

# Synthesis and Crystal Structure of the Germatrane E-N(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>O<sub>3</sub>GeC(Br)=C(Br)Ph

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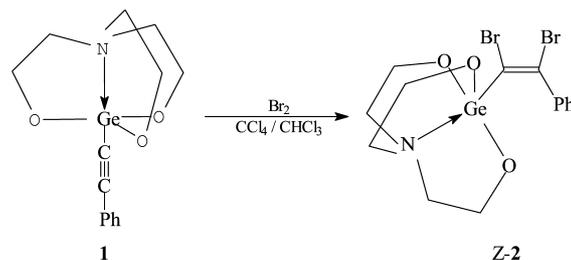
The reaction of (phenylacetylenyl)triethoxygermane, (EtO)<sub>3</sub>GeC≡CPh (**3**), with bromine in CHCl<sub>3</sub>/CCl<sub>4</sub> solution leads to a mixture of Z- and E- (EtO)<sub>3</sub>GeC(Br)=C(Br)Ph (**4**) in the ratio Z/E = 3/1. Treatment of this product with N(CH<sub>2</sub>CH<sub>2</sub>OH)<sub>3</sub> affords a mixture of Z- and E-N(CH<sub>2</sub>CH<sub>2</sub>O)<sub>3</sub>GeC(Br)=C(Br)Ph (**2**) in high yield. Compound E-**2** was isolated in 16% yield. The molecular composition and the structure of all new compounds have been established by elemental analyses, <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy. The crystal structure of E-**2** is reported. The possible reasons for the different Z/E ratios in the products of the bromination of **3** and N(CH<sub>2</sub>CH<sub>2</sub>O)<sub>3</sub>GeC≡CPh (**1**) are discussed using DFT calculations.

*Key words:* Germatrane, Bromination, Alkynes, DFT Calculations

## Introduction

Metallatrane are a systematically studied class of compounds containing hypervalent atoms of the main group elements [1]. Metallatrane of Group 14 elements, N(CH<sub>2</sub>CH<sub>2</sub>O)<sub>3</sub>MX (M = Si, Ge, Sn), received particular attention due to the interest in the nature of a possible M←N transannular interaction [1–3]. In this context, a great number of metallatrane with various substituents at the hetero atom were synthesized. At present, much more attention is directed towards the chemical transformations of these compounds, especially to those with retention of the atrane framework of the molecule. Nevertheless, the total number of such reports is relatively small.

As part of our investigations along this line, we have studied a number of metallatrane in which a phenylacetylene group is bound to the hetero atom and reported that treatment of N(CH<sub>2</sub>CH<sub>2</sub>O)<sub>3</sub>-GeC≡CPh (**1**) with molecular bromine leads to the formation of only one product, viz. the Z-isomer of N(CH<sub>2</sub>CH<sub>2</sub>O)<sub>3</sub>GeC(Br)=C(Br)Ph (**Z-2**) (Scheme 1) [4]. Formation of any amount of E-N(CH<sub>2</sub>CH<sub>2</sub>O)<sub>3</sub>GeC(Br)=C(Br)Ph (**E-2**) in this reaction was not observed.

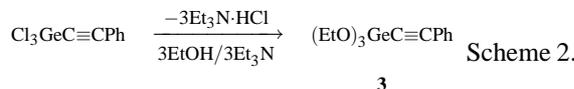


Scheme 1.

In order to find a reasonable explanation for such an unusual behaviour, an attempt has been made to use another approach for the preparation of E-**2**. We decided to carry out an electrophilic bromination reaction not at the final stage of the synthetic chain, but as the stage preceding the atrane fragment generation. The following motivation prompted us to start this investigation: (i) to examine the possibility of E-**2** formation in principle; (ii) to investigate the structure of E-**2** that seems to be important for ascertainment of the influence of apical substituent stereochemistry and electronic properties on geometrical features of atrane cage. Here we report on the synthesis and structure of E-N(CH<sub>2</sub>CH<sub>2</sub>O)<sub>3</sub>GeC(Br)=C(Br)Ph (**E-2**).

