Synthesis, Structure and Chemical Transformations of Ethynylgermatranes

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Ethynylgermatranes have been prepared from monosubstituted acetylenes by a three-step synthesis without isolation of the hydrolytically unstable intermediate chlorogermanes and ethoxygermanes. Boiling an equimolar mixture of tetrachlorogermane Cl_4Ge, acetylene RC≡CH and triethylamine in hexane leads to germylation of the C_{sp}–H bond and the formation of ethynyl-substituted trichlorogermanes. Subsequent alkoxylation of chlorogermanes by ethanol in the presence of triethylamine affords triethoxygermanes that then take part in transalkoxylation with triethanolamine to give ethynylgermatranes. The molecular structures of all ethynylgermatranes and the hexacarbonyldicobalt complex of 1-heptynylgermatrane have been determined by X-ray crystallography.

Introduction

Derivatives of pentacoordinate germanium are the subject of considerable current research activity, particularly germatranes that contain an intramolecular N→Ge bond.[1−4] Investigations have focused on the relationship between the transannular N→Ge bond length and such factors as the character of the substituent at the germanium atom, the atrane skeleton structure, as well as crystal packing (crystal density, Z of unit cell, etc). However, the scope of their synthesis is limited. The few reported examples of ethynylgermatranes (unsubstituted ethynylgermatrane, 1-octynylgermatrane, and phenylethynylgermatranes)[5−8] were obtained by the "stannyl" method, by treating ethynyltrichlorogermanes $RC{\equiv}CGeCl_3$ with the tris(trialkylstannyl) ether of triethanolamine or by addition of triethanolamine to $RC{\equiv}CGeCl_3$ in the presence of triethylamine; phenylethynylgermatrane has also been prepared by the reaction of bromogermatrane with lithium phenylacetylenide.[5] The C≡C triple bond in ethynylgermatranes should allow various chemical transformations; however, only the bromination of phenylethynylgermatrane by NBS and bromine has been studied.[5] To the best of our knowledge, only the molecular structures of 1-phenylethynylgermatrane, and its chloroform solvate, and 4-fluorophenylethynylgermatrane have been determined by X-ray crystallography.[5,6,8] In this paper we focus on the synthesis of ethynylgermatranes via germylation of monosubstituted acetylenes by tetrachlorogermane in the presence of an organic base. Various chemical transformations of the acetylene fragment have been carried out, including complexation with octacarbonyldicobalt, [2+3] dipolar cycloaddition, and electrophilic substitution. The molecular structures of all synthesized ethynylgermatranes as well as of the hexacarbonyldicobalt complex of 1-heptynylgermatrane are also reported.

Results and Discussion

The ethynylgermatranes **4a−d** were prepared from monosubstituted acetylenes **1a−d** by a three-step synthesis without isolation of the hydrolytically unstable intermediate chlorogermanes **2a−d** and ethoxygermanes **3a−d**. Boiling an equimolar mixture of tetrachlorogermane $GeCl_4$, acetylene RC≡CH and triethylamine in hexane[9,10] leads to germylation of the $C_{sp}-H$ bond and formation of ethynyl-substituted trichlorogermanes **2a−d**. Subsequent alkoxylation of chlorogermanes by ethanol in the presence of triethylamine affords triethoxygermanes **3a−d** which are then involved in transalkoxylation with triethanolamine to give ethynylgermatranes **4a−d** (Scheme 1). The yield of germatranes **4a−d** depends on the structure of the substituent R. The highest yield was observed for (trimethylsilyl)ethynylgermatrane (**4d**) (85%); with 1-heptynylgermatrane (**4a**) and (1-cyclohex-1-enyl)ethynylgermatrane (**4b**) the yields were 48 and 55%, respectively. The lowest yield was for 3-methoxypropyn-1-ylgermatrane (**4c**) (12%). Our attempts to prepare germatrane from methyl propiolate failed, since tetrachlorogermane acts as a Lewis acid in the reaction with HC≡CCOOMe to form 1,3,5-tris(methoxycarbonyl)benzene by [2+2+2] cycloaddition (Scheme 2).

