10**. Thermal ellipsoid (50% probability level) drawing with hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge−C(1) 1.952(2), Ge−O 1.7879(13), Ge−C(13) 1.979(2), Ge−C(28) 1.987(2), C(1)−C(2) 1.343(3); Ge−C(1)−C(2) 132.20(14), O−Ge−C(1) 110.22(7), O−Ge−C(13) 101.27(7), O−Ge−C(28) 114.26, C(13)−Ge−C(28) 109.99(7).

(3) and 0.57(3). The occupancies of atoms C(37B)−C(39B) and C(37″)−C(39″) refined to 0.721(12) and 0.279(12).

We thought that this result could have originated from the hot methanol wash of the proposed fluorogermane, so we decided to use the same procedure with ethanol as the trapping agent. If this experiment led again to compound **11**, it would mean that we had replaced the fluoride with a methoxy group when it was exposed to hot methanol. Conversely, if the experiment resulted in compound **12**, the formal ethanol trapping product of **1**, it would be clear that we were trapping **1** and not **3**. In fact, when ethanol was added to the reaction solution at −78 °C, the product was the ethanol adduct **12**, which was also studied by X-ray crystallography (Figure 3). The isopropyl group C(22)−C(24) was disordered and modeled in two orientations with refined occupancies of 0.322(12) for the unprimed atoms and 0.678(12) for the primed atoms.

As our syntheses continued, it became clear that water was a fast, efficient trapping reagent that could be utilized for gas chromatographic studies to verify that the 1-germapropadiene **1** was still in solution. In a similar manner, water was added to the reaction solution at −78 °C, yielding the water adduct of the germapropadiene, **10** (eq 4). The latter was also investigated by X-ray crystallography (Figure 4).



$$\mathbf{1} \xrightarrow[-78\ ^\circ\mathrm{C}]{\mathrm{ROH,\ Et_2O}} \mathrm{Tip_2Ge(OR)CH{=}C(Ph)tBu} \quad (4)$$

10-12

10: R= H
11: R= Me
12: R= Et

It is interesting that the Ge−C(1)−C(2) bond angles (**10** = 132.2°, **11** = 133.4°, **12** = 131.1°) are considerably greater than the 120° value for sp^2-hybridized carbons. Steric factors evidently force the C=C(t-Bu)Ph fragment away from the larger Tip groups.

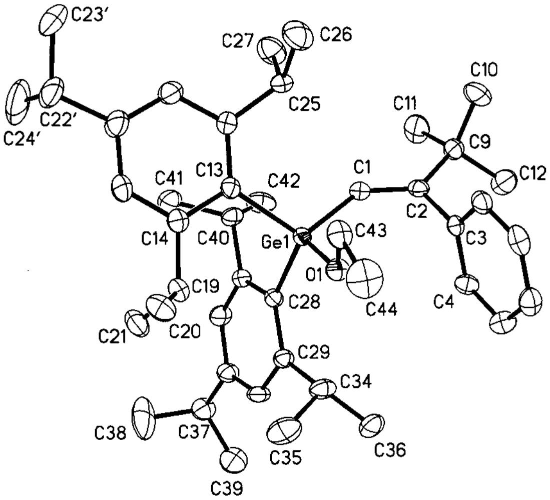


Figure 3. Molecular structure of methoxygermane, **11**. Thermal ellipsoid (50% probability level) drawing with hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge−C(1) 1.970(5), Ge−O 1.812(3), Ge−C(13) 1.994(4), Ge−C(28) 2.005(5), O−C(43) 1.424(6), C(1)−C(2) 1.340(6); O−Ge−C(1) 111.2(2), O−Ge−C(13) 105.4(2), O−Ge−C(28) 111.6(2), Ge−O−C(43) 119.2(3), C(1)−Ge−C(13) 118.1(2), C(1)−Ge−C(28) 100.7(2), C(13)−Ge−C(28) 109.9(2), Ge−C(1)−C(2) 133.4(4).