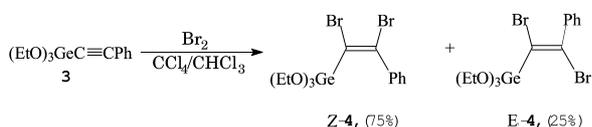
## Results and Discussion

(Triethoxygermyl)phenylacetylene (**3**), not described before, was obtained as shown in Scheme 2 in 94% yield.



To the best of our knowledge, no example of the bromination reaction of R<sub>3</sub>GeC≡CPh-type compounds was reported earlier in the literature, and only few brominations of silylsubstituted alkynes have been studied [5]. The stereochemistry of the dibromoalkenes obtained was not the subject of these investigations. Only in the case of Me<sub>3</sub>SiC≡CSiMe<sub>3</sub> the product of the reaction with bromine was assigned a *trans*-configuration [5c]. As to AlkC≡CAr, most of these compounds react with bromine in chloroalkane solution under kinetic control to give mixtures of *cis*- and *trans*-dibromoalkene derivatives, the latter considerably prevailing [6]. A literature data analysis led us to assume that the *trans*-isomer of (EtO)<sub>3</sub>GeC(Br)=C(Br)Ph (**E-4**), the precursor of the targeted E-N(CH<sub>2</sub>CH<sub>2</sub>O)<sub>3</sub>GeC(Br)=C(Br)Ph (**E-2**), can also be prepared by the action of bromine on (phenylacetylenyl)triethoxygermane (**3**).

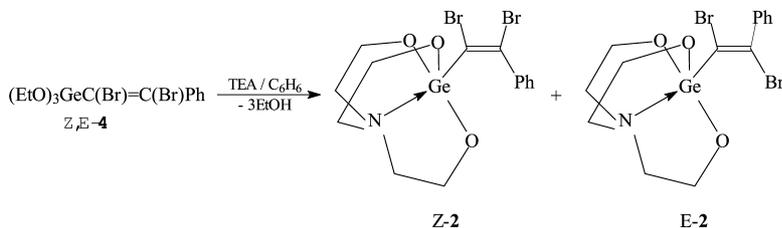
With bromine in CHCl<sub>3</sub>/CCl<sub>4</sub> solution, compound **3** affords a mixture of *Z*- and *E*-isomers of **4** in good yield (Scheme 3).



Scheme 3.

No decomposition products have been detected and the ratio of stereoisomers is about *Z*/*E* = 3/1 (from <sup>1</sup>H NMR data).

Treatment of this mixture of *Z*,*E*-isomers of **4** with an equivalent amount of triethanolamine (TEA) according to standard procedures [2] gives a mixture



Scheme 4.

of germatranes **Z-2** and **E-2** in high yield in a similar ratio (Scheme 4). We succeeded in separating the two isomeric products by crystallization from hot toluene. A white precipitate containing mainly the *Z-2* isomer was obtained, while the *E-2* isomer could be isolated in 16% yield as a pure solid after adding pentane to the filtrate.

