ELECTRONIC SUPPLEMENTARY INFORMATION for

Addition of a Cyclopropyl Alkyne to Tetramesityldigermene: Evidence for a Biradical Intermediate

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Structure Elucidation of Compounds ***5a,b***

The mass spectrum of digermacyclobutene **5a** contains a highest-mass ion with *m/z* 808, corresponding to a 1 : 1 adduct between digermene **2** and alkyne **1**. The precise mass of **5a** agrees well with the calculated mass. As expected, the ^{1}H and ^{13}C NMR spectra of **5a,b** each contain eight signals which can be assigned to the *para* and *ortho* methyl groups of the four different mesityl substituents. The signals observed at 7.59 and 7.43 ppm in the ^{1}H NMR spectra of **5a** and **5b**, respectively, were assigned to the vinylic ^{1}H of the digermacyclobutene ring system based on their distinctive chemical shifts (Table S1). The signals at 177.89, 172.19 ppm (*C*=CH) and 148.91, 158.02 ppm (C=*C*H) in the ^{13}C NMR spectra of **5a,b**, respectively, were assigned to the vinylic carbons of the cyclobutene ring by ^{1}H-^{13}C *g*HMBC and ^{1}H-^{13}C *g*HSQC/*g*HMQC correlation spectroscopy. The chemical shifts of these signals are consistent with those reported for other digermacyclobutenes (Table S1) and, furthermore, the spectral features of the ^{1}H and ^{13}C NMR spectra of **5a,b** are similar to those of the analogous silicon compound previously reported by our group[1] (Table S2). All other NMR spectroscopic data are consistent with the proposed structure of **5a,b**. The *cis* stereochemical relationship of the phenyl and methoxy substituents for **5a** was determined based on the magnitude of the coupling constant (J = 7.2 Hz) between the cyclopropyl ring hydrogens. The value of this coupling constant falls within the typical range observed for cyclopropyl hydrogens having a *cis* relationship (6–8 Hz).[2,3,4,5,6] The stereochemical relationship of the methyl group attached to the cyclopropyl ring is assumed to remain *cis* to both the phenyl and methoxy subsitutents. For **5b**, the magnitude of the coupling constant between the same two cyclopropyl hydrogens was determined to be 4.2 Hz. This value is in the range expected for hydrogens with a *trans* orientation (2-4 Hz).[7] Thus, we assign a *trans* relationship to the methoxy and phenyl substituents on the cyclopropyl ring of

digermacyclobutene **5b**. The stereochemical relationship of the methyl group attached to the cyclopropyl ring of **5b** in relation to the methoxy and phenyl substituents cannot be defined based on the spectroscopic data obtained.

Table S1. ^{1}H and ^{13}C Vinylic Chemical Shifts (ppm) of Digermacyclobutenes.

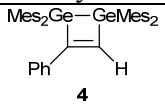
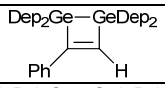
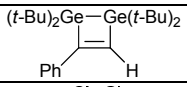
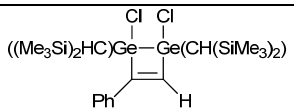
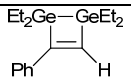
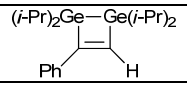
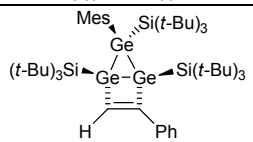
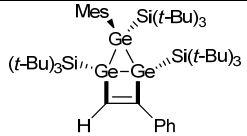
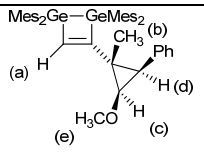
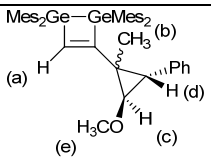
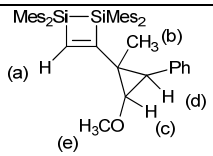
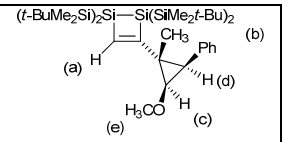
Digermacyclobutene	*H*C=CPh	HC=*C*Ph	H*C*=CPh	Reference
 **4**	7.84 ($CDCl_3$) 8.07 (C_6D_6)	169.83	157.21	8, this work
	7.88 ($CDCl_3$)			9
	7.82 ($CDCl_3$)	173.43	152.29	10
	7.85 (C_6D_6)	177.64	158.53	11
	7.69 ($CDCl_3$)	161.74	149.72	12
	7.70 (CD_2Cl_2)	171.6 ($CDCl_3$)	150.4 ($CDCl_3$)	12
	7.52 (C_6D_6)	167.4	153.0	13
	7.24 (C_6D_6)	170.8	155.9	13

Table S2. Comparison of ^{1}H and ^{13}C Chemical Shifts (ppm) of **5a,b**, 1,1,2,2-Tetramesityl-3-(2-methoxy-1-methyl-3-phenylcyclopropyl)-1,2-disilacyclobut-3-ene,[1] and 1,1,2,2-Tetrakis(*t*-butyldimethylsilyl)-3-(*trans,trans*-2-methoxy-1-methyl-3-phenylcyclopropyl)-1,2-disilacyclobut-3-ene.[4]

	 **5a**	 **5b**		
Nucleus	δ(ppm), *J* (Hz)	δ(ppm), *J* (Hz)	δ(ppm), *J* (Hz)	δ(ppm), *J* (Hz)
H_a	7.59	7.43	6.88	6.50
H_b	1.35	1.67	1.59	1.37
H_cC(OMe)	3.56 (d) *J* = 7.2	4.03 (d) *J* = 4.2	3.98 (d) *J* = 4.7	3.48 (d) *J* = 6.7
(Ph)CH_d	2.50 (d) *J* = 7.2	2.16 (obscured d)	2.42 (d) *J* = 5.2	2.38 (d) *J* = 6.7
H_e	3.08	3.13	3.17	3.24
HC=*C*	177.89	172.19	173.98	174.65
H*C*=C	148.91	158.02	155.25	140.07
C(C_bH$_3$)	13.19	22.55	obscured	13.74
C(C_bH$_3$)	33.12	40.33	37.32	32.35
H_dC_dPh	35.87	41.82	43.06	35.81
H_cC_cOMe	70.68	70.76	73.06	71.83
O*C*H$_3$	58.39	57.63	57.79	58.59
i-Ph*C*	137.05	approx. 138.4	137.14	137.27
i-Mes*C*	139.00, 138.69, 138.32	139.65, 141.26	134.9, 134.18, 133.97, 133.34	Not Applicable

Structure Elucidation of Compound ***6***

Digermacyclohepta-1,2-diene **6**, contaminated with digermacyclobutene **5b**, was isolated from the crude reaction mixture. The spectroscopic data could only be recorded on a mixture of **6**/**5b**, and hence, there was a lot of overlap in the aromatic region of the ^{1}H and ^{13}C spectra of **6**/**5b**. Thus, assignment of the aryl ^{1}H and ^{13}C signals to either **6** or **5b** was difficult; however, many important signals could be unambiguously assigned to either **6** or **5b**.

An absorption at 1942 cm^{-1} * is present in the IR spectrum of **6** and was assigned to the allene moiety of digermacyclohepta-1,2-diene **6**.[14] The signal at 209.2 ppm+ in the ^{13}C NMR spectrum of **6** is also characteristic of the chemical shifts observed for the central carbon of an allene moiety.[15] Analysis of both the two-dimensional ^{1}H-^{1}H TOCSY and ^{1}H-^{1}H *g*COSY spectra of **6** shows a correlation between the broad singlet at 5.85 ppm (1H) and the broad singlet at 1.97 (3H) present in the ^{1}H NMR spectrum of **6**. The *g*HSQC spectrum of **6** revealed that the singlet at 5.85 ppm in the ^{1}H dimension correlates to a signal at 93.80 ppm in the ^{13}C dimension. In the *g*HMQC spectrum of **6**, the signal at 1.97 ppm in the ^{1}H dimension correlates to a signal at 11.08 ppm in the ^{13}C dimension. Thus, these signals can be assigned to the hydrogen and methyl group on the allene moiety of **6** as depicted in Fragment 1 (Chart S1). As further evidence for this assignment, the signal at 1.97 ppm (assigned to the allenic methyl group) in the ^{1}H dimension of the *g*HMBC of **6** correlates to the signal at 96.26 ppm in the ^{13}C dimension, consistent with a two-bond coupling between the methyl hydrogens and the geminal allenic carbon.