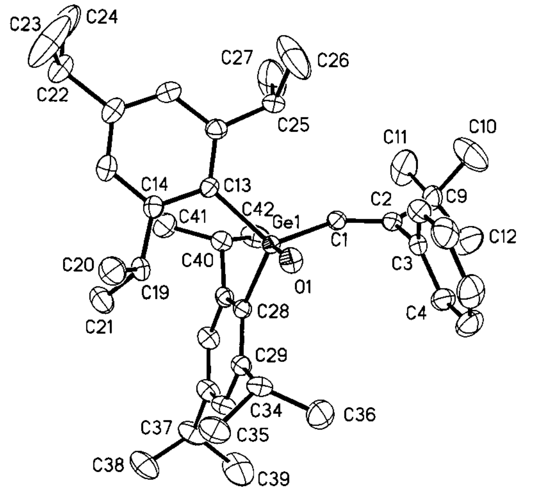


Figure 4. Molecular structure of ethoxygermane, **12**. Thermal ellipsoid (50% probability level) drawing with hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge−C(1) 1.958(2), Ge−O 1.7850(12), Ge−C(13) 1.985(2), Ge−C(28) 1.982(2), O−C(43) 1.426(2), C(1)−C(2) 1.331(2); O−Ge−C(1) 110.77(7), O−Ge−C(13) 105.27(7), O−Ge−C(28) 110.22(6), Ge−O−C(43) 119.09(11), O−C(43)−C(44) 108.8(2), C(1)−Ge−C(13) 114.50(7), C(1)−Ge−C(28) 106.53(7), C(13)−Ge−C(28) 109.58(7), Ge−C(1)−C(2) 131.1(2).

Reactions with Carbonyl Compounds. Germenes can react with carbonyl groups by 2+2 cycloaddition (eq 5) to form 1,2-oxagermetanes.[10] To find out if **1** behaves in a similar manner, we first treated it with benzophenone. No reaction occurred at 0 °C even after 3 days. The 1-silapropadiene **4** did react with benzophenone to form a 1,2-oxasiletane, but only when reacted at room temperature for 8 h.

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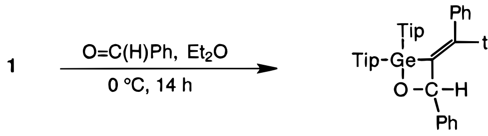
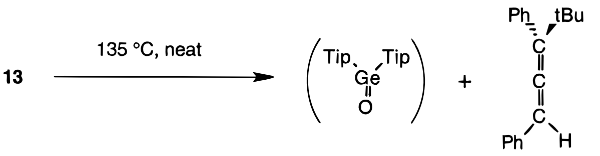
[10] (a) Lazraq, M.; Couret, C.; Escudié, J.; Satgé, J.; Drager, M. **1991**, *10*, 1771. (b) Wiberg, N.; Kim, C. K. *Chem. Ber.* **1986**, *119*, 2980.



13 (5)

Realizing that benzophenone was probably too hindered to react with **1** at 0 °C, we next tried the reaction with benzaldehyde. An overnight reaction of **1** with benzaldehyde at 0 °C gave the desired 2+2 cycloaddition product **13** (eq 5). This is the first example of a 1,2-oxagermetane with an exocyclic double bond. Compound **13** was studied by single-crystal X-ray diffraction (Figure 5), which revealed the angle between the planes of Ge−C(1)−C(43) and Ge−C(1)−O to be 9.8°. It is of note that the O−Ge−C(1) bond angle is only 74.1°. One isopropyl group was disordered and modeled in two orientations with occupancies of 0.666(9) and 0.334(9) for C(38), C(39) and C(38′), C(39′), respectively.

Oxagermetanes that are not very sterically hindered typically decompose by cleavage of the Ge−C and O−C bonds of the ring, producing a germanone and an alkene.[11] Compound **13** shows no sign of this mode of decomposition to the germanone and the allene (eq 6) up to 135 °C, but the 100% intensity peak for the mass spectrum corresponds to the allene fragment.