<sup>1</sup>H and <sup>13</sup>C NMR spectra of **2-4** are consistent with the suggested structures. In the <sup>1</sup>H NMR spectra of germatranes **Z-2** and **E-2**, signals of the methylene protons of the atrane skeleton appear as a set of two pseudo-triplets, forming an AA'XX' spin system. This pattern is a general feature of the atrane framework for a variety of metallatranes. The δ <sup>1</sup>H values (CDCl<sub>3</sub>) of the OCH<sub>2</sub> and NCH<sub>2</sub> protons of the atrane skeleton in **Z-2** are shifted to higher field by 0.38 and 0.21 ppm, respectively, as compared to the related germatrane **E-2**. Similarly, the δ <sup>1</sup>H values (CDCl<sub>3</sub>) of the OCH<sub>2</sub> and CH<sub>3</sub> protons of the ethoxy groups in **Z-4** are shifted to higher field by 0.35 and 0.24 ppm, respectively, as compared to **E-4**. In accordance with results of the X-ray diffraction study for **E-2** (below) and **Z-2** [4] as well as with quantum chemical calculations for the geometry of **Z-2** and **Z-4** (below), the phenyl group is in a steric proximity to the methylene group in the *Z*-isomer, in contrast to the situation in the *E*-isomer. Thus, the shortest distance between one of the protons of the OCH<sub>2</sub> group in germatrane **Z-2** and the center of the phenyl ring is about 2.5 Å, while in **E-2** it is more than 7 Å (X-ray data). It appears that the ring current influence leads to high field shifts of the signals of the freely rotating N(CH<sub>2</sub>CH<sub>2</sub>O)<sub>3</sub>Ge and (CH<sub>3</sub>CH<sub>2</sub>O)<sub>3</sub>Ge groups. Previously such high field shifts of the signals of the 9-exo-R-group hydrogen atoms in chromium tricarbonyl complexes of 9-substituted fluorenes were observed in "collision complexes" with benzene-d<sub>6</sub> (the so called ASIS-effect) [7a]. The same phenomenon has also been observed in the <sup>1</sup>H NMR spectra of germatranes in benzene-d<sub>6</sub> [7b] and has been explained in terms of the formation of a charge-transfer complex between germatranes and C<sub>6</sub>D<sub>6</sub>. Thus, the presence of

Table 1. Crystal data, data collection, structure solution and refinement parameters for E-2.

Empirical formula	C <sub>14</sub> H <sub>17</sub> Br <sub>2</sub> GeNO <sub>3</sub>
Formula weight	479.70
Crystal size [mm]	0.72 × 0.33 × 0.21
Crystal system	monoclinic
Space group	<i>P</i> 2 <sub>1</sub> , <i>Z</i> = 2
Unit cell dimensions [Å]	<i>a</i> = 7.0106(9) Å <i>b</i> = 15.816(3) Å <i>c</i> = 7.2960(9) Å $\beta$ = 98.01(1)°
Volume [Å <sup>3</sup> ]	801.1(2)
Density (calculated), [g cm <sup>-3</sup> ]	1.989
Absorption coefficient [mm <sup>-1</sup> ]	6.908
F(000)	468
Diffractometer	Stoe IPDS II
Temperature [K]	193(2)
Radiation ( $\lambda$ , Å)	0.71073
Scan mode	$\omega$
$\Theta$ -Range [deg]	2.58 to 25.00
Index ranges	$-8 \leq h \leq 8$ , $-18 \leq k \leq 16$ , $-8 \leq l \leq 8$
Reflections collected	5739
Independent reflections	2505
Solution method	Direct methods [17]
Refinement method	Full-matrix least-squares on F <sup>2</sup> [18]
Data / restraints / parameters	2505 / 1 / 191
Goodness-of-fit on F <sup>2</sup>	1.063
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> (all data)	0.0366, 0.0923
Largest diff. peak and hole, [e / Å <sup>-3</sup> ]	0.522 and -0.660

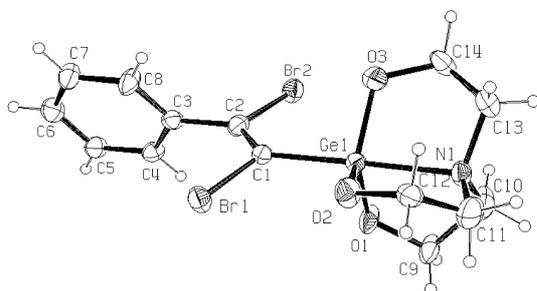


Fig. 1. Molecular structure of E-2.

these high field shifts in the spectra of compounds **2** and **4** can serve as an additional evidence for the *cis*-structure of these dibromides. It should be noted that  $\delta^{13}\text{C}$  values of the corresponding atrane skeleton carbons are practically the same for both isomers.

The crystal and molecular structure of E-2 was studied by X-ray analysis in this work, following the recent investigation of Z-2 [4]. To the best of our knowledge, compounds Z-2 and E-2 are the first Z,E-pair of isomers of 1-alkenylgermatranes which have been

Table 2. Selected bond lengths (Å) for E-2.