The assignments of the ^{1}H NMR signals due to individual mesityl *ortho* and *para* methyl groups of **6** were made based on the integration of the signals in the ^{1}H NMR spectrum of **6**, and by analysis of the correlations apparent in the ^{1}H-^{1}H TOCSY spectrum of **6**. All of the signals assigned to the mesityl methyl groups of **6** are broad; presumably, this is due to slow rotation of the aryl groups on the NMR time scale.

An AB spin system in the ^{1}H NMR spectrum of **6** (J_{AB} = 12 Hz) was observed at 4.86 and 5.03 ppm. As expected, a correlation between these signals was observed in the ^{1}H-^{1}H *g*COSY and ^{1}H-^{1}H TOCSY NMR spectra of **6**. The ^{1}H signals at 4.86 and 5.03 ppm correlate to carbon

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* The allene stretching vibration of Ph_3Ge-(H)C=C=CH_2 is found at 1942 cm^{-1} and at 1940 cm^{-1} for Ph_3Ge-(H)C=C=C(H)CH_3.[14]

+ The ^{13}C NMR chemical shift was extracted from the ^{1}H-^{13}C *g*HMBC spectrum of **6**.

signals at 77.41 and 56.49 ppm, respectively, in the ^{13}C dimension of the ^{1}H-^{13}C *g*HSQC and ^{1}H-^{13}C *g*HMQC spectra of **6**. Thus, these signals were assigned to inequivalent strongly coupled vicinal hydrogens as shown in Fragment 2 (Chart S1).

In the ^{1}H-^{13}C *g*HMBC spectrum of **6**, a correlation between the signal at 4.86 ppm in the ^{1}H dimension and the signal at 209.2 ppm in ^{13}C dimension is observed, and suggests a two to three bond relationship between this hydrogen and the central allenic carbon. A second correlation is observed between the ^{1}H signal at 4.86 ppm and the signal at 11.08 ppm (assigned to the allenic methyl carbon) in the ^{13}C dimension in the *g*HMBC spectrum of **6**. The signal at 5.03 ppm in the ^{1}H dimension displays a correlation with the signal at 96.26 ppm (assigned to the methyl substituted terminal allenic carbon) in the ^{13}C dimension of the *g*HMBC spectrum of **6**, but it does not correlate to the ^{13}C signals at 209.2 or 11.08 ppm. The ^{1}H signal at 5.03 ppm also correlates to a ^{13}C signal at 130.60 ppm (assigned to an *ipso*-mesityl carbon by further correlation of the ^{13}C signal at 130.60 ppm with mesityl methyl hydrogens in the ^{1}H dimension of the *g*HMBC spectrum of **6**). Based on these observations, Fragments 1 and 2 (Chart S1) can be connected as shown in Fragment 3 (Chart S1).

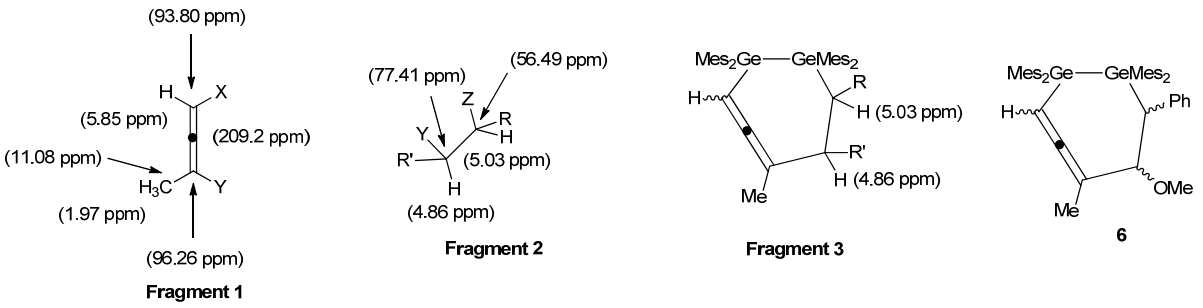


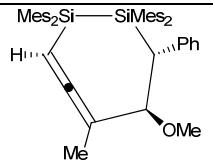
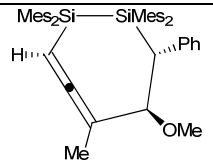
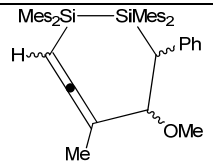
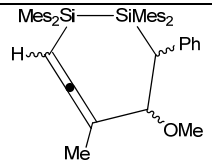
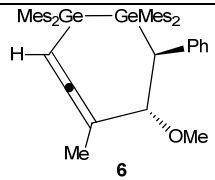
Chart S1

The signal at 5.03 ppm (^{13}C at 56.49 ppm) in the ^{1}H dimension of the ^{1}H-^{13}C *g*HMBC spectrum of **6** correlates to a signal at 141.79 ppm in the ^{13}C dimension, which was assigned to the *ipso*-phenyl carbon based on additional correlations observed between this signal and signals

assigned to phenyl hydrogens in the *g*HMBC spectrum of **6**. Moreover, the chemical shift of this signal (141.79 ppm) is consistent with those observed in the analogous 1,1,2,2-tetramesityl-6-methoxy-5-methyl-7-phenyl-1,2-disilacyclohepta-3,4-dienes (**11**) (Table S3).[1] Thus, the signal at 5.03 ppm in the ^{1}H NMR spectrum of **6** must be assigned to the hydrogen geminal to the phenyl substituent. Similarly, the signal at 4.86 ppm (^{13}C at 77.41 ppm) in the ^{1}H dimension of the *g*HMBC spectrum of **6** correlates to the signal at 56.33 ppm in the ^{13}C dimension, assigned to the methoxy group (assigned by *g*HSQC correlations). Therefore, the signal at 4.86 ppm in the ^{1}H NMR spectrum of **6** was assigned to the hydrogen geminal to the methoxy substituent. Furthermore, the ^{13}C chemical shifts of the signals at 56.49 and 77.41 ppm are consistent with having a phenyl or a methoxy substituent, respectively (see Table S3). Together, all of these observations establish the structure and regiochemistry of **6** (Chart S1).

The coupling constant between the vicinal hydrogens on the seven-membered ring **6** is 12 Hz. We note that the magnitude of this coupling constant is the same as the coupling constant for the analogous hydrogens in one isomer of the analogous 1,2-disilacyclohepta-3,4-diene **11** (Isomer A, Table S3). The stereochemical relationship between the hydrogens on the seven-membered ring of analogous 1,2-disilacyclohepta-3,4-diene **11** (Isomer A, Table S3) was unambiguously assigned to be *trans* by X-ray crystallography.[1] Thus, we assign the stereochemistry of the hydrogens on the seven-membered ring in **6** to be *trans*. Curiously, only one isomer of the 1,2-digermacyclohepta-3,4-diene was isolated; there was no evidence in the crude reaction mixture or any isolated fractions for additional isomers. Perhaps, a longer lived biradical allowed for selectivity during ring closure.

Table S3. Comparison of ^{1}H and ^{13}C Chemical Shifts (ppm) of **6** and analogous 1,2-disilacyclohepta-3,4-dienes **11**.[1]

	 Isomer A	 Isomer A	 Isomer B	 Isomer C	 6
solvent	$(CD_3)_2CO$	C_6D_6	C_6D_6	C_6D_6	C_6D_6
*H*C=C=CCH$_3$	5.50	5.72	5.79	6.22	5.85
HC=C=CC*H*$_3$	1.80	1.94 (br d)	1.87	1.32	1.97
*H*COMe	4.60 (AB) J = 11.7 Hz	4.81	4.52 (AB) J = 10.2 Hz	4.17 (AB) J = 10.7 Hz	4.86 (AB) J = 12 Hz
*H*CPh	4.54 (AB) J = 12 Hz	4.81	3.26 (AB) J = 10.2 Hz	4.49 (AB) J = 10.7 Hz	5.03 (AB) J = 12 Hz
OC*H*$_3$	3.00	2.89	2.87	2.93	2.92
H*C*=C=CCH$_3$	91.91		89.6	90.5	93.80
HC=*C*=CCH$_3$	213.14		211.2	210.2	209.2
HC=C=*C*CH$_3$	96.39		94.5	95.0	96.26
HC=C=C*C*H$_3$	10.60		16.4	16.3	11.08
H*C*OMe	77.07		85.6	84.4	77.41
O*C*H$_3$	56.62		52.0	51.9	56.33
H*C*Ph	52.42		47.8	44.1	56.49
i-Ph*C*	142.63		143.9	143.4	141.79
i-Mes*C*	134.86, 138.7, 138.86, 138.58		unable to be determined	unable to be determined	130.60 (rest unable to be determined)

*Structure Elucidation of Compound **8***

Despite much effort through preparative thin layer chromatography, crystallization and trituration, a pure sample of **8** could not be obtained, although **8** was the major component of the mixture. The structure of **8** was deduced from the IR, Raman, and mass spectra, as well as the ^{1}H, ^{13}C, 1-D TOCSY, ^{1}H-^{1}H *g*COSY, ^{1}H-^{1}H TOCSY, ^{1}H-^{13}C *g*HSQC/ *g*HMQC, and ^{1}H-^{13}C *g*HMBC NMR spectra recorded in both C_6D_6 and acetone-d_6. Because the sample was not pure, the structure of **8** is considered tentative. The NMR chemical shifts of **8** discussed here are those recorded in C_6D_6.

