

Synthesis and chemistry of aryloxygermylene-amine complexes

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Abstract

The synthesis of stable monomeric dimesityloxygermylene-amine $(\text{MesO})_2\text{Ge-NR}_3$ [$\text{NR}_3 = \text{Et}_2\text{NH}$, $(\text{C}_6\text{H}_{11})_2\text{NH}$, Et_3N , dabco, tmeda] and chloromesityloxygermylene-amine $\text{MesO}(\text{Cl})\text{Ge-tmeda}$ complexes is presented. All compounds have been fully characterized by spectroscopic methods. The insertion reaction of $(\text{MesO})_2\text{Ge-tmeda}$ **1a** with dimethyl disulfide, bis(trimethylsilyl)peroxide and iodomethane is reported. Cycloaddition reactions with dimethylbutadiene are especially effective without any activation and with dimethyl acetylenedicarboxylate led selectively to compounds **7** and **8**. In the latter case, the transient formation of a germirene has been evidenced by a trapping reaction. The structures of **3**, **7** and **8** were determined by single-crystal X-ray diffraction.
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1. Introduction

In organometallic chemistry, metalla-alkynes such as $\text{M}_{14}\equiv\text{C}$ ($\text{M}_{14} = \text{Si}, \text{Ge}, \text{Sn}, \text{Pb}$) are of great interest: first the study of a new bond involving carbon remains an attractive challenge, and also these compounds have potential applications such as precursors of organometallic polymers or as new ligands for transition metal complexes with possible application in catalysis.

Until now mainly symmetric dimetalla-alkynes $\text{M}_{14}\equiv\text{M}_{14}$ have been described [1–4]. In this field, Sekiguchi et al. published recently the first compound, characterized by X-ray analysis, with a silicon-silicon triple bond (bond order: 2.62) [1a], which was an unresolved challenge for more than 20 years. Analogs of alkynes with multiple bonds germanium–germanium [2a], tin–tin [3] and lead–lead [4], have already been proposed by Power et al. but in both cases (Ge and Sn) the length values of the metal–

metal bond are in the same range as for a typical double bond. Especially in the case of the diplumbyne, this compound is often described as a diplumbylene due to the bond, which is longer than a single lead–lead bond. Recently, Tokitoh et al. synthesized another digermine with a Ge–Ge bond order also between 2 and 3 [2d].

By contrast, dissymmetric metalla-alkynes $\text{M}_{14}\equiv\text{C}$ have not been stabilized until now and only two transient derivatives have been described and evidenced by trapping reactions: our group published the first germa-alkyne $\text{Ge}\equiv\text{C}$ – obtained from a diazogermylene [5]. A similar reaction was used by Kira and co-workers to obtain a transient stanna-alkyne $\text{Sn}\equiv\text{C}$ – from a diazostannylene [6]. Our objective is to increase the stability of metalla-alkynes by varying the ligands bonded to the metal and to the carbon.

Apeloig and Karni, using “ab initio” calculations, have shown that an oxygen atom connected to the silicon atom will stabilize a sila-alkyne particularly in relation to its silylidene isomer [7]. Taking into account of these conclusions we planed to prepare an aryloxydiazogermylene $\text{ArO-Ge}(\text{CN}_2)\text{R}'$, a potential precursor of an aryloxygerma-alkyne $\text{ArO-Ge}\equiv\text{C-R}'$. The mesityloxy group (2,4,6-trimethyl-

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phenyloxy) appeared to us to be a convenient ligand due to the presence of the oxygen atom and its steric bulk.

We present in this paper the synthesis of the dimesityloxygermylene and the chloromesityloxygermylene as precursors for the mesityloxy(trimethylsilyl)diazogermylene. Many aspects of the chemistry of these new germanium (II) compounds are also presented.

2. Results and discussion

Cyclic [8] or non-cyclic [9] oxygenated germynes have been known for more than 30 years. These species possess dioxygenated structures but also monooxygenated ones such as RO–Ge–Y with Y = halogen [8a,9a,9b,9h,10].