N(1)–Ge(1)	2.167(6)	C(5)–C(6)	1.40(1)
O(1)–Ge(1)	1.788(5)	C(6)–C(7)	1.39(1)
O(2)–Ge(1)	1.792(5)	C(7)–C(8)	1.38(1)
O(3)–Ge(1)	1.780(5)	C(9)–O(1)	1.426(9)
C(1)–C(2)	1.331(9)	C(9)–C(10)	1.57(1)
C(1)–Br(1)	1.905(7)	C(10)–N(1)	1.48(1)
C(1)–Ge(1)	1.995(6)	C(11)–N(1)	1.44(1)
C(2)–C(3)	1.483(9)	C(11)–C(12)	1.51(1)
C(2)–Br(2)	1.904(7)	C(12)–O(2)	1.413(9)
C(3)–C(8)	1.37(1)	C(13)–C(14)	1.47(1)
C(3)–C(4)	1.399(9)	C(13)–N(1)	1.52(1)
C(4)–C(5)	1.37(1)	C(14)–O(3)	1.442(9)

Table 3. Selected bond angles (deg) for E-2.

O(1)–C(9)–C(10)	108.9(6)	O(3)–Ge(1)–O(2)	113.3(3)
N(1)–C(10)–C(9)	106.4(7)	O(1)–Ge(1)–O(2)	117.6(3)
N(1)–C(11)–C(12)	108.0(7)	O(3)–Ge(1)–C(1)	97.0(2)
O(2)–C(12)–C(11)	110.8(7)	O(1)–Ge(1)–C(1)	93.8(2)
C(14)–C(13)–N(1)	107.2(6)	O(2)–Ge(1)–C(1)	97.5(3)
O(3)–C(14)–C(13)	110.5(6)	O(3)–Ge(1)–N(1)	83.9(2)
C(11)–N(1)–C(10)	117.2(8)	O(1)–Ge(1)–N(1)	84.2(2)
C(11)–N(1)–C(13)	112.8(7)	O(2)–Ge(1)–N(1)	83.8(3)
C(10)–N(1)–C(13)	110.9(7)	C(1)–Ge(1)–N(1)	178.0(3)
C(11)–N(1)–Ge(1)	105.3(5)	C(2)–C(1)–Br(1)	116.3(5)
C(10)–N(1)–Ge(1)	104.5(4)	C(2)–C(1)–Ge(1)	127.7(5)
C(13)–N(1)–Ge(1)	104.7(4)	Br(1)–C(1)–Ge(1)	115.9(3)
C(9)–O(1)–Ge(1)	118.4(4)	C(1)–C(2)–C(3)	128.2(6)
C(12)–O(2)–Ge(1)	116.6(5)	C(1)–C(2)–Br(2)	119.0(5)
C(14)–O(3)–Ge(1)	116.4(5)	C(3)–C(2)–Br(2)	112.7(5)
O(3)–Ge(1)–O(1)	125.8(3)		

structurally characterized. Moreover, scanning of the Cambridge Structural Database (Ver. 5.22) [8] shows that no molecular structures of a pair of *cis*- and *trans*-isomers containing a (Br)C=C(Br) fragment have been documented.

The molecular structure of E-2 is shown in Figure 1. Table 1 summarizes crystal data as well as details of the data collection and the structural refinement; important bond lengths and angles are given in Tables 2 and 3. The coordination polyhedron of the germanium atom in E-2 is a distorted trigonal bipyramid with the N(1) and C(1) atoms in the axial positions and the three oxygen atoms in equatorial sites. This is similar to the geometry found previously for Z-2 [4]. The germanium atom is displaced by 0.19 Å (for E-2; 0.20 Å for Z-2) from the plane defined by the three equatorial oxygen atoms towards the carbon atom. The N–Ge–C(1) angle is almost linear (178.0(3)° for E-2 and 178.0(7)° for Z-2). The Ge–C(1) distance observed in E-2 [1.995(6) Å] is slightly longer than that in Z-2 [1.98(2) Å] while the Ge–N bond in E-2 [2.167(6) Å] is significantly shorter than that in Z-2 [2.23(1) Å]. The Ge–N distance in E-2 lies within the typical range for germa-