14 15 (6)

Compared to compounds **8**, **10**, **11**, and **12**, which have more freedom of rotation around the Ge−C(1) bond, the four-membered ring of the 1,2-oxagermetane locks **13** into a rigid conformation, as evidenced by the complexity of ^{1}H and ^{13}C NMR spectra. Compounds **10**−**12** typically show the hydrogen atom on the tertiary carbons of the isopropyl groups on the Tip ligands in a ratio of 4:2 (ortho:para). In contrast, the ^{1}H NMR spectrum of compound **13** shows six separate inequivalent signals for the six isopropyl hydrogens. This is also revealed in the many doublets for the isopropyl methyl groups of the Tip ligands compared to compounds **10**−**12**. The ^{13}C NMR spectrum is also much more complex than the spectra of compounds **10**−**12**. The ^{13}C NMR peak for C(43) is easily identifiable at +85.79 ppm, well downfield of the other aliphatic carbons.

The reaction of **1** with acetone was also investigated. Addition of carefully dried acetone to the reaction solution at −78 °C led not to a carbonyl adduct of **1**, but to the water adduct **10**. The latter could arise by initial formation of a germyl enol ether,[10a] followed by hydrolysis during the workup, as shown in Scheme 2. However, the ^{1}H and ^{13}C NMR of the solution before workup showed no evidence of a germyl enol ether; instead the NMR spectra appeared identical to that of **10**. Acetone can dimerize to form diacetone alcohol, which can decompose to mesityl oxide and water. Thus it seems likely that **1** may serve to dehydrate acetone directly.

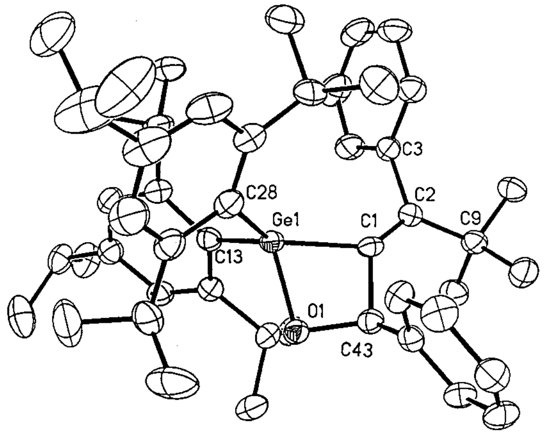
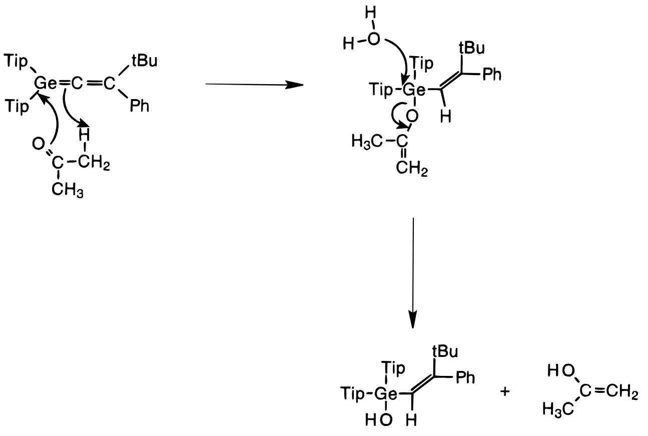


Figure 5. Molecular structure of 1,2-oxagermetane, **13**. Thermal ellipsoid (50% probability level) drawing with hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge−C(1) 1.970(3), Ge−O 1.843(2), Ge−C(13) 1.975(3), Ge−C(28) 1.971(3), C(1)−C(2) 1.348(4), C(1)−C(43) 1.545(4), O−C(43) 1.454(4); O−Ge−C(1) 74.10(11), Ge−O−C(43) 96.48(17), O−C(43)−C(1) 100.1(2), C(43)−C(1)−Ge 88.5(2), Ge−C(1)−C(2) 134.1(2), C(2)−C(1)−C(43) 132.9(3), C(13)−Ge−C(28) 112.64(14), O−Ge−C(28) 105.46(13), O−Ge−C(13) 110.54(12), C(1)−Ge−C(13) 119.74(14), C(1)−Ge−C(28) 123.99(14), C(1)−C(2)−C(3) 118.4(3), C(1)−C(2)−C(9) 125.4(3), C(3)−C(2)−C(9) 116.1(3).