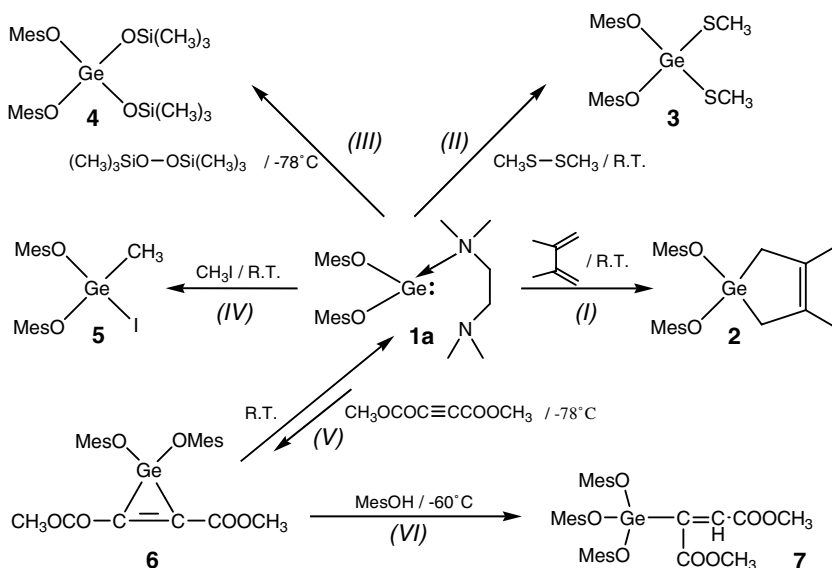
Most of these compounds are mainly characterized by classic reactions in the field of germylene chemistry (insertion or cycloaddition reactions). Only a few have been studied by X-ray analysis in a monomeric form: Acac–Ge–I (acac = acetylacetonate) [10], Ge(OCH₂CH₂NMe₂)₂ [9g], Ge(OCH₂CH₂NMe₂)Cl [9h], Ge(OCH₂CH₂NMe₂)-OCOCH₃ [9h]; in all these structures a supplementary coordination of an oxygen or a nitrogen atom of the ligand to the germanium is evidenced in the solid state. In the case of non-coordinated germynes, the structure of Ge[OC(*t*-Bu)₃]₂ (**A**) is revealed [9d]. For aryloxygermylenes only some derivatives have been structurally described until now: (4-Me-2,6-*t*-Bu₂C₆H₃-O)₂Ge (**B**) synthesized by Lappert et al. [9c], (2,6-Ph₂C₆H₃-O)₂Ge (**C**) [9j] and (2,3,5,6-Ph₄C₆H-O)₂Ge (**D**) described by Weinert et al. [9j], (C₆H₃-2,6-(C₆H₃-2,6-*i*-Pr₃)₂)₂Ge (**E**) recently isolated by Power et al. [9k].

Comparing Ge–O bond lengths between the alkyoxygermylene **A** [Ge–O: 1.896(6); 1.832(1) Å] and the aryloxygermylenes **B** (1.802(8); 1.812(7) Å); **C** (1.817(1); 1.822(1) Å); **D** (1.826(1); 1.827(1) Å) and **E** (1.8296(14) Å) gives some information on the electronic environment of

the germanium atom in such germynes. The Ge–O bonds in aryloxygermylenes **B**, **C**, **D** and **E** are appreciably shorter than in the alkyoxygermylene **A**, indicating a back-donation from the oxygen to the germanium atom increasing the nucleophilic character of the germanium. Moreover, shorter Ge–O bonds must increase the ligand–ligand steric repulsion and explain the larger O–Ge–O bond angle in **B** [92.0(4)°], **C** [92.10(5)°], **D** [91.09(7)°] and **E** [92.54(6)°] compared to **A** [85.9(4)°], enhancing the sp² character of the germanium atom in the aryloxy compounds.

The dimesityloxygermylene (MesO)₂Ge: (Mes = 2,4,6-trimethylphenyl) was synthesized in high yield by reaction between GeCl₂-dioxane and mesitol (2,4,6-trimethylphenol) in the presence of a secondary or tertiary amine. Using this method the germylene was obtained as a monomeric species complexed by one equivalent of amine. Recently, Oláh et al. [11] have demonstrated that germynes which possess electrophilic character can have strong interactions with hard Lewis bases such as amines. In our case, several secondary or tertiary amines (Et₂NH, (C₆H₁₁)₂NH, *i*-Pr₂NH, Et₃N, dabco, tmeda) were used, all leading to nearly quantitative yields. Only diisopropylamine gives a different result with formation of the already reported dimeric form of the dimesityloxygermylene [9j]. Indeed, the recent attempts of Weinert et al. to synthesize dimesityloxygermylene by a protonolysis reaction between Lappert's germylene Ge[N(SiMe₃)₂]₂ and mesitol (MesOH) led to a dimeric structure [Ge(OMes)₂]₂ in the solid state [9j].