tranes [2.081(5)–2.32(1) Å] [9,10] and clearly verifies the existence of the Ge–N transannular bond. The environment at the nitrogen atom is approximately tetrahedral with C–N–C and C–N–Ge angles ranging between 104.5(4)° and 117.2(8)°. The nitrogen atom is displaced by 0.38 Å from the plane defined by the three carbon atoms towards the germanium atom. The latter value for E-2 is essentially greater as that for Z-2 (0.34 Å). All five-membered rings of the atrane skeleton adopt an “envelope”-like conformation; for E-2 all carbon atoms in the  $\alpha$ -positions to the nitrogen atom occupy “flap” sites, while the C- $\beta$  atoms form the base of an envelope plane. On the contrary, for Z-2 C- $\beta$  atoms are in “flap” positions while C- $\alpha$  atoms are in the base of an envelope plane.

Considering compounds **2** as derivatives of *cis*- and *trans*-dibromoethylene, we should note a slight lengthening of the double C(1)=C(2) bond from Z-2 (1.30(2) Å) [4] to E-2 (1.331(9) Å). The C=C bond in E-2 is notably longer than that in the closely related *trans*-dibromides (PPh<sub>4</sub>[Cl<sub>4</sub>W(Ph–C≡C–CBr=CBr–Ph)] – 1.26(2) Å, and in Ph–CBr=CBr–NO<sub>2</sub> – 1.20(2) Å [11a,b], and close to that previously found for *trans*-Ph–CBr=CBr–Ph – 1.32(4) Å [11c]. The C(2)–C(3) bond length in E-2 (1.483(9) Å) is considerably shorter than that in Z-2 (1.53(2) Å) [4]. The other key geometrical parameters of these fragments are very close for E-2 and Z-2. Deviations of the C, Ge, and Br atoms from a mean plane formed by the substituted double bond (Chart 1) are less than 0.06 Å for both molecules. The phenyl ring is not coplanar with the double bond C(1)=C(2) in both E-2 and Z-2 [4]. Recently, the same feature was found for Ph–CBr=CBr–NO<sub>2</sub> [11b].

In order to get a better understanding of the *cis*-, *trans*-product ratio in our bromination reactions we have performed DFT calculations on compounds **2** and **4** up to the PBE level of theory [14]. Selected calculated geometrical parameters (Chart 1) are listed in Table 4.

Geometry optimization of E-2 and Z-2 leads to structural parameters which are in good agreement with the X-ray data. However, the calculated values of the Ge–N distances for these compounds are somewhat longer than that found in the solid state. Explanation of this disagreement is the weakness of the transannular bond in germatranes, which are exposed to crystal field effects in solid state [3b]. The elongation of the Ge–O and Ge–C bonds in E-2 and Z-2 in comparison with the same bonds in tetracoordinated germanium derivatives

Table 4. Calculated bond lengths (Å) for E-2, Z-2, E-4, Z-4.

	E-2	Z-2	E-4	Z-4
N–Ge	2.350	2.350	–	–
O–Ge (average)	1.831	1.833	1.791	1.790
C(1)–Ge(1)	1.989	1.994	1.970	1.971
C(1)–C(2)	1.342	1.345	1.345	1.348
C(1)–Br(1)	1.932	1.916	1.924	1.914
C(2)–C(3)	1.475	1.476	1.472	1.473
C(2)–Br(2)	1.947	1.941	1.945	1.933

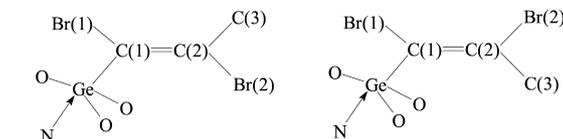


Chart 1.