Scheme 2



Conclusions

Germapropadiene **1** follows the reactivity pattern of the analogous silapropadiene **4**, but with a few significant differences. Both heteropropadienes add alcohols across the M=C double bond in a similar manner. Because of the instability of **1**, it did not react with benzophenone as **4** did (to form a 1,2-oxasiletane). The less bulky carbonyl compound benzaldehyde however added to the germapropadiene to form a 1,2-oxagermetane. The most pronounced differences between the two analogues lie in their stabilities and modes of decomposition. Compound **1** survives only to 0 °C in solution, whereas compound **4** is much more stable, decomposing only at 130 °C. The silapropadiene decomposes to a single product, a silacyclobutane (**5**), but the germapropadiene rearranges to two products, a germacyclobutane (**8**) and a germacyclopentane (**9**).

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[11] Satgé, J. *Adv. Organomet. Chem.* **1982**, *21*, 241.

Table 1. Crystallographic Data for Compounds 8 and 10−13

	8	**10**	**11**	**12**	**13**
formula	$C_{42}H_{60}GeO$	$C_{42}H_{62}GeO$	$C_{43}H_{64}GeO$	$C_{44}H_{66}GeO$	$C_{49}H_{66}GeO$
fw	637.49	655.51	669.53	683.56	743.61
cryst size (mm^3)	0.38 × 0.34 × 0.30	0.35 × 0.35 × 0.25	0.36 × 0.18 × 0.14	0.60 × 0.20 × 0.10	0.35 × 0.35 × 0.02
a (Å)	12.6624(7)	31.267(2)	9.6460(9)	33.6377(7)	20.9235(12)
b (Å)	17.2347(12)	12.3157(6)	11.8734(8)	47.2748(2)	10.8125(6)
c (Å)	17.8359	22.6568(11)	38.0722(4)	10.4827(3)	19.2080(9)
α (deg)	84.572(3)	90	84.459(4)	90	90
β (deg)	87.898(4)	113.9091(7)	87.213(4)	90	91.876(2)
γ (deg)	79.855(2)	90	69.440(4)	90	90
cryst syst	triclinic	monoclinic	triclinic	orthorhombic	monoclinic
space group	$P\bar{1}$	$C2/c$	$P\bar{1}$	$Fdd2$	$P2_1/c$
vol (Å^3)	3813.5(4)	7975.9(7)	4063.1(5)	16669.8(6)	4343.2(4)
D_{calcd} (gcm^{-3})	1.110	1.092	1.095	1.089	1.137
Z	4	8	4	16	4
wavelength (Å)	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
temp (K)	133(2)	133(2)	133(2)	133(2)	133(2)
abs coeff (mm^{-1})	0.829	0.796	0.782	0.764	0.738
abs correction	semiempirical	semiempirical	semiempirical	semiempirical	empirical
min/max trans	0.813/0.956	0.734/0.831	0.678/0.962	0.576/0.746	0.7821/0.9854
no. of reflns collected	42 178	19 062	35 860	20 266	16 591
no. of indep reflns	18 394	9611	13 932	7843	7537
no. of obsd reflns	12 036	7129	8809	6733	4918
no. of params	797	397	855	455	479
restraints	94	0	92	101(disorder)	32(disorder)
q range (deg)	3.0−25.0	3.0−25.0	3.0−25.0	3.0−25.0	2.36−25.00
Goof on F^2	1.014	0.984	1.015	0.918	0.912
largst diff peak (e Å^{-3})	2.671	0.578	3.161	0.373	0.672
largst diff hole (e Å^{-3})	−0.757	−0.410	−1.392	−0.278	−0.529
R1 (%)	0.0586	0.0367	0.0694	0.0252	0.0510
wR2 (%)	0.1506	0.0954	0.1812	0.0489	0.1237
largest & mean *D*/esd	−0.005/0.000	−0.001/0.000	−0.001/0.000	−0.002/0.000	0.006/0.000

Experimental Section

^1H and ^{13}C NMR spectra were recorded on a Bruker AC-300 spectrometer. Chemical shifts are given relative to external standards (^1H and ^{13}C, tetramethylsilane). All ^{13}C spectra were ^1H decoupled. High-resolution electron-impact ionization mass spectrometry was performed on an MS80 Kratos spectrometer. Elemental analyses were carried out at INEOS, Russian Academy of Sciences, Moscow. X-ray crystal structure determinations were performed on a Siemens P4 diffractometer equipped with a CCD area detector, using Mo Kα radiation. The structures of all compounds were solved by direct methods and refined by full-matrix least-squares refinement with anisotropic displacement parameters. Hydrogen atoms in all models were refined using a riding model with isotropic displacement parameters. Details of the data collection and refinement are given in Table 1.