As with other acetylene derivatives,[11−14] 1-heptynylgermatrane (**4a**) easily reacts with octacarbonyldicobalt in hexane (20 min at −5 °C). The hexacarbonyldicobalt complex of 1-heptynylgermatrane **5**, isolated in almost quantitative yield (93%) (Scheme 1), is stable in the solid state but com-

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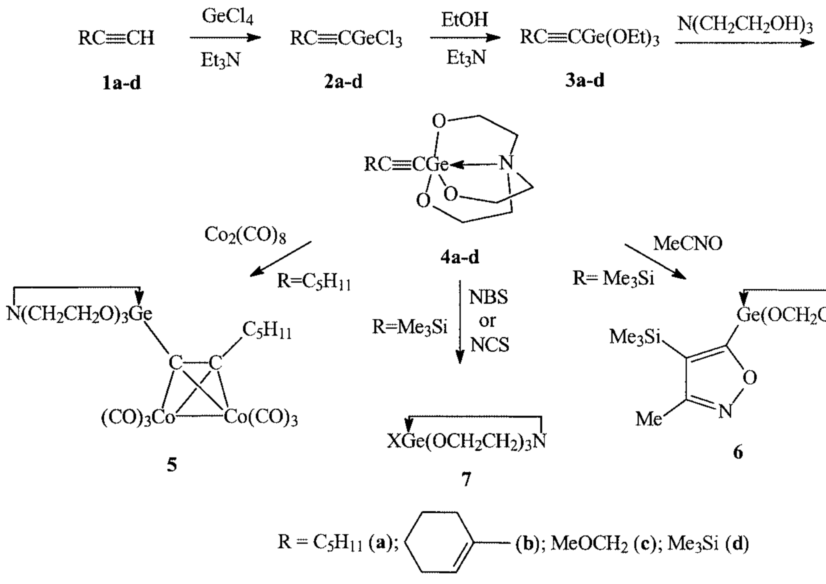
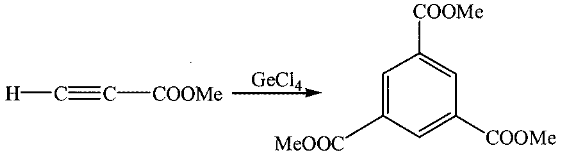


Scheme 1. Synthesis and transformations of ethynylgermatranes



Scheme 2. [2+2+2] Cyclization of methyl propiolate in the presence of tetrachlorogermane

pletely decomposes in organic solvents (even in nonpolar ones such as hexane or benzene) after 2−3 h.

[2+3] Dipolar cycloaddition of acetonitrile oxide to the C≡C triple bonds of heptynylgermatrane (**4a**) and (trimethylsilyl)ethynylgermatrane (**4d**) has been investigated. Acetonitrile oxide, prepared in situ by the Mukaiyama−Hoshito method,[15] reacts with **4d** regioselectively to give only one of the two possible regioisomeric products, i.e. 5-germatranylisoxazole (**6**) in 75% yield. Conversely, for **4a** only a trace amount of the isoxazole derivative was detected by GC-mass spectrometry (Scheme 1).

The reaction of **4d** with NCS and NBS in DMF proceeds with cleavage of the Ge−C bond and formation of chloro- and bromogermatranes **7** (X = Cl, Br).[16] Our attempts to desilylate **4d** by different desilylation agents (Bu_4NF/Et_2O, $K_2CO_3/MeOH$, Amberlyst 15/THF, TsOH/MeOH) failed to cleave the Si−C bond, and so the initial germatrane **4d** was recovered.