Complexes of dimesityloxygermylene with amines are waxy materials impossible to crystallize but were obtained in high purity suitable for the study of their reactivity. For this purpose, the (MesO)₂Ge–tmeda complex (**1a**) was preferably used for the chemical characterization of the monomeric dimesityloxygermylene.



Scheme 1.

Classic reactions were performed from **1a** and 2,3-dimethyl-1,3-butadiene to lead to the germacyclopentene **2** or with dimethyl disulfide with formation of the corresponding adduct **3** (reactions I and II, Scheme 1). In reaction I, which occurs at room temperature without any activation, dimesityloxygermylene-amine complexes show higher reactivity than usually observed with germylenes (for example see [8f]). The disulfide adduct **3** (reaction II) was also characterized by X-ray diffraction analysis (Fig. 1). Ge–O (1.760 and 1.766 Å) and Ge–S bond lengths (2.160 and 2.193 Å) are in the range of the standard values for germanium (IV) compounds. Due to the difference in size of the oxygen and sulfur atoms the O–Ge–O angle (101.82°) is logically sharper than the S–Ge–S angle (113.34°). We can also see that **3** is tetracoordinated in the solid state and there is no interaction of the germanium with any heteroatom from another molecule. Similar reactions could be expected with peroxides, and in fact these reactions depend on the peroxide used. No reaction was observed with di-*tert*-butyl peroxide but on the other hand **1a** reacts easily at –78 °C with bis(trimethylsilyl)peroxide to lead to the expected tetragermoxane **4** (reaction III). Germylene **1a** can also undergo another type of reaction by insertion into the carbon–iodine bond of methyl iodide (reaction IV). The iodogermane **5** was easily obtained and fully characterized by spectroscopic methods.

More complex was the reaction V between **1a** and dimethyl acetylenedicarboxylate. The addition was effected at –78 °C. Surprisingly the expected germirene **6** was not stable at room temperature decomposing to the two starting materials in accordance with a cycloreversion reaction, already known in germirene chemistry [12a]. The low thermal stability of **6** probably arises from both the electron-rich germanium in **1a** and the presence of electron withdrawing groups on the acetylenic compound. Indeed

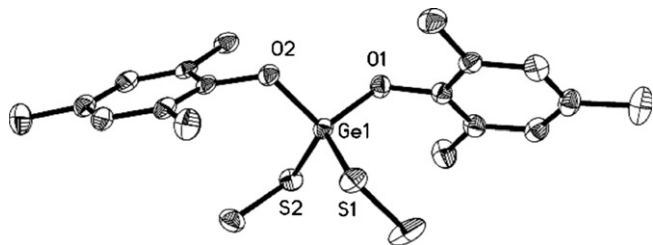


Fig. 1. Molecular structure of **3** in the solid state. Thermal ellipsoids are at the 50% probability level. Hydrogen atoms are omitted for clarity.

most of the known stable three membered rings of this class of compounds have less electronegative or even electropositive substituents on the carbon atoms [12]. Formation of **6** at low temperature (–60 °C) was evidenced by its quenching, at this temperature, by one equivalent of mesitol leading to the ring-opened alkenylgermane **7**. In this last reaction, the two *Z* and *E* stereoisomers of **7** were obtained in different amounts. Despite steric considerations the *Z* isomer was the major one (*Z*: 65%; *E*: 35%). This surprising result can be understood from the X-ray structure of **7**. In the *Z* isomer there is a strong coordination between the oxygen of the carbonyl of the β-ester group and the germanium atom. A similar interaction probably occurs to obtain the *Z* configuration of the carbanionic intermediate which is generated during the nucleophilic opening of **6** by the mesitol (Scheme 2).