E-4 and Z-4 is in accordance with a theory of “hypervalent compounds” [12]. These results demonstrate that the employed computational method affords quite reliable and reasonable data for the germanium derivatives in question. In both cases (for **2** and **4**) the calculated energy of the Z-isomer is lower than that of the E-isomer (1.31 and 2.05 kcal/mol, respectively). Therefore, the formation of Z-isomers in both bromination reactions is the thermodynamically favoured process.

Bianchini *et al.* proposed a reaction profile for the electrophilic bromination reactions of alkylaryl-acetylenes [6b]. We have adopted this profile for our compounds and carried out the optimization of the structures of the reagents, the final products and the intermediates formed during the reaction process according to this mechanism. Table 5 summarizes differences between the sum of zero-point energies of the products (separate Br<sub>2</sub> and Z-2 or Z-4 adducts) and species corresponding to each step of the bromination reaction scheme (Figure 2). Step I corresponds to a separate molecule of acetylene and two molecules of bromine. The next stage (step II) is a  $\pi$ -complex (R<sub>3</sub>GeC≡CPh·Br<sub>2</sub>) and one separate molecule of bromine, which is engaged in another  $\pi$ -complex (step III: R<sub>3</sub>GeC≡CPh·2Br<sub>2</sub>) during the reaction. It should be noted that the formation of the bridged bromirenium ion and Br<sub>3</sub><sup>−</sup> (step IVb) as intermedi-

Table 5.  $\Delta E$  values (kcal/mol) between the sum of zero-point energies of the products (separate Br<sub>2</sub> and Z-2 or Z-4 adducts) and species corresponding to each step of the bromination reaction scheme.

Step according to reaction scheme	I	II	III	IVa	IVb
Bromination of <b>1</b>	28.61	21.69	10.96	81.64	96.50
Bromination of <b>3</b>	27.21	21.68	14.75	94.48	112.98

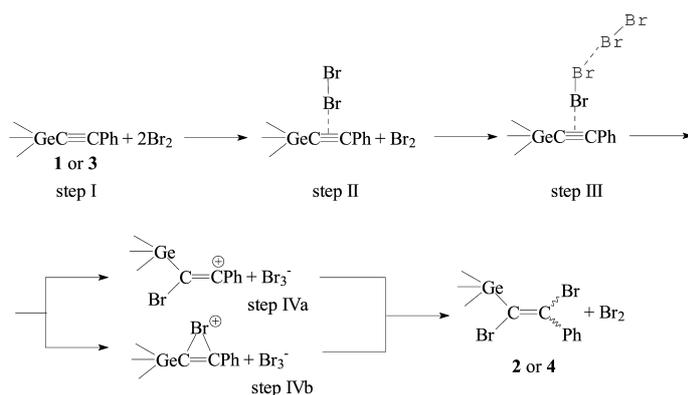


Fig. 2. Reaction scheme of the electrophilic addition of bromine to alkynes [6b].

ates is unfavourable in comparison to the formation of an open-ion intermediate (R<sub>3</sub>Ge(Br)C=C<sup>+</sup>Ph) and Br<sub>3</sub><sup>-</sup> (step IVa) for both reactions (bromination of **1** and **3**). Thus, no stereoselectivity of the bromine addition to the triple bond is to be expected in both cases. The formation of only *Z*-**2** in the reaction of **1** with bromine can be attributed to the steric hindrance for Br<sub>3</sub><sup>-</sup> in the attack of the open vinyl cation from the opposite site. This steric crowding is appreciably less in the bromine addition to **3** where the *E*-**4** adduct is formed together with the *Z*-**4** adduct.

However, final elucidation of the bromination reaction pathways of element substituted alkynes requires additional theoretical and experimental investigations. Further experiments with R<sub>3</sub>MC≡CPh are in progress.