In the IR spectrum of **8**, no stretch attributable to an allene moiety is present; furthermore, there is no signal observed between 200 and 215 ppm in the ^{13}C NMR spectrum of **8**. Thus, the possibility that **8** is a diastereomer of digermacyclohepta-1,2-diene **6** was eliminated. There is a very broad stretch at 3439 cm^{-1} in the IR spectrum of **8** which can be assigned to a hydroxyl moiety. No absorption that could be attributed to a Ge-H stretching vibration was apparent in the IR or Raman spectra of **8**.

There are several signals apparent in the ^{1}H and ^{13}C NMR spectra of **8** which can be assigned to four different mesityl groups. In the mass spectrum of **8**, the typical fragmentation signals for a Mes_2Ge-$GeMes_2$ moiety are present, and thus, a Ge-Ge connection is present in the structure of **8**.

In the ^{1}H NMR spectrum of **8**, there are four prominent signals at 1.67 ppm (3H), 4.34 ppm (1H), 5.94 ppm (1H), and 6.81 ppm (1H). Analysis of the 1-D TOCSY spectra of **8** revealed that these 4 signals belong to the same spin system. The ^{1}H-^{1}H gCOSY and ^{1}H-^{1}H 2-D TOCSY spectra of **8** suggest that some of these signals are more strongly coupled than others. Notably, there is no signal in the ^{1}H NMR spectrum of **8** that could be assigned to a methoxy group, which implies the loss of methoxy or methanol from compound **8** at some point during its formation.

The signal at 4.34 ppm (1H) in the ^{1}H NMR spectrum of **8** shows some fine structure which can be described as a broad triplet. In the ^{1}H-^{13}C *g*HSQC/*g*HMQC spectra of **8**, the signal at 4.34 ppm in the ^{1}H dimension correlates to a signal at 46.65 ppm in the ^{13}C dimension. Based on the chemical shift of this ^{13}C signal, it can be concluded that this hydrogen is on a saturated carbon. Furthermore, a ^{13}C chemical shift of 46.65 ppm is too upfield to be consistent with oxygen substitution on the same carbon; however, the chemical shift is consistent with phenyl substitution on the same carbon (Table S3). The ^{13}C signal at 46.65 ppm correlates to the signals in the ^{1}H dimension of the *g*HMBC spectrum of **8** assigned to the phenyl hydrogens (multiplet at 6.95-6.87 ppm). Because the signal at 144.29 ppm in the ^{13}C dimension also correlates to signals in the ^{1}H dimension of the *g*HMBC spectrum of **8** assigned to the phenyl hydrogens, the signal at 144.29 ppm was assigned to the *ipso* carbon of the phenyl group. Based on these observations, we assign these data to a HCPh moiety (Fragment 1, Chart S2).

The broad singlet at 5.94 ppm (1H) in the ^{1}H dimension correlates to a signal at 139.76 ppm in the ^{13}C dimension of the ^{1}H-^{13}C *g*HSQC and *g*HMQC spectra of **8**. This ^{13}C shift falls within the typical chemical shift range for sp^{2}-hybridized carbons (Fragment 2, Chart S2). The ^{1}H signal at 5.94 ppm also displays weak correlations to ^{13}C signals at 161.81, 145.04, and 144.29 ppm in the ^{1}H-^{13}C *g*HMBC spectrum of **8**. Since the signal at 144.29 also correlates to the signal at 4.34 ppm (*H*CPh) in the *g*HMBC spectrum of **8**, fragments 1 and 2 are connected, and thus, a =CHCHPh moiety is present in **8**.

The signal at 1.67 ppm (3H) in the ^{1}H NMR spectrum of **8** is also broad, with a fine splitting pattern which can be ascribed to a doublet of doublets. This ^{1}H signal correlates to a signal at 20.05 ppm in the ^{13}C dimension of the *g*HSQC and *g*HMQC spectra of **8**, and thus, can be assigned to a methyl group. The ^{1}H signal at 1.67 ppm also correlates to signals at 161.81, 145.04, and 139.76 (=*C*HCHPh) ppm in the ^{13}C dimension of the ^{1}H-^{13}C *g*HMBC

spectrum of **8**. The ^{13}C signal at 145.04 ppm is assigned to the vinylic carbon attached to the methyl group (Fragment 3, Chart S2). Because the ^{13}C signal at 145.04 ppm is also found to correlate to the signal at 5.94 ppm (=C*H*CHPh) in the ^{1}H dimension of the gHMBC spectrum of **8**, Fragments 1, 2, and 3 (Chart S2) are connected to one another in the following manner: H_3CC=CHCHPh.

The signal at 6.81 ppm in the ^{1}H NMR spectrum of **8** is broad. In the ^{1}H-^{13}C *g*HMQC spectrum of **8**, the signal at 6.81 ppm in the ^{1}H dimension correlates to a signal at 141.79 ppm in the ^{13}C dimension. The chemical shift of the ^{13}C signal at 141.79 ppm is consistent with a vinylic sp^2-hydbridized carbon (Fragment 4, Chart S2). In the *g*HMBC spectrum of **8**, the ^{1}H signal at 6.81 ppm strongly correlates to signals at 161.81, 145.04, and 139.76 ppm in the ^{13}C dimension. The signals at 139.76 (=*C*HCHPh) and 145.04 (H_3C*C*=C) ppm have previously been assigned, and thus, the spin-system consisting of the 4 predominant ^{1}H signals can be connected as depicted in Fragment 5 (Chart S2).

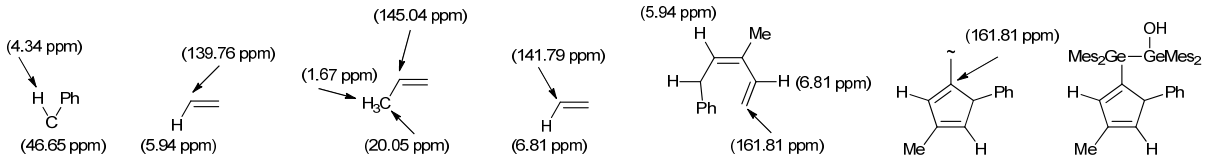


Chart S2

Notably, the ^{1}H signals at 5.94, 1.67, and 6.81 ppm all correlate to a signal at 161.81 ppm in the ^{13}C dimension of the *g*HMBC spectrum of **8**. However, the ^{13}C signal at 161.81 ppm did not correlate to any signal in the ^{1}H dimension of the *g*HSQC/*g*HMQC spectra of **8**. Thus, we can attribute the ^{13}C signal at 161.81 ppm to a substituted vinylic carbon (Fragment 5, Chart S2). Given that the signal at 4.34 ppm in the ^{1}H NMR spectrum of **8** correlates to the signal at 6.81 ppm in the TOCSY and gCOSY spectra of **8**, it is likely that the structure is a substituted cyclopentadiene (Fragment 6, Chart S2). To complete the structure of **8**, it is reasonable to assume, based on the fact that a Y-Mes$_2$Ge-GeMes$_2$-X moiety is present in **8**,

that the ^{13}C signal with a chemical shift of 161.81 ppm, has a digermyl substituent. In the mass spectrum of **8**, a signal at *m/z* 777 is observed. This corresponds to our proposed cyclopenta-1,3-diene fragment plus a Mes_2Ge-$GeMes_2$ moiety. Since no GeH moiety was detected by ^1H NMR, IR or Raman spectroscopy, we believe that a hydroxyl moiety is present as the remaining substituent, and thus, we propose the structure for **8** as shown in Chart S2.