The structures of the germatranes were confirmed by ^1H and ^{13}C NMR spectroscopy (Table 1). The ^1H spectra of

Table 1. ^1H and ^{13}C NMR spectroscopic data of ethynylgermatranes and their derivatives

Compound	δ ^1H, ppm			δ ^{13}C, ppm			
	CH_2N	CH_2O	R	CH_2N	CH_2O	GeCCR	R
4a	2.84 (t, J = 5.6 Hz, 6 H)	3.82 (t, J = 5.6 Hz, 6 H)	0.82 (t, J = 6 Hz, 3 H), 1.17−1.65 (m, 5 H), 2.20 (t, J = 6.4 Hz, 3 H)	51.5	56.6	80.5, 101.7	13.7, 19.5, 22.0, 28.2, 31.1
4b	2.87 (t, J = 5.6 Hz, 6 H)	3.84 (t, J = 5.6 Hz, 6 H)	1.45−1.60 (m, 4 H), 1.96−2.06 (m, 2 H), 2.1−2.2 (m, 2 H), 6.21 (sept, J = 1.8 Hz, 1 H)	51.3	56.5	87.0, 101.5	21.3, 22.1, 25.5, 28.8, 120.2, 136.2
4c	2.90 (t, J = 5.6 Hz, 6 H)	3.85 (t, J = 5.6 Hz, 6 H)	3.37 (s, 3 H), 4.12 (s, 2 H)	52.4	57.6	92.2, 96.5	58.4, 61.1
4d	2.87 (t, J = 5.6 Hz, 6 H)	3.84 (t, J = 5.6 Hz, 6 H)	0.15 (s, 9 H)	51.3	56.7	106.9, 108.3	−0.1
5	2.87 (t, J = 5.6 Hz, 6 H)	3.81 (t, J = 5.6 Hz, 6 H)	0.90 (t, J = 7 Hz, 3 H), 1.3−1.5 (m, 5 H), 1.6−1.7 (m, 3 H)	52.6	57.0	80.2, 108.5 201.0 (CO), 206.7 (CO)	14.0, 22.4, 31.4, 31.5, 34.6
6	2.89 (t, J = 5.6 Hz, 6 H)	3.83 (t, J = 5.6 Hz, 6 H)	0.34 (s, 9 H), 2.41 (s, 3 H, Me-C)	51.5	56.4	119.3, 128.8, 12.1 (Me), 161.1 (C=N)	−1.1

all germatrane derivatives (**4−6**) are characterized by two triplets of CH_2N (δ = 2.84−2.90 ppm) and CH_2O (δ = 3.81−3.85 ppm) groups. The signals of carbon atoms in the atrane fragment are in the δ = 51.3−52.6 and 56.4−57.6 ppm regions of the ^{13}C NMR spectra, and the signals of carbonyl-ligand carbon atoms in **5** are shifted to low field (δ = 201.0 and 206.7 ppm). As reported previously,[17] complexation of the C≡C triple bond does not strongly affect the carbon atoms' chemical shifts.

Molecular Structures of the Germatranes

Molecular structure data have been reported for more than 60 germatranes and their structural analogues.[2,18] However, only three of these structures contain an ethynylgermatrane fragment (phenylethynylgermatrane, and its $CHCl_3$ solvate, and 4-fluorophenylethynyl analogue[5,6,8]). These compounds are characterized by transannular N→Ge distances of 2.178, 2.160, and 2.175 Å, respectively, which are short in comparison with those in other alkyl-, alkenyl-, and arylgermatranes (2.20−2.24 Å). To further investigate the influence of various acetylene substituents RC≡C on the transannular N→Ge bond length the molecular structures of ethynylgermatranes **4a−d** and of the hexacarbonyldicobalt complex **5** have been determined by X-ray crystallography.