## Experimental Section

All solvents were dried by standard methods and distilled prior to use. All manipulations were carried out in an argon atmosphere using standard Schlenk techniques; Cl<sub>3</sub>GeC≡CPh was prepared according to the literature [13]. NMR spectra were recorded at 25 °C on Bruker AC 300 and Varian VXR 400 spectrometers, CDCl<sub>3</sub> was used as solvent and as internal deuterium lock. Chemical shifts in the <sup>1</sup>H and <sup>13</sup>C NMR spectra are given in ppm relative to internal TMS. Elemental analyses were carried out by the Microanalytical Laboratory of the Chemistry Department of Moscow State University. Mass spectra (EI-MS) were recorded on a VARIAN CH-7a instrument using electron impact ionisation at 70 eV; all assignments are made with reference to the most abundant isotopes.

### (Phenylacetylenyl)triethoxygermane (**3**)

A solution of 15 ml (10.9 g, 0.108 mol) of Et<sub>3</sub>N in 130 ml of EtOH was added dropwise to a stirred solution of Cl<sub>3</sub>GeC≡CPh (10.0 g, 0.036 mol) in ether (100 ml) at 0 °C.

The reaction mixture was allowed to warm to room temperature and then refluxed for 3 h. After all volatile materials were removed *in vacuo*, benzene was added to the residue. The precipitate of Et<sub>3</sub>N·HCl was filtered off. Removal of the solvent from the filtrate followed by distillation of the liquid residue gave 10.6 g (94%) of **3** as a colorless liquid.

B. p. 110–112 °C/1 Torr. – *n*<sub>D</sub><sup>20</sup> 1.5045. – <sup>1</sup>H NMR (400 MHz): δ = 1.23 (t, 9H, CH<sub>3</sub>), 3.91 (q, 6H, OCH<sub>2</sub>); 7.20–7.33 (m, 3H, aromatic protons), 7.43–7.48 (m, 2H, aromatic protons). – <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz): δ = 18.44 (CH<sub>3</sub>), 60.71 (OCH<sub>2</sub>), 80.06 (CGe), 106.45 (PhC), 120.60, 128.27, 129.83, 132.30 (aromatic carbons). – C<sub>14</sub>H<sub>20</sub>GeO<sub>3</sub> (308.90): calcd. C 54.44, H 6.53, Ge 23.50; found C 54.28, H 6.31, Ge 23.83.

### Bromination of (phenylacetylenyl)triethoxygermane (**3**). Synthesis of 1,2-dibromo-1-(triethoxygermyl)-2-phenylethene (**4**).

A solution of bromine (1.55 g, 0.0097 mol) in 15 ml of CCl<sub>4</sub> was dropped slowly with stirring to a solution of (phenylacetylenyl)triethoxygermane (**3**) (3.0 g, 0.0097 mol) in 15 ml of chloroform. Subsequent stirring of the reaction mixture for 4 h at room temperature led to a gradual disappearance of the red color of Br<sub>2</sub>. Solvents were removed *in vacuo*, and distillation of the liquid residue under reduced pressure afforded 3.28 g (72% yield) of 1,2-dibromo-1-(triethoxygermyl)-2-phenylethene (**4**). Compound (**4**) was obtained as a mixture of *Z*- and *E*-isomers with a 75:25 ratio (according to <sup>1</sup>H-NMR) and used without further purification.

B. p. 144–145°C/1 Torr. – <sup>1</sup>H NMR (300 MHz): δ = 1.08 (t, 9H, CH<sub>3</sub>, major isomer), 1.32 (t, 9H, CH<sub>3</sub>, minor isomer), 3.68 (q, 6H, OCH<sub>2</sub>, major isomer), 4.03 (q, 6H, OCH<sub>2</sub>, minor isomer), 7.34–7.43 (m, 10H, C<sub>6</sub>H<sub>5</sub>, both isomers). – <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz): δ = 18.37 (CH<sub>3</sub>, major isomer), 18.68 (CH<sub>3</sub>, minor isomer), 60.67 (OCH<sub>2</sub>, major isomer), 61.04 (OCH<sub>2</sub>, minor isomer), 118.01, 128.16, 128.37, 128.98, 129.19, 129.94, 130.88, 139.77, 151.27, 152.79 (aro-

matic C and C=C for both isomers, two other carbon atoms were not found in the spectra).