All reactions were carried out under an atmosphere of dry argon in flame- or oven-dried glassware. Bis(2,4,6-triisopropylphenyl)phenylethynylfluorogermane (**2**) and 1,1-bis(2,4,6-triisopropylphenyl)-3-*tert*-butyl-3-phenyl-1-germa-1,2-propadiene (**1**) were prepared as described in the literature.[6] Diethyl ether was distilled from sodium/benzophenone prior to use. Acetone was dried by refluxing over anhydrous $CaSO_4$ overnight and distilling onto 4 Å molecular sieves. Methanol and ethanol were refluxed overnight with Mg and I_2 and distilled the next day. Benzophenone, benzaldehyde, and t-BuLi were used as received.

Formation of Germapropadiene 1 at −75 °C. A solution of **2** (0.10 g, 0.17 mmol) in 0.7 mL of dry diethyl ether was prepared in an NMR tube sealed with a septum and cooled to −75 °C. The ^{13}C NMR spectrum was that previously recorded for **2**.[6] A solution of *tert*-butyllithium (1.7 M in pentane, 0.10 mL, 0.170 mmol) was added at −75°, leading to immediate formation of an orange-red color, characteristic for **1**. The ^{13}C NMR spectrum was identical to that of **1**.

1-(2,4,6-Triisopropylphenyl)-4,6-(diisopropylphenyl)-1-(2-phenyl-3,3-dimethylbut-1-enyl)-2,2-dimethylgermacyclobutane (8). A solution of **1** (1.00 g, 1.67 mmol) in diethyl ether was prepared as described in the literature.[6] The solution was slowly allowed to warm from 0 °C to room temperature overnight. Reaction yields were analyzed by gas chromatography, which showed that compounds **8** and **9** were present in a ratio of 3:2, with only traces of other products. The solvent was removed in vacuo, and the compounds were separated by flash column chromatography (silica gel, hexane/diethyl ether (99.5:0.5)). Removal of solvent by rotary evaporation gave **8** as a solid (crude yield = 0.33 g, 31%). This was recrystallized once from a 2-methoxyethanol/diethyl ether mixture to give 0.24 g of crystals of **8** (0.38 mmol, 23%). Mp (2-methoxyethanol): 150 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 1.02−1.03 (br m, 6 H), 1.12 (s, 12 H), 1.23 (d, 3 H, $J = 6.4$ Hz), 1.24 (d, 3 H, $J = 6.8$ Hz), 1.26 (d, 6 H, $J = 6.8$ Hz), 1.30 (d, 9 H, $J = 6.6$ Hz), 1.37 (d, 3 H, $J = 6.8$ Hz), 1.49 (s, 3 H), 2.86 (sept., 2 H, $J = 7.0$ Hz), 3.11−3.24 (m, 3 H), 5.82 (s, 1 H), 6.73 (d, 1 H, $J = 1.2$ Hz), 6.98 (s, 2 H), 7.04−7.07 (m, 3 H), 7.18−7.24 (m, 3 H). ^{13}C NMR (75.3 MHz, $CDCl_3$): δ 22.8, 23.7, 23.91, 23.95, 24.1, 24.2, 25.2, 26.3, 26.9, 28.0, 30.6, 33.3, 34.0, 34.5, 37.8, 39.5, 117.1, 121.2, 122.4, 125.7, 125.9, 127.1, 128.6, 136.2, 142.3, 147.0, 149.3, 150.8, 151.9, 152.9, 161.8, 164.5. Anal. Calcd for $C_{42}H_{60}$-Ge: C, 79.13; H, 9.49; Ge, 11.39. Found: C, 79.20; H, 9.48; Ge, 11.16. MS[EI] [$m/z(I_{rel})$]: 638 [7.3, M$^+$], 581 [100, − t-Bu], 434 [74.0, − Tip and H].