The germanium atom of germatranes **4a−d** and **5** has the typical atrane trigonal-bipyramidal geometry with nitrogen and carbon atoms in apical positions and three equatorial oxygen atoms. The axial nitrogen atom is pyramidalized so that its lone pair points towards the germanium atom. Selected bond lengths and angles are presented in Table 2. The transannular N→Ge bond length in ethynylgermatranes **4** varies between 2.202(3) Å (for the disordered germatrane **4a**) and 2.115 Å [for 3-methoxypropyn-1-ylgermatrane, (**4c**)]. The last value is one of the shortest distances detected for germatranes with Ge−C bonds. The shorter intramolecular bond length of 2.108 Å was found only for trifluoromethylgermatrane.[19] The Ge−C bonds in germatranes **4** lie between 1.905 and 1.962 Å. The longest Ge−C distance is observed in 3-methoxypropyn-1-ylgermatrane (**4c**) (Figure 1). This indicates that the decrease of the N→Ge bond in the fragment N→Ge−C is accompanied by elongation of the Ge−C bond.

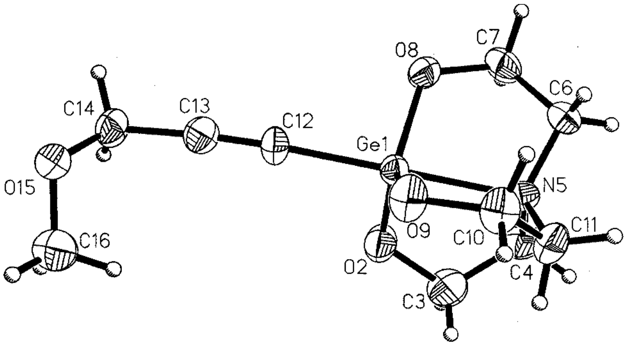


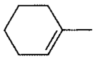
Figure 1. Molecular structure of 3-methoxypropyn-1-ylgermatrane (**4c**)

The unit cell of germatrane **4a** contains two independent molecules; one of which is strongly disordered due to the pentyl substituent. Disorder is also observed in the crystal structure of the cyclohexenylethynyl derivative **4b**. The usual disorder for the atrane system occurs for C-4, C-6, and C-11 atoms. Carbon atom C-17 in the six-membered cycle is also disordered. The occupation *g* factor for disordered atoms is 0.5.

Crystals of (trimethylsilyl)ethynylgermatrane (**4d**) were obtained as a solvate with toluene. To prevent toluene evaporating rapidly from the crystal surface, which would destroy the mono crystal of **4d** within 1 h, the X-ray analysis was carried out under an epoxide glue film. The unit cell contains four molecules of germatrane **4d** and two of toluene.

Cobalt complex **5** (Figure 2) crystallized from light petroleum as scarlet prisms. The six-coordinate cobalt atoms have a pseudotetrahedral polyhedron. The Co−Co bond distance is 2.487(1) Å. The dihedral angle between planes C-12, C-13, Co-1 and C-12, C-13, Co-2 is 84.7(1)°. Molecules of complex **5** are in special positions: atoms Ge-1,

Table 2. Selected bond lengths and angles of ethynylgermatranes [**4** $RC{\equiv}CGe(OCH_2CH_2)_3N$] and the dicobalhexacarbonyl complex

Compound	R	r (N→Ge), Å	r (Ge – C), Å	r (C≡C), Å	∠ NGeC, deg.	∠ GeCC, deg.
4a[a]	C_5H_{11}	2.176(3)	1.914(4)	1.185(5)	178.4(2)	178.7(4)
		2.202(3)	1.908(4)	1.184(5)	179.0(2)	177.5(4)
4b		2.176(4)	1.905(6)	1.194(7)	179.1(2)	172.9(6)
4c	CH_2OMe	2.115(7)	1.962(9)	1.199(13)	179.9(3)	173.7(9)
4d	Me_3Si (PhMe)	2.164(7)	1.922(9)	1.185(13)	178.1(3)	179.2(10)
5		2.195(5)	1.926(6)	1.325(8)	176.1(3)	139.6(5)

[a] For two independent molecules.

N-5, C-12, C-13, C-14, C-15, C-16, C-17 lie in crystallographic plane *m*. However, the molecules are not symmetrical; therefore, disorder occurs in the crystal structure. The occupation *g* factor for disordered atoms is 0.5. According to the literature data, complex **5** is the first example of a cluster structure containing a germatranyl fragment.