Experimental Section

General Procedures. Unless otherwise indicated, all reactions were carried out in flame-dried glassware under an inert atmosphere of argon using a dual manifold vacuum line or prepared under a nitrogen atmosphere using an MBraun Labmaster 130 glovebox. Photolyses (350 nm) were performed in a Rayonet Photochemical Reactor (Southern New England Co.). Samples were cooled by circulating methanol through a vacuum-jacketed Pyrex immersion well using an Endocal model ULT-70 low temperature external bath circulator. THF was purged with nitrogen and then passed through an alumina column (Innovative Technologies Ltd.) prior to use. Toluene was purged with nitrogen and then passed through an alumina column and copper catalyst (Innovative Technologies Ltd.) prior to use. Phenylacetylene was distilled from calcium hydride. Pre-coated silica glass plates suitable for preparative thin-layer chromatography were purchased from EM Science. Tetramesityldigermene (**2**)[16] and (*trans*,*trans*-2-methoxy-1-methyl-3-phenylcyclopropyl)ethyne (**1**)[5] were prepared according to the literature procedures. Typically, alkyne **1** is contaminated with (*trans*,*trans*-2-methoxy-1-methyl-3-phenylcyclopropyl)ethene.[5] By GC analysis, alkyne **1** used in these experiments contained 15% of the alkene.

NMR spectra were recorded on Varian Mecury 400 or Inova 400 or 600 NMR spectrometers. The standards used were as follows: residual C_6D_5H (7.15 ppm) and $(CD_2H)(CD_3)CO$ (2.04 ppm) for ^1H NMR spectra; C_6D_6 central transition (128.00 ppm) and

$(CD_3)_2CO$ central transition (29.80 ppm) for ^{13}C NMR spectra. C_6D_6 was used for all spectra, unless otherwise noted. *J* values are reported in Hertz. Mass spectra were recorded on a Finnegan MAT model 8400 mass spectrometer with an ionizing voltage of 70 eV (reported in mass-to-charge units, *m/z*, with ion identity and intensities relative to the base peak in parentheses). IR spectra were recorded as thin films on a Bruker FT-IR spectrometer.

Addition of Phenylacetylene to Tetramesityldigermene (2). Digermene **2** (0.081 mmol), produced by photolysis of hexamesitylcyclotrigermane (**3**) (50 mg, 0.054 mmol) in THF (4 mL) at -70 ^oC, was dissolved in toluene (4 mL) after removal of the THF. Phenylacetylene (0.1 mL, excess) was added to the solution of **2** and the mixture was heated to 100 ^oC for 18 h. The colour of the reaction mixture changed from bright yellow to orange. The volatiles were removed by rotary evaporation *in vacuo* to give digermacyclobutene **4** as an orange powder contaminated with a significant amount of phenylacetylene (**4** : phenylacetylene, 40 : 60, 55.9 mg). Compound **4** was identified by comparison of the ^1H NMR spectral data in $CDCl_3$ with the reported literature values.[8]

4: ^1H NMR (C_6D_6, ppm): 8.07 (1H, s, *H*C=C), 6.99-7.05, 6.91-6.88 (m, 5H, Ph*H*), 6.68 (2H, s, Mes C*H*), 6.66 (2H, s, Mes C*H*), 2.39 (12H, s, Mes *o*-CH_3), 2.30 (12H, s, Mes *o*-CH_3), 2.07 (6H, s, Mes *p*-CH_3), 2.05 (6H, s, Mes *p*-CH_3).

Addition of (*trans*,*trans*-2-Methoxy-1-methyl-3-phenylcyclopropyl)ethyne (1) to Tetramesityldigermene (2). Digermene **2** (0.65 mmol), produced by photolysis of hexamesitylcyclotrigermane **(3)** (0.40 g, 0.43 mmol) in THF (15 mL) at -70 ^oC, was dissolved in toluene (10 mL) after removal of the THF. A solution of alkyne **1** (15.6 mg, 0.84 mmol) in toluene (2 mL) was added to the solution of **2**. The mixture was heated to 100 ^oC for 5 days in a Schlenk tube. After this time, the colour of the solution had faded from bright to pale yellow. The solvent was removed by rotary evaporation to yield a light yellow oil. The crude product was separated by preparative thin-layer chromatography (silica gel; 60/40

hexanes/CH_2Cl_2). Each band isolated from the plate was separated again by preparative thin-layer chromatography to give 1,1,2,2-tetramesitylmethoxydigermane (**7**),[17] digermacyclobutene **5a** contaminated with alkyne **1** and/or the corresponding alkene (0-10%),[5] an inseparable mixture of digermacyclobutene **5b** and digermacyclohepta-1,2-diene **6** (1:3 ratio), and digermylcyclopenta-1,3-diene (**8**) contaminated with small amounts of unidentified impurities (ratio of products in the crude mixture was 12 : 25 : 12 : 22 : 29, respectively).[℘] Minor amounts of (hydroxydimesitylgermyl)dimesitylgermane,[18] 2,2,4,4-tetramesityl-2,4-digermadioxetane,[19] and 1,1,2,2-tetramesitylmethoxydigermanol ($Mes_2Ge(OMe)Ge(OH)Mes_2$) were also isolated, as well as minor amounts of unidentified compounds. The thermal stabilities of **5a** and **8** were examined by heating the isolated compounds in toluene at 105 °C under nitrogen for 17 hours: both compounds showed no change.

5a: IR (cm^{-1}): 3022 (w), 2959 (m), 2921 (s), 2820 (w), 1601 (s), 1448 (s), 1444 (s), 1379 (m), 1371 (m), 1026 (s), 847 (m). ^{1}H NMR (ppm): 7.59 (1H, s, *H*C=C), 7.46 (2H, d, *o*-Ph*H*, J = 7.8 Hz), 7.17 (2H, t, *m*-Ph*H*, J = 7.8 Hz), 7.05 (1H, t, *p*-Ph*H*, J = 7.8 Hz), 6.69 (2H, s, Mes C*H*), 6.66 (2H, s, Mes C*H*), 6.65 (4H, s, Mes C*H*), 3.56 (1H, d, C*H*OMe, J = 7.2 Hz), 3.08 (3H, s, OCH_3), 2.50 (1H, d, C*H*Ph, J = 7.2 Hz), 2.47 (6H, s, Mes *o*-CH_3), 2.43 (6H, s, Mes *o*-CH_3) 2.42, 2.41 (12H, each s, Mes *o*-CH_3), 2.08 (3H, s, Mes *p*-CH_3), 2.06 (3H, s, Mes *p*-CH_3), 2.05 (3H, s, Mes *p*-CH_3), 2.03 (3H, s, Mes *p*-CH_3), 1.35 (s, CH_3). ^{13}C NMR (ppm): 177.89 (HC=*C*), 148.91 (H*C*=C), 143.25, 143.21, 143.14, 142.93 (*o*-Mes*C*), 139.00, 138.69, 138.32 (*i*-Mes*C*), 138.19, 138.15, 138.09, 137.95, 137.89 (1 x *i*-Mes*C*, 4 x *p*-Mes*C*), 137.05 (*i*-Ph*C*), 130.73 (*o*-Ph*C*), 129.27, 129.25, 129.11, 129.06 (Mes *C*H), 128.29 (*m*-Ph*C*), 126.09 (*p*-Ph*C*), 70.68 (H*C*OMe), 58.39 (O*C*H$_3$), 35.87 (H*C*Ph), 33.12 (*C*CH$_3$), 25.16, 25.03, 24.87,

[℘] Due to the extensive chromatography performed and combination of bands from the preparative thin-layer chromatography plates, meaningful isolated yields could not be determined.