#### *E-1,2-Dibromo-1-germatranyl-2-phenylethene (E-2)*

Triethanolamine (0.57 g, 0.0039 mol) was added dropwise to a stirred solution of **4** (1.81 g, 0.0039 mol) in 15 ml of benzene. Immediate precipitation of a white solid was observed. The reaction mixture was stirred at room temperature for 4 h, then the solvent was removed *in vacuo*. The white solid (1.76 g, 95%) obtained was found to contain a mixture of isomeric dibromides Z,E-2 in *ca.* 3:1 ratio (<sup>1</sup>H NMR). Recrystallization of the solid from toluene (15 ml) afforded mainly the Z-2 isomer (1.02 g, 55% yield). Pentane (5 ml) was added to the filtrate. A white precipitate was collected by filtration, washed with pentane and dried *in vacuo*. The white solid (0.30 g, 16% yield) was the almost pure E-2 isomer.

<sup>1</sup>H NMR (300 MHz): δ = 2.91 (t, 6H, NCH<sub>2</sub>), 3.91 (t, 6H, OCH<sub>2</sub>), 7.25–7.41 (m, 5H, C<sub>6</sub>H<sub>5</sub>). – <sup>13</sup>C {<sup>1</sup>H} NMR (75 MHz): δ = 52.63 (NCH<sub>2</sub>), 57.18 (OCH<sub>2</sub>), 122.79, 128.03, 128.37, 128.68, 129.13, 141.18 (aromatic C and C=C). – MS (EI, 70 eV): *m/z* (%) = 479 (5) [M<sup>+</sup>], 400 (69) [M<sup>+</sup>-Br], 370 (10) [M<sup>+</sup>-Br-CH<sub>2</sub>O], 220 (100) [M<sup>+</sup>-CBrCBrC<sub>6</sub>H<sub>5</sub>], 190 (33) [M<sup>+</sup>-CBrCBrC<sub>6</sub>H<sub>5</sub>-CH<sub>2</sub>O], 180 (10) [C<sub>8</sub>H<sub>5</sub>Br<sup>+</sup>], 160 (16) [M<sup>+</sup>-CBrCBrC<sub>6</sub>H<sub>5</sub>-2CH<sub>2</sub>O], 146 (49) [M<sup>+</sup>-CBrCBrC<sub>6</sub>H<sub>5</sub>-CH<sub>2</sub>O-CH<sub>2</sub>CH<sub>2</sub>O]. – C<sub>14</sub>H<sub>17</sub>Br<sub>2</sub>GeNO<sub>3</sub> (479.69): calcd. C 35.05, H 3.57, N 2.92; found C 35.38, H 4.23, N 2.67.

#### *X-ray single crystal structure determination*

All non-hydrogen atoms of E-2 were refined anisotropically; the hydrogen atoms were placed in calculated positions and refined using a riding model. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publi-

cation no. CCDC 196476. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code + 44(1223)336-033; E-mail: deposit@ccdc.cam.ac.uk].

#### *Calculations*

The nonempirical generalized gradient approximation (GGA) for the exchange-correlation functional of Perdew *et al.* was employed [14]. Calculations were performed using the program "PRIRODA" developed by Laikov, which implements an economical computational procedure [15]. Large orbital basis sets of contracted Gaussian-type functions of the size (5s1p):[3s1p] for H, (11s6p2d):[4s3p2d] for C, (11s6p2d):[4s3p2d] for N, (11s6p2d):[4s3p2d] for O, (19s16p9d):[6s5p3d] for Ge, and (19s16p9d):[6s5p3d] for Br were used. Full geometry optimization was performed for a number of structures followed by vibrational frequency calculation using analytical first and second derivatives. Each structure has been characterized by the vibrational analysis. We have estimated the energy of the bromirenium ion as the energy of the structure with equivalent distances between the bromine atom and each carbon atom of the triple bond. We calculated a set of such structures with this distance ranging from 1.75 to 2.5 Å and the structure with the lowest energy was found at a distance of 2.15 Å for both **1** and **3**. The present theoretical method has given useful results in the organometallic chemistry of Si, Cr, Ti, Zr, Sb, and Bi [16].

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