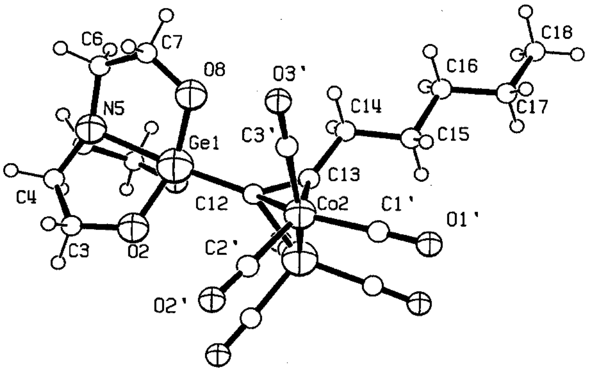


Figure 2. Molecular structure of the hexacarbonyldicobalt complex of 1-heptynylgermatrane (**5**)

Conclusions

Ethynylgermatranes have been prepared from monosubstituted acetylenes by a three-step synthesis from initial acetylenes RC≡CH. With methyl propiolate, tetrachlorogermane acts as Lewis acid to form 1,3,5-tri(methoxycarbonyl)benzene by [2+2+2] cycloaddition. 1-Heptynylgermatrane easily reacts with octacarbonyldicobalt in hexane, almost quantitatively, yielding the hexacarbonyldicobalt complex. The reaction of trimethylsilylethynylgermatrane with NCS and NBS in DMF proceeds with cleavage of the Ge−C bond and formation of chloro- and bromogermatranes. The transannular N→Ge bond lengths (2.115−2.202 Å) of the germatranes are strongly influenced by the RC≡C substituent, with 3-methoxypropyn-1-ylgermatrane having the shortest bond (2.115 Å).

Experimental Section

Instrumental: ^1H and ^{13}C NMR spectra were recorded with a Varian Mercury 200 spectrometer at 200.06 and 50.31 MHz, respectively, at 303 K. The chemical shifts are given relative to TMS from the solvent impurity ($CHCl_3$ in $CDCl_3$) signal (δ_H = 7.25 ppm). Mass spectra were recorded with a Hewlett Packard apparatus (70 eV). The melting points were determined with a "Digital melting point analyser" (Fisher) and are uncorrected. 1-Heptyne, 1-ethynylcyclohexene, methyl 2-propynyl ether, trimethylsilylacetylene, triethanolamine and octacarbonyldicobalt [$Co_2(CO)_8$] were purchased from Aldrich.