24.76 (Mes *o*-CH_3), 20.95, 20.93, 20.91 (Mes *p*-CH_3), 13.19 (CH_3). EI-MS (*m/z*): 808 (M^+ ($^{72}Ge^{74}Ge$), 23), 776 (M^+ - $HOCH_3$, 21), 622 ($Mes_4{}^{72}Ge^{74}Ge$, 17), 497 (M^+ - $Mes_2{}^{72}GeH$, 14), 467 (M^+ - $Mes_2{}^{72}GeOCH_3$, 65), 431 ($Mes_3{}^{74}Ge$, 100), 343 ($Mes_2{}^{74}GeOCH_3$, 83), 311 ($Mes_2{}^{72}GeH$, 78), 193 ($Mes^{74}Ge$, 65). High-resolution EI-MS: Exact mass calcd for $C_{49}H_{58}{}^{72}Ge^{74}GeO$ 808.292, found 808.295.

5b and 6: IR (cm^{-1}): 2981 (m), 2920 (s), 2852 (w), 2818 (w), 2730 (w), 1942 (w), 1602 (m), 1496 (w), 1449 (s), 1406 (w), 1377 (w), 1290 (w), 1087 (m), 1029 (m), 848 (m), 698 (m). ^1H NMR (ppm): 7.43 (1H, s, *H*C=C, **5b**), 7.08-7.04 (m, PhH, **5b** and **6**), 6.92 (1H, s, Mes C*H*, **6**), 6.88-6.83 (m, Ph*H*, **5b** and **6**), 6.80-6.77 (m, Ph*H*, **5b** and **6**), 6.76 (2H, s, Mes C*H*, **6**), 6.71 (4H, s, Mes C*H*, **5b**), 6.66 (2H, s, Mes C*H*, **5b**), 6.61, 6.59 (3H, each s, Mes C*H*, **6**), 6.58 (2H, s, Mes C*H*, **5b**), 6.32 (1H, s, Mes C*H*, **6**), 6.09 (1H, s, Mes C*H*, **6**), 5.85 (1H, s, *H*C=C=C, **6**), 5.03 (1H, AB, *H*CPh, **6**, J = 12 Hz), 4.86 (1H, AB, *H*COMe, **6**, J = 12 Hz), 4.03 (1H, d, *H*COMe, **5b**, J = 4.2 Hz), 3.13 (3H, s, OCH_3, **5b**), 3.05 (6H, bs, Mes CH_3, **6**), 2.92 (3H, s, OCH_3, **6**), 2.58 (3H, bs, Mes CH_3, **6**), 2.47 (3H, bs, Mes CH_3, **6**), 2.45 (6H, s, Mes *o*-CH_3, **5b**), 2.43 (3H, bs, Mes CH_3, **6**), 2.31 (3H, bs, Mes CH_3, **6**), 2.29 (6H, s, Mes *o*-CH_3, **5b**), 2.21 (6H, s, Mes *o*-CH_3, **5b**), 2.19 (3H, bs, Mes CH_3, **6**), 2.17 (6H, s, Mes *o*-CH_3, **5b**), 2.16 (1H, *H*CPh, **5b**), 2.12 (3H, s, Mes *p*-CH_3, **5b**), 2.08 (3H, s, Mes *p*-CH_3, **5b**), 2.07 (3H, s, Mes *p*-CH_3, **5b**), 2.06 (3H, bs, Mes CH_3, **6**), 2.05 (3H, bs, Mes CH_3, **6**), 2.00 (3H, s, Mes *p*-CH_3, **5b**), 1.99 (3H, bs, Mes CH_3, **6**), 1.97 (3H, bs, CH_3, **6**), 1.67 (3H, s, CH_3, **5b**), 1.54 (3H, bs, Mes CH_3, **6**), 1.28 (3H, bs, Mes CH_3, **6**). ^{13}C NMR (ppm): 209.2$^+$ (C=*C*=C, **6**), 172.19 (HC=*C*, **5b**), 158.02 (H*C*=C, **5b**), 149.37, 144.24, 143.68, 143.48, 143.15, 143.11, 142.42, 141.86 (all Mes*C*, **5b** and **6**), 141.79 (*i*-PhC, **6**), 141.26 (*i*-MesC, **5b**), 139.65 (*i*-MesC, **5b**), 138.95, 138.50, 138.48, 138.42, 138.01, 137.82, 137.74, 137.55, 137.50, 137.06, 136.40 (all Mes*C*, **5b** and **6**), 130.77 (Ph*C*H, **5b** and **6**), 130.60 (*i*-MesC, **6**), 129.27, 129.11 (Mes *C*H, **5b**), 129.00, 128.95, 128.88, 128.79, 128.73 (Mes *C*H, Ph*C*H, **5b** and **6**), 128.49

(bs, Mes *C*H, **6**), 128.36 (Ph*C*H, **5b** and **6**), 128.29 (Mes*C*H, **6**), 128.08, 125.97, 125.12 (Ph*C*H, **5b** and **6**), 96.26 (bs, HC=C=*C*CH_3, **6**), 93.80 (H*C*=C=CCH_3, **6**), 77.41 (H*C*OMe, **6**), 70.76 (H*C*OMe, **5b**), 57.63 (O*C*H_3, **5b**), 56.49 (H*C*Ph, **6**), 56.33 (O*C*H_3, **6**), 41.82 (H*C*Ph, **5b**), 40.33 (*C*CH_3, **5b**), 29.69 (bs, Mes *C*H_3, **6**), 29.55 (bs, Mes *C*H_3, **6**), 28.28 (bs, Mes *C*H_3, **6**), 26.04 (bs, Mes *C*H_3, **6**), 25.96 (bs, Mes *C*H_3, **6**), 25.86 (Mes *C*H_3, **5b**), 25.00 (Mes *C*H_3, **5b**), 24.70 (bs, Mes *C*H_3, **6**), 24.48 (Mes *C*H_3, **5b**), 24.45 (Mes *C*H_3, **5b**), 22.70 (bs, Mes *C*H_3, **6**), 22.55 (*C*H_3, **5b**), 22.39 (bs, Mes *C*H_3, **6**), 21.03, 20.95, 20.84, 20.81, 20.74, 20.68 (Mes *C*H_3, **5b** and **6**), 11.08 (*C*H_3, **6**). EI-MS (*m/z*): 808 (M^+ ($^{72}Ge^{74}Ge$), 36), 776 (M^+ - $HOCH_3$, 17), 622 ($Mes_4{}^{72}Ge^{74}Ge$, 11), 498 (M^+ - $Mes_2{}^{72}Ge$, 11), 467 (M^+ - $Mes_2{}^{72}GeOCH_3$, 66), 431 ($Mes_3{}^{74}Ge$, 78), 343 ($Mes_2{}^{74}GeOCH_3$, 100), 311 ($Mes_2{}^{74}Ge$ - H, 85), 221 ($Mes^{72}GeOCH_3$ - H, 21), 192 ($Mes^{74}Ge$ - H, 67). High-resolution EI-MS: Exact mass calcd for $C_{49}H_{58}{}^{72}Ge^{74}GeO$ 808.292, found 808.293.

8: IR (cm^{-1}): 3439 (br s), 2920 (m), 2853 (m), 1643 (s), 1602 (s), 1449 (m), 1410 (w), 1380 (w). Raman (cm^{-1}): 3020 (m), 2918 (s), 2862 (m), 2730 (w), 1602 (s), 1554 (m), 1447 (m), 1378 (s), 1291 (s), 1031 (m), 1000 (m), 952 (w), 586 (m), 558 (s). ^{1}H NMR (ppm, C_6D_6): 6.95-6.87 (5H, m, Ph*H*), 6.83 (2H, bs, Mes*H*), 6.81 (1H, s, *H*C=CGe), 6.74 (2H, bs, Mes*H*), 6.633 (2H, s, Mes C*H*), 6.626 (2H, s, Mes C*H*), 5.94 (1H, bs, *H*C=CCH_3), 4.34 (1H, t, *H*CPh, *J* = 2.4), 2.56 (6H, s, Mes *o*-CH_3), 2.35 (6H, s, Mes *o*-C*H*$_3$), 2.12 (6H, s, Mes *p*-C*H*$_3$), 2.09 (bs, Mes *o*-C*H*$_3$), 2.06 (6H, s, Mes *p*-C*H*$_3$), 2.02 (6H, s, Mes *o*-C*H*$_3$), 1.67 (3H, dd, C*H*$_3$, *J* = 3.0, 1.2). ^{1}H NMR (ppm, $(CD_3)_2CO$, -40 °C): 6.97-6.82 (6H, m, Ph*H*),[ϒ] 6.77, 6.75, 6.74 (5H, each s, Mes C*H*),[ϒ] 6.69 (2H, s, Mes C*H*), 6.67 (1H, s, Mes C*H*), 6.63 (1H, s, Mes C*H*), 6.47 (1H, s, *H*C=CGe), 6.44 (1H, s, Mes C*H*), 6.29 (1H, s, Mes C*H*), 5.82 (1H, bs, *H*C=CCHPh), 4.17 (1H, bs, *H*CPh), 2.71 (3H, s, Mes C*H*$_3$), 2.37 (3H, s, Mes C*H*$_3$), 2.25 (3H, s, Mes C*H*$_3$), 2.24 (3H, s, Mes C*H*$_3$), 2.23 (3H, s, Mes C*H*$_3$), 2.16 (3H, s, Mes C*H*$_3$), 2.14 (6H, s, Mes

[ϒ] Integration of the aromatic region in the ^{1}H NMR spectrum of **8** (in $(CD_3)_2CO$) was slightly greater than expected due to contamination with an unknown compound.