1-(2,4,6-Triisopropylphenyl)-4,6-(diisopropylphenyl)-1-(2-phenyl-3,3-dimethylbut-1-enyl)-3-methylgermacyclopentane (9). Compound **9** (larger R_f value than **8**) was isolated from the same reaction mixture as **8** during flash column chromatography (crude yield = 0.20 g, 0.31 mmol, 19%). This was recrystallized from a 2-methoxyethanol/diethyl ether mixture, yielding 0.14 g (0.22 mmol, 13%) of **9** as a white solid. Mp (2-methoxyethanol): 133 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 0.95−0.98 (m, 3 H), 1.00 (br s, 12 H), 1.07 (d, 6 H, $J = 5.3$ Hz), 1.17 (d, 3 H, $J = 6.8$ Hz), 1.22−1.29 (m, 18 H), 1.59 (s, 3 H), 2.61 (sept., 1 H, $J = 6.8$ Hz), 2.70 (sept., 2 H, $J = 6.6$ Hz), 2.84 (sept., 1 H, $J = 6.8$ Hz), 2.85 (sept., 1 H, $J = 6.8$ Hz), 6.36 (s, 1 H), 6.68 (d, 2 H, $J = 7.2$ Hz), 6.73 (d, 1 H, $J = 1.3$ Hz), 6.83 (s, 2 H), 6.88 (t, 2 H, $J = 7.5$ Hz), 6.96 (d, 1 H, $J = 1.3$ Hz), 7.05 (t, 1 H, $J = 7.4$ Hz). ^{13}C NMR (75.3 MHz, $CDCl_3$): δ 23.1, 24.0, 24.2, 25.4, 26.4, 26.7, 27.7, 29.6, 33.1, 34.1, 34.2, 34.6, 38.3, 39.1, 117.0, 120.5, 122.3, 123.9, 126.1, 126.4, 129.4, 135.5, 141.6, 142.4, 149.1, 150.7, 151.7, 153.0, 161.8, 164.7. Anal. Calcd for $C_{42}H_{60}Ge$: C, 79.13; H, 9.49. Found: C, 78.95; H, 9.66. MS[EI] [$m/z(I_{rel})$]: 638 [9.7, M^+], 581 [100, − t-Bu], 434 [79.1, − Tip and H].

1,1-Bis(2,4,6-triisopropylphenyl)hydroxygermyl-2-phenyl-3,3-dimethylbut-1-ene (10). Method A. To a deep red ethereal solution of **1** (1.01 g, 1.68 mmol) at −78 °C was added water (0.20 mL, 11.1 mmol, 6.6 equiv), decolorizing the solution immediately. The solution was warmed to room temperature overnight. The solvents were removed in vacuo, and the solid 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 (195−210 °C/0.02 Torr) gave **10** as a colorless oil (crude yield = 0.77 g, 71%). The oil was recrystallized once from 2-methoxyethanol/diethyl ether solution giving colorless crystals of **10** (0.57 g, 0.89 mmol, 53%).