Table 3. Main X-ray crystallographic details for **4a−d**

	4a	**4b**	**4c**	**4d**	**5**
Crystal shape	prism	plate	needle	prism	prism
Crystal colour	colourless	colourless	colourless	colourless	purple
Crystal size (mm^3)	0.23 × 0.25 × 0.30	0.05 × 0.15 × 0.45	0.07 × 0.10 × 0.55	0.25 × 0.43 × 0.45	0.25 × 0.33 × 0.37
Chemical formula	$C_{13}H_{23}GeNO_3$	$C_{14}H_{21}GeNO_3$	$C_{10}H_{17}GeNO_4$	$C_{11}H_{21}GeNO_3Si\cdot(C_7H_8)_{0.5}$	$C_{19}H_{23}Co_2GeNO_9$
Molecular weight	313.92	323.91	287.84	315.97 + 0.5·92.15	599.83
Crystal system	monoclinic	orthorhombic	orthorhombic	orthorhombic	orthorhombic
Space group	$P2_1/c$	*Pbca*	$Pna2_1$	$P2_12_12_1$	*Pnma*
a (Å)	10.4850(3)	11.2133(2)	13.151(8)	6.7256(1)	16.1811(5)
b (Å)	20.2849(5)	11.8230(2)	9.824(4)	11.6160(2)	10.6651(4)
c (Å)	14.0695(4)	22.4887(4)	9.107(4)	28.2106(8)	14.0561(5)
α(°)	90	90	90	90	90
β(°)	93.448(1)	90	90	90	90
γ(°)	90	90	90	90	90
Volume ($Å^3$)	2986.98(14)	2981.44(9)	1176.6(9)	2203.94(8)	2425.7(1)
Z	8	8	4	4	4
d_{calcd}, (g/cm^3)	1.396	1.443	1.625	1.091	1.642
Absorption coefficient (mm^{-1})	2.052	2.058	2.603	1.450	2.629
F(000)	1312	1344	592	756	1208
Diffractometer used	Nonius KappaCCD	Nonius KappaCCD	Syntex $P2_1$	Nonius KappaCCD	Nonius KappaCCD
Radiation, λ (Å)	Mo-K_α (0.71073)	Mo-K_α (0.71073)	Mo-K_α (0.71073)	Mo-K_α (0.71073)	Mo-K_α (0.71073)
Temperature (K)	298(2)	298(2)	293(2)	298(2)	298(2)
Total reflections	11246	7482	1372	3758	5178
Independent reflections	7356	4348	1372	2305	2894
Used reflections	4444	3092	1155	1730	1986
Threshold expression	$I > 3.0\sigma(I)$	$I > 2.0\sigma(I)$	$I > 2.0\sigma(I)$	$I > 3.0\sigma(I)$	$I > 2.0\sigma(I)$
R(int)	0.033	0.035	–	0.039	0.036
$2\theta_{max}$(°)	55.0	60.0	55.0	50.0	55.0
Index ranges	$-13 \le h \le 13$	$-15 \le h \le 15$	$0 \le h \le 17$	$-7 \le h \le 7$	$-20 \le h \le 21$
	$-26 \le k \le 26$	$-16 \le k \le 16$	$0 \le k \le 12$	$-13 \le k \le 13$	$-13 \le k \le 13$
	$-18 \le l \le 18$	$-31 \le l \le 31$	$0 \le l \le 11$	$-33 \le l \le 33$	$-18 \le l \le 18$
Refined parameters	337	208	144	182	203
R-factor	0.0498	0.0589	0.0438	0.0671	0.0447
R(F) for all data	0.0870	0.0916	0.0535	0.0910	0.0742
w*R*(F^2) for all data	0.1281	0.1838	0.1169	0.1952	0.1145
$\Delta\rho_{max}$ ($e/Å^3$)	0.978	0.423	0.713	0.809	0.514
Deposition number CCDC	185235	186941	185234	186942	185863

General Method for Synthesis of Ethynylgermatranes (4a−d): A solution of tetrachlorogermane (4.28 g, 0.02 mol) in dry hexane (10 mL) was added dropwise to a mixture of acetylene **1** (0.02 mol) and triethylamine (0.022 mol) in dry hexane (50 mL). The reaction mixture was boiled under reflux for 2 h and filtered from triethylamine hydrochloride. A mixture of ethanol (0.07 mol) and triethylamine (0.07 mol) was added to the filtrate. The resultant triethylamine hydrochloride precipitate was filtered off after stirring for 2 h at room temperature. The filtrate was then added to a solution of triethanolamine (0.02 mol) in hexane (10 mL). The transalkoxylation reaction was exothermic. After cooling to room temperature the resultant ethynylgermatrane (**4**) precipitate was filtered off and recrystallized from toluene. The products were obtained as white crystalline solids.

For X-ray analysis crystals of germatranes **4a−d** were grown from toluene. Crystals of the hexacarbonyldicobalt complex were obtained by rapid crystallization from dry light petroleum. The crystal structures were solved by direct methods[20−22] and refined with the help of computer programs.[23,24] The main crystallographic data of the germatranes are given in Table 3.