C*H*$_3$), 2.12 (6H, s, Mes C*H*$_3$), 2.09 (3H, s, Mes C*H*$_3$), 1.77 (3H, s, Mes C*H*$_3$), 1.43 (3H, bs, C*H*$_3$). ^{13}C NMR (ppm, C_6D_6): 161.81 (HC=*C*Ge), 145.04 (HC=*C*CH$_3$), 144.59 (*o*-Mes*C*), 144.29 (*i*-Ph*C* and *o*-Mes*C*), 143.27, 142.92 (*o*-Mes*C*), 141.79 (H*C*=CGe), 141.25, 140.40 (*i*-Mes*C*), 139.76 (H*C*=CCHPh), 138.49, 138.18 (*p*-Mes*C*), 138.01, 137.28 (*i*-Mes*C*), 129.27, 129.19, 128.61 (*m*-Mes*C*), 128.22, 127.66, 124.98 (Ph*C*H), 46.65 (H*C*Ph), 24.62, 22.76, 20.99, 20.94, 20.93, 20.89 (Mes *C*H$_3$), 20.05 (*C*H$_3$). CI-MS (*m/z*): 845 (0.5), 777 (M^+ (^{72}Ge^{74}Ge) - OH, 1), 622 (Mes$_4$^{72}Ge^{74}Ge, 1), 586 (M^+ - Mes^{72}GeOH, 3), 431 (Mes$_3$^{74}Ge, 14), 313 (Mes$_2$^{74}Ge + H, 34), 192 (Mes^{72}GeH, 9), 121 (MesH + H, 100). High-resolution CI-MS: Exact mass calcd for $C_{48}H_{55}$^{72}Ge^{74}Ge (M^+ - OH) 777.274, found 777.272.

Mes$_2$Ge(OMe)Ge(OH)Mes$_2$: IR (cm^{-1}): 3474 (br), 2920 (s), 2851 (w), 1601 (w), 1449 (w), 1054 (w), 1019 (w), 847 (w). ^{1}H NMR (ppm): 6.70, 6.69 (8H, each s, Mes C*H*), 3.53 (3H, s, OC*H*$_3$), 2.43 (12H, s, Mes *o*-C*H*$_3$), 2.40 (12H, s, Mes *o*-C*H*$_3$), 2.09 (6H, s, Mes *p*-C*H*$_3$), 2.08 (6H, s, Mes *p*-C*H*$_3$). CI-MS (*m/z*): 669 (M^+ (^{72}Ge^{74}Ge) – H, 2), 653 (M^+ – OH, 8), 639 (M^+ - OCH$_3$, 10), 623 (M^+ - O$_2$CH$_3$, 3), 551 (M^+ - Mes, 4), 431 (Mes$_3$^{74}Ge, 8), 343 (Mes$_2$^{74}GeOCH$_3$, 40), 329 (Mes$_2$^{74}GeOH, 20), 313 (Mes$_2$^{74}GeH, 26), 121 (MesH + H$^+$, 100).

Figure S1. ^{1}H NMR Spectrum of Compound 5a.

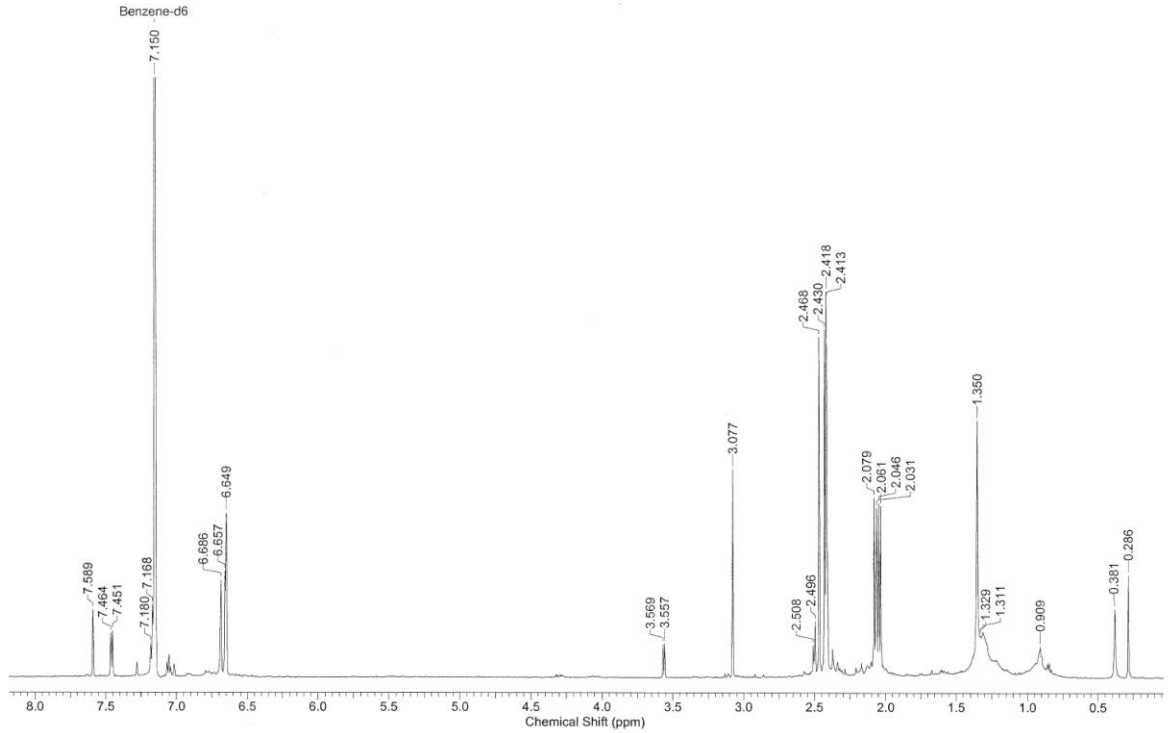


Figure S2. ^{1}H NMR Spectrum of Compound 5b/6 (integrated for 6).