Method B. To a deep red ethereal solution of **1** (1.00 g, 1.67 mmol) at −78 °C was added dry acetone (0.25 mL, 3.4 mmol, 2.0 equiv), decolorizing the solution immediately. The solution was warmed to room temperature overnight. A workup procedure analogous to that of method A gave **10** as a colorless oil. The oil was recrystallized once from hot methanol and then once from a hot 2-methoxyethanol/diethyl ether solution, giving colorless crystals of **10** (0.66 g, 1.01 mmol, 60%). Mp (2-methoxyethanol): 138 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.97 (d, 12 H, $J = 6.6$ Hz), 1.01 (d, 12 H, $J = 6.8$ Hz), 1.11 (s, 9 H), 1.18 (d, 12 H, $J = 7.0$ Hz), 2.80 (sept., 2 H, $J = 7.0$ Hz), 3.42 (sept., 4 H, $J = 6.8$ Hz), 6.31 (s, 1 H), 6.92 (s, 4 H), 7.18−7.20 (m, 2 H), 7.31−7.34 (m, 3 H). ^{13}C NMR (75.3 MHz, $CDCl_3$): δ 23.9, 24.4, 24.6, 29.5, 33.0, 34.2, 38.6, 121.6, 126.1, 127.3, 127.8, 129.2, 136.5, 141.5, 149.4, 153.1, 161.5. Anal. Calcd for $C_{42}H_{62}GeO$: C, 76.95; H, 9.53; Ge, 11.07. Found: C, 76.70; H, 9.53; Ge, 10.84. MS[EI] [$m/z(I_{rel})$]: 638 [3.5, − H_2O], 581 [14.6, − H_2O and t-Bu], 452 [88.9, − Tip and H], 434 [100, − H_2O, H and Tip].

1,1-Bis(2,4,6-triisopropylphenyl)methoxygermyl-2-phenyl-3,3-dimethylbut-1-ene (11). To a solution of **1** (0.50 g, 0.83 mmol) at −78 °C was added dry methanol (0.50 mL, 12.5 mmol, 15 equiv), decolorizing the solution immediately. The solution was warmed to room temperature overnight. A workup procedure analogous to that of **10** (method A) gave **11** as a colorless oil. The oil was recrystallized once from hot methanol and 2-methoxyethanol twice, giving colorless needles of **11** (0.12 g, 0.18 mmol, 22%). Mp (2-methoxyethanol): 108 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.93 (d, 12 H, $J = 6.8$ Hz), 0.95 (d, 12 H, $J = 6.6$ Hz), 1.08 (s, 9 H), 1.18 (d, 12 H, $J = 7.0$ Hz), 2.49 (s, 3 H), 2.80 (sept., 2 H, $J = 6.8$ Hz), 3.41 (sept., 4 H, $J = 6.8$ Hz), 6.23 (s, 1 H), 6.90 (s, 4 H), 7.16−7.19 (m, 2 H), 7.25−7.28 (m, 3 H). ^{13}C NMR (75.3 MHz, $CDCl_3$): δ 23.86, 23.92, 24.4, 29.9, 32.9, 34.1, 38.8, 52.8, 121.7, 125.9, 126.2, 126.6, 129.6, 134.9, 141.9, 149.5, 153.6. Anal. Calcd for $C_{43}H_{64}GeO$: C, 77.13; H, 9.63; Ge, 10.84. Found: C, 76.70; H, 9.55; Ge, 10.97. MS[EI] [$m/z(I_{rel})$]: 638 [9.8, − MeOH], 581 [35.0, − MeOH and t-Bu], 466 [84.2, − Tip and H], 434 [100, − MeOH, H and Tip].

1,1-Bis(2,4,6-triisopropylphenyl)ethoxygermyl-2-phenyl-3,3-dimethylbut-1-ene (12). To a solution of **1** (1.00 g, 1.67 mmol) at −78 °C was added dry ethanol (1.00 mL, 17.0 mmol, 10 equiv). The solution was warmed to room temperature overnight and worked up in the same manner as **10** (method A), yielding **12** as a colorless oil. The oil was recrystallized once from hot methanol and once from 2-methoxyethanol/diethyl ether to give colorless crystals of **12** (0.59 g, 0.86 mmol, 51%). Mp: 110 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.56 (t, 3 H, $J = 6.8$ Hz), 0.91 (d, 12 H, $J = 6.5$ Hz), 0.94 (d, 12 H, $J = 6.5$ Hz), 1.07 (s, 9 H), 1.18 (d, 12 H, $J = 6.8$ Hz), 2.68 (q, 2 H, $J = 7.0$ Hz), 2.80 (sept., 2 H, $J = 6.8$ Hz), 3.40 (m, 4 H), 6.25 (s, 1 H), 6.89 (s, 4 H), 7.15−7.17 (m, 2 H), 7.25−7.27 (m, 3 H). ^{13}C NMR (75.3 MHz, $CDCl_3$): δ 18.2, 23.87, 23.91, 24.2, 24.5, 29.9, 32.9, 34.1, 38.8, 59.4, 121.7, 125.8, 126.1, 126.7, 129.4, 135.1, 141.8, 149.4, 153.7, 161.7. Anal. Calcd for $C_{44}H_{66}GeO$: C, 77.31; H, 9.73; Ge, 10.62. Found: C, 77.56; H, 9.53; Ge, 10.68. MS-[EI] [$m/z(I_{rel})$]: 638 [9.7, − EtOH], 581 [26.7, − EtOH and t-Bu], 480 [62.7, − Tip and H], 434 [100, − EtOH, H and Tip].