From the X-ray structure of the *Z* isomer of **7** (Fig. 2), we can observe that three bonds around the germanium atom (Ge–O5, Ge–O7, Ge–C1) are in equatorial positions (sum of angles: 352°) and the angle between Ge–O3 and Ge–O6 bonds (173°) is in accordance with an almost apical

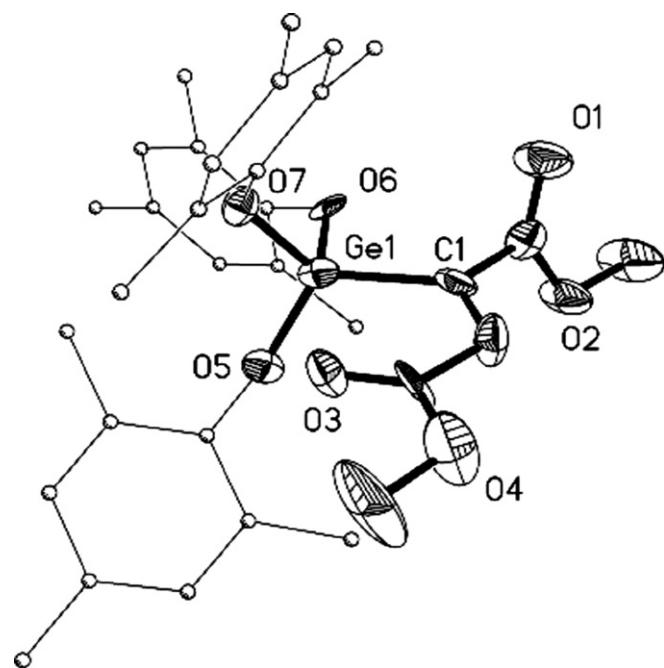
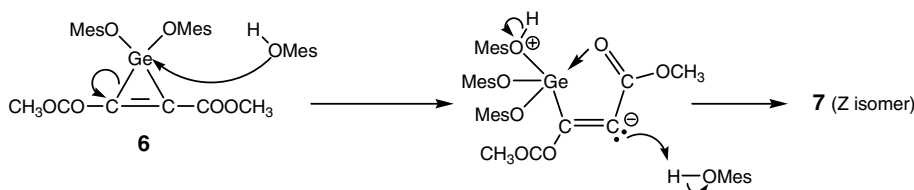
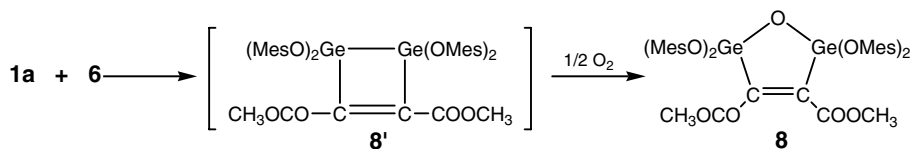


Fig. 2. Molecular structure of **7** in the solid state. Thermal ellipsoids are at the 50% probability level. Hydrogen atoms are omitted for clarity.



Scheme 2.



Scheme 3.

position in a trigonal bipyramidal structure. The existence of a strong coordination can also explain the Ge–O3 distance (2.403 Å), much shorter than the sum of the Van der Waals radii of the germanium and oxygen atoms (2.15 and 1.50 Å, respectively) [13]. Additionally with the acetylenic compound, a minor side-reaction was observed which led to the formation of the transient digermacyclobutene **8'** (Scheme 3). This can be explained by a reaction of the germirene **6** with a second equivalent of **1a**. In accordance with the chemistry of α -dimetallated four membered rings [14], the digermacyclobutene possesses a very highly reactive Ge–Ge bond which can explain its rapid oxidation leading to the 1,3-digermaoxolene **8** which was isolated in trace amounts.

It was not possible to purify **8** but single crystals could be selected from the mixture and characterized by X-ray analysis. From the structure (Fig. 3) we can observe again longer intracyclic germanium–oxygen bond lengths

(1.756(2) and 1.772(2) Å) than the aryloxy exocyclic Ge–O bond lengths (1.745(3), 1.746(3), 1.748(3), 1.752(3) Å), a difference already noticed in oxygenated germlyenes (vide supra). The intracyclic C=C double bond has a classic value (1.326(5) Å). Another feature of the structure of **8** concerns the two ester groups which show a surprising disorder. The ring is almost planar, indeed the dihedral angles C37–C38–Ge2–O1 and C38–C37–Ge1–O1 are -1.3° and 1.0° , respectively.