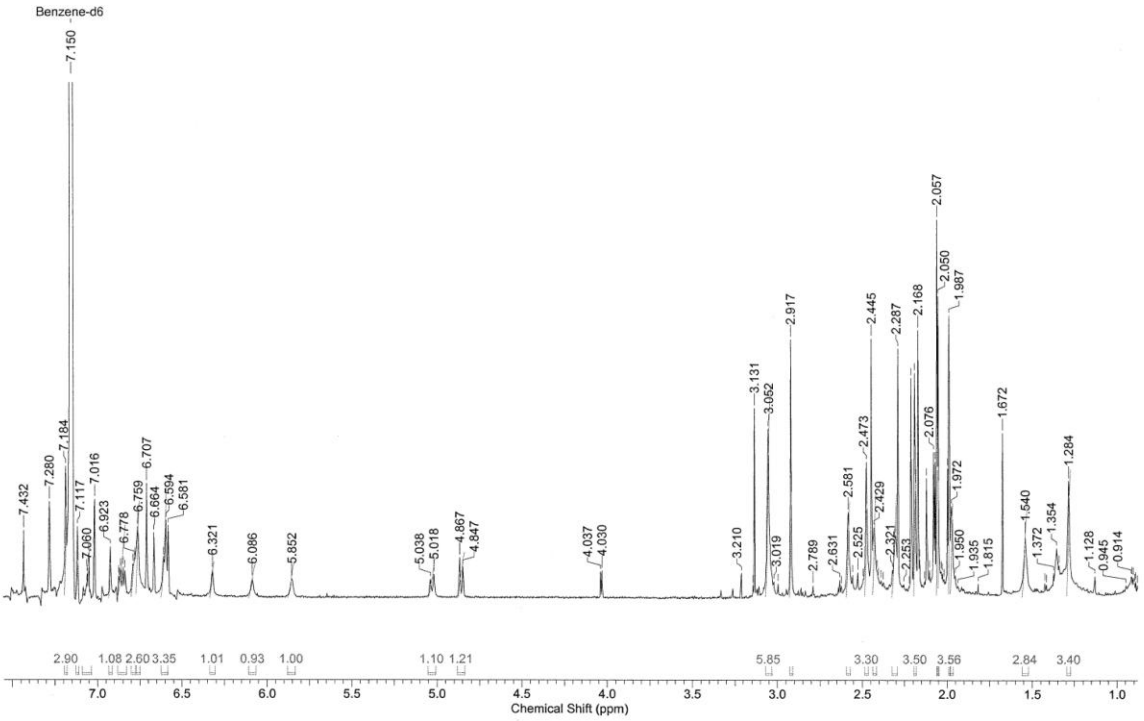


Figure S3. Expansion of the ^{1}H NMR Spectrum of Compound 5b/6: 6.4-7.4 ppm

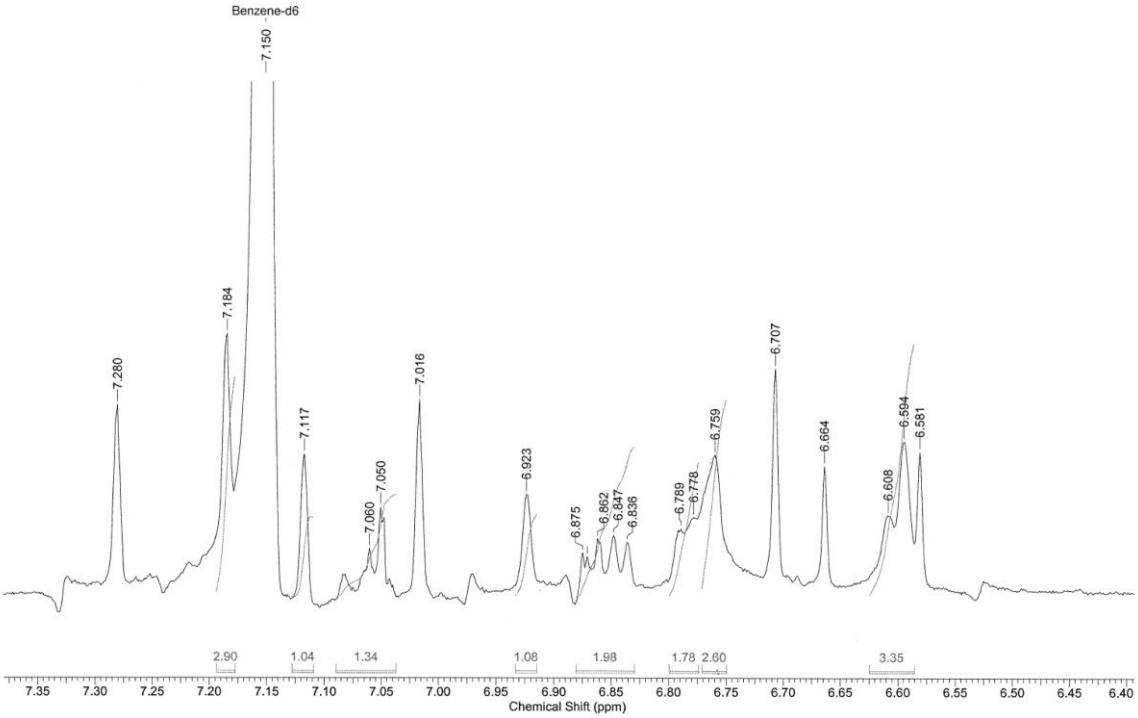


Figure S4. Expansion of the ^{1}H NMR Spectrum of Compound 5b/6: 4.8-6.4 ppm

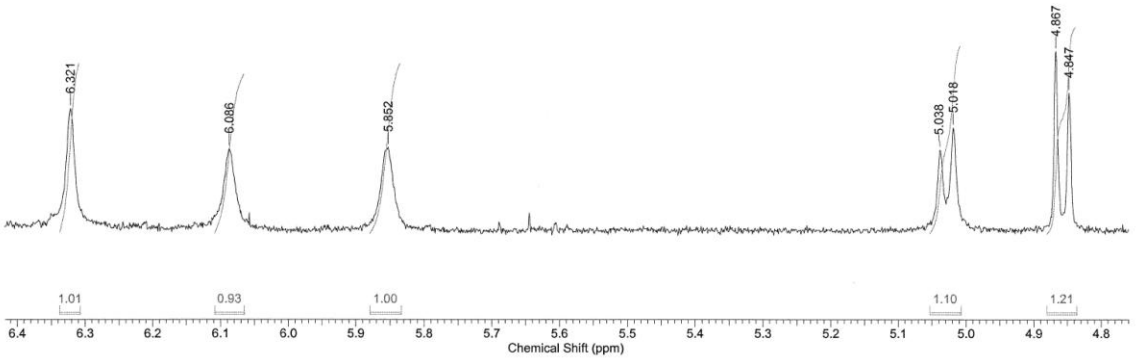


Figure S5. Expansion of the ^{1}H NMR Spectrum of Compound 5b/6: 2.2-3.2 ppm

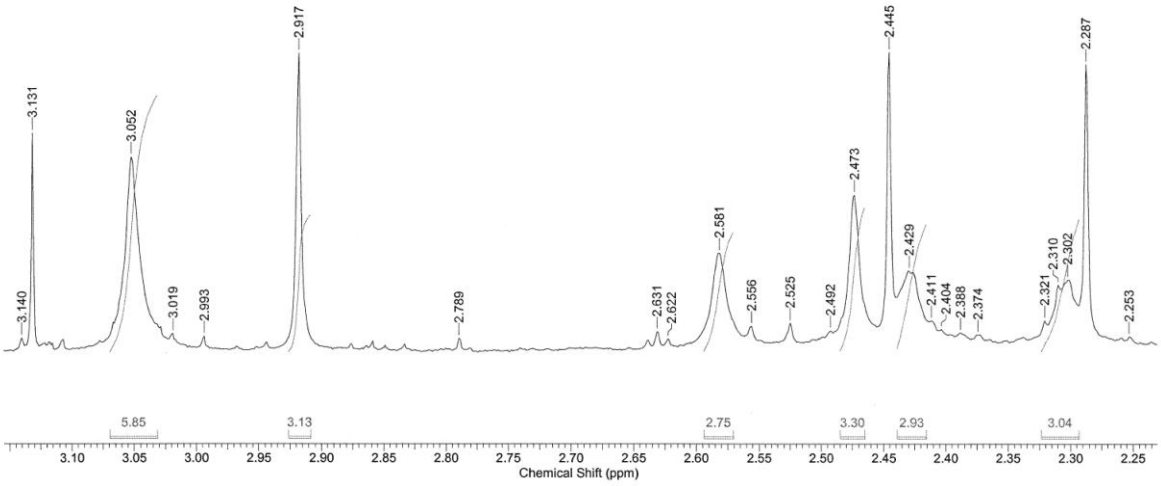


Figure S6. Expansion of the ^{1}H NMR Spectrum of Compound 5b/6: 1.9-2.3 ppm