2,2-Bis(2,4,6-triisopropylphenyl)-3-(3,3-dimethyl-2-phenylbut-1-ylidene)-4-phenyl-1,2-oxagermetane (13). To a deep red ethereal solution of **1** (1.00 g, 1.67 mmol) at −78 °C was added dry benzaldehyde (0.34 mL, 3.3 mmol, 2.0 equiv), turning the solution orange. The solution was left at 0 °C overnight. The solvents were removed in vacuo, and the solid was purified by flash column chromatography (silica gel, hexane/diethyl ether (99.5:0.5)). Removal of solvent by rotary evaporation gave **13** as a solid (crude yield = 0.92 g, 74%). The solid was recrystallized once from a hot 2-methoxyethanol/diethyl ether mixture to give colorless crystals of **13** (0.73 g, 0.98 mmol, 59%). Mp: 134 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.13 (d, 3 H, $J = 6.3$ Hz), 0.53 (d, 3 H, $J = 7.2$ Hz), 0.56 (d, 3 H, $J = 7.0$ Hz), 0.85 (d, 3 H, $J = 6.4$ Hz), 0.95 (s, 9 H), 1.00 (d, 3 H, $J = 6.4$ Hz), 1.18 (d, 3 H, $J = 7.0$ Hz), 1.19 (d, 3 H, $J = 6.8$ Hz), 1.25 (d, 6 H, $J = 7.0$ Hz), 1.27 (d, 3 H, $J = 6.4$ Hz), 1.47 (d, 3 H, $J = 6.6$ Hz), 1.50 (d, 3 H, $J = 6.8$ Hz), 1.94 (sept., 1 H, $J = 6.6$ Hz), 2.60 (sept., 1 H, $J = 6.4$ Hz), 2.65 (sept., 1 H, $J = 6.8$ Hz), 2.83 (sept., 1 H, $J = 7.0$ Hz), 2.85 (sept., 1 H, $J = 7.0$ Hz), 4.46 (sept., 1 H, $J = 6.6$ Hz), 6.49 (s, 1 H), 6.74−6.91 (m, 5 H), 7.09−7.13 (m, 7 H), 7.39−7.42 (m, 2 H). ^{13}C NMR (75.3 MHz, $CDCl_3$): δ 22.9, 23.2, 23.9, 24.0, 25.2, 25.4, 25.54, 25.57, 25.7, 30.8, 31.4, 34.0, 34.17, 34.21, 35.3, 36.3, 38.5, 85.8, 121.50, 121.54, 122.19, 122.24, 126.3, 126.7, 127.8, 128.8, 136.8, 139.5, 143.2, 145.2, 150.2, 150.5, 150.6, 153.4, 153.9, 154.1, 154.2, 155.2. Anal. Calcd for $C_{49}H_{66}GeO$: C, 79.10; H, 8.95; Ge, 9.76. Found: C, 78.88; H, 8.90; Ge, 9.93. MS[EI] [$m/z(I_{rel})$]: 744 [5.9, M^+], 729 [9.9, − Me], 638 [14.4, − Ph(H)CO], 581 [22.8, − Ph(H)CO, − t-Bu], 497 [100, − PhCC=C(t-Bu)Ph].

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Supporting Information Available: Tables giving atomic coordinates, hydrogen coordinates, anisotropic displacement parameters, bond lengths, bond angles, and torsion angles, and figures of the unit cell diagram of **8**, **10**, **11**, **12**, and **13** (59 pages). Ordering information is given on any current masthead page.

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