1-Heptynylgermatrane (4a): Yield: 3.02 g (48%). M.p. 89 °C. MS: m/z = 315 [M^+]. $C_{13}H_{23}GeNO_3$ (313.94): calcd. C 49.74, H 7.38, N 4.46; found C 49.51, H 7.30, N 4.45.

(1-Cyclohex-1-enyl)ethynylgermatrane (4b): Yield: 3.56 g (55%). M.p. 211−212 °C. MS: m/z = 325 [M^+]. $C_{14}H_{21}GeNO_3$ (323.93): calcd. C 51.91, H 6.53, N 4.32; found C 51.83, H 6.58, N 4.36.

(3-Methoxypropyn-1-yl)germatrane (4c): Yield: 0.69 g (12%). M.p. 193−194 °C. MS: m/z = 289 [M^+]. $C_{10}H_{17}GeNO_4$ (287.86): calcd. C 41.73, H 5.95, N 4.86; found C 41.77, H 5.99, N 4.84.

(Trimethylsilyl)ethynylgermatrane (4d): Yield: 5.44 g (86%). M.p. 237 °C. MS: m/z = 317 [M^+]. ^{29}Si NMR (CDCl$_3$): $\delta = -18.6$ ppm. $C_{11}H_{21}GeNO_3Si$ (315.98): calcd. C 41.81, H 6.70, N 4.43; found C 41.76, H 6.63, N 4.44.

Hexacarbonyldicobalt Complex of 1-Heptynylgermatrane (5): A solution of octacarbonyldicobalt (0.342 g, 1 mmol) in hexane (10 mL) was added to a solution of 1-heptynylgermatrane (**4a**, 0.314 g, 1 mmol) in hexane (10 mL) at −5 °C. The reaction mixture was stirred 20 min, then hexane was removed and the crude product obtained was purified on silica gel using CH_2Cl_2 as eluent (R_f = 0.55). Yield: 0.56 g (93%). M.p. 102−104 °C. $C_{19}H_{23}Co_2GeNO_9$ (599.46): calcd. C 38.07, H 3.87, N 2.34; found C 38.06, H 3.79, N 2.29.

3-Methyl-4-trimethylsilyl-5-germatranylisoxazole (6): Nitroethane (0.005 mol) and triethylamine (two drops) in dry benzene (20 mL) were added dropwise to a mixture of trimethylsilylethynylgermatrane **4d** (1.58 g, 0.005 mol) and phenylisocyanate (0.01 mol). The mixture was heated for 5 h at 70−80 °C. After cooling to room temperature, diphenylurea was filtered off, the solvent evaporated, and the resultant residue purified on silica gel using dichloromethane as eluent (R_f = 0.45). Yield 1.39 g (75%). M.p. 115 °C. MS: m/z = 374 [M^+]. ^{29}Si NMR (CDCl$_3$): $\delta = -6.4$ ppm. $C_{13}H_{24}GeN_2O_4Si$ (373.04): calcd. C 41.86, H 6.48, N 7.51; found C 41.81, H 6.50, N 7.54.

Method for Synthesis of 1,3,5-Tris(methoxycarbonyl)benzene: A solution of tetrachlorogermane (4.28 g, 0.02 mol) in dry hexane (10 mL) was added dropwise to a mixture of methylpropiolate (1.68 g, 0.02 mol) and triethylamine (2.22 g, 0.022 mol) in dry hexane (50 mL). The reaction mixture was refluxed for 2 h and filtered from triethylamine hydrochloride. The crude product was purified on silica using hexane as eluent. Yield: 52%. The structure was confirmed by MS-GC and ^{1}H NMR spectroscopy.

Reaction of (Trimethylsilyl)ethynylgermatrane with NCS and NBS: NCS or NBS (1 mmol) was added portion-wise, during 1 h at room temperature, to a solution of **4d** (0.315 g, 1 mmol) in DMF (10 mL). After the usual workup the crude product **7** was purified by flash chromatography using ethyl acetate/hexane (5:1) as eluent. Yield: 87−90%.

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