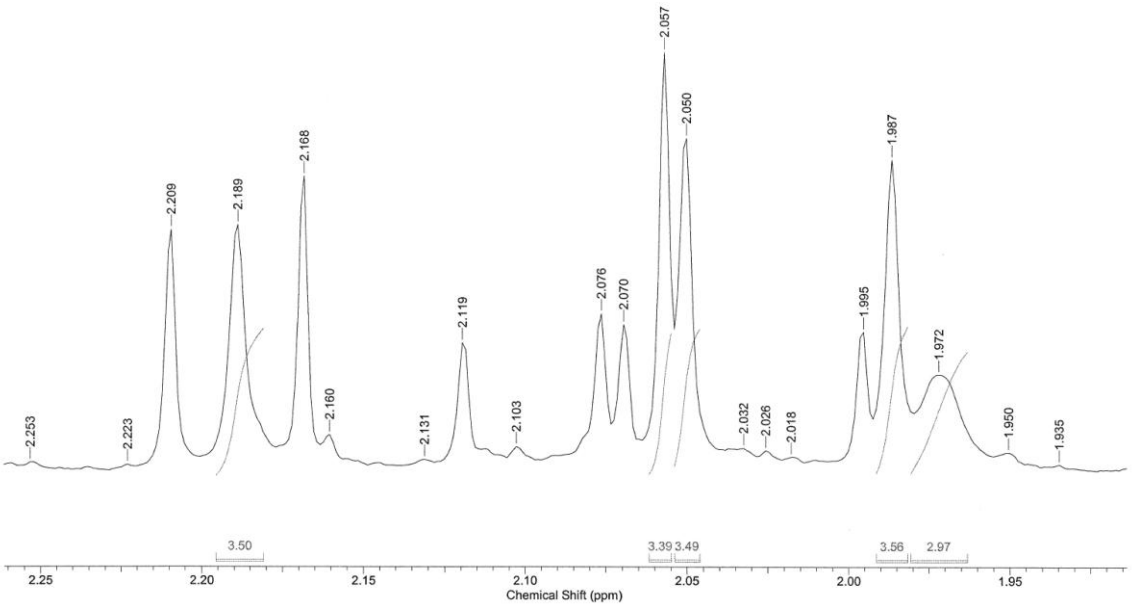


Figure S7. Expansion of the ^{1}H NMR Spectrum of Compound 5b/6: 1.2-1.6 ppm

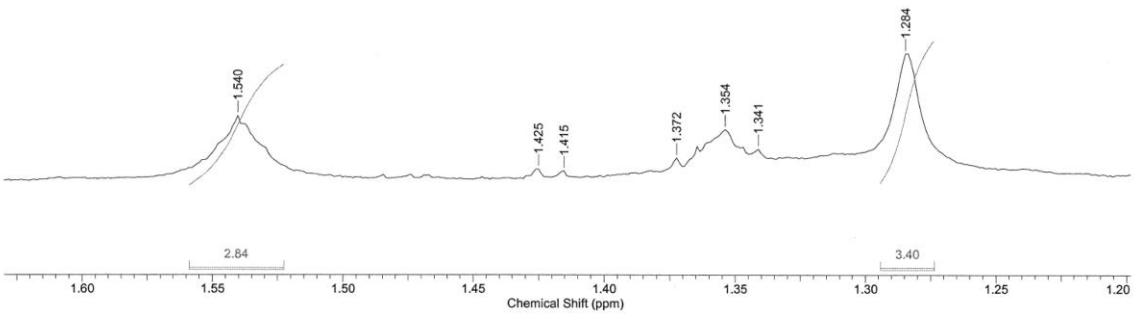


Figure S8. ^{1}H NMR Spectrum of Compound 8

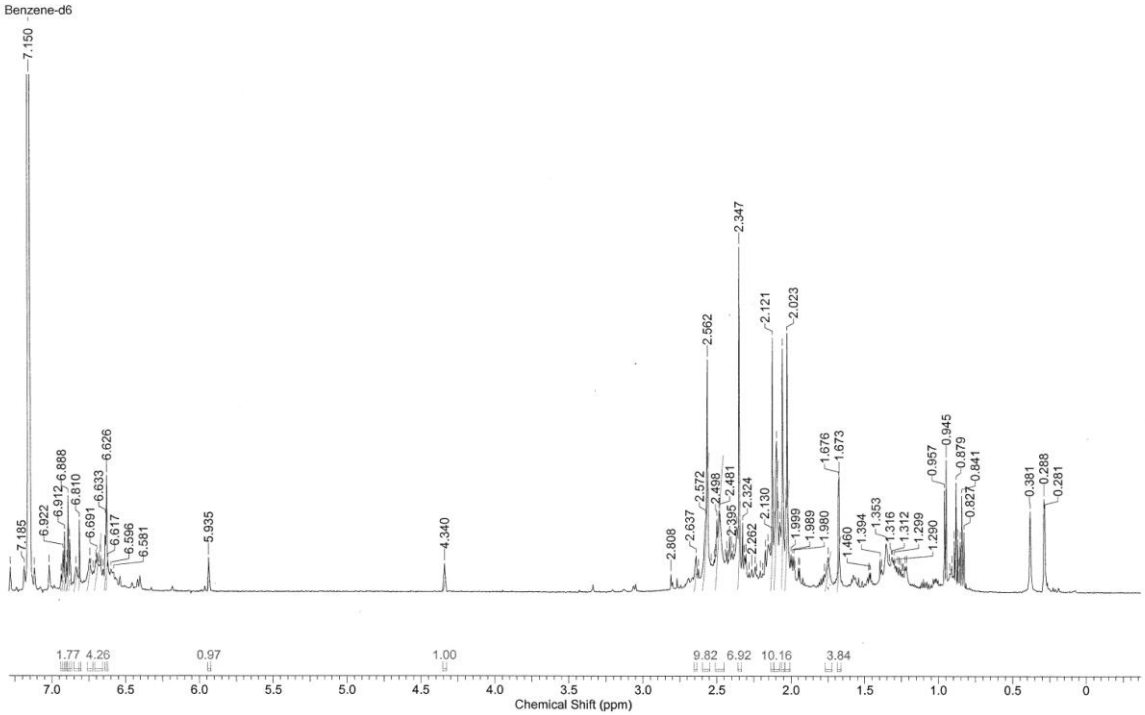
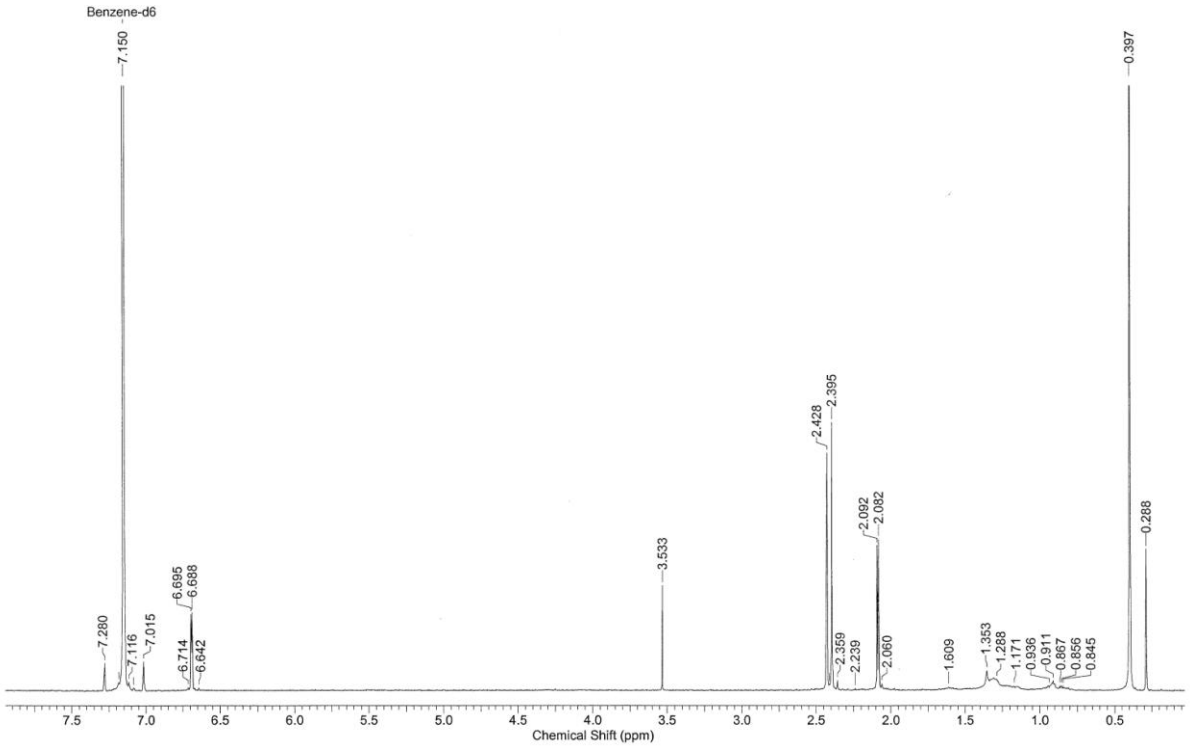


Figure S9. ^{1}H NMR Spectrum of $Mes_2Ge(OMe)Ge(OH)Mes_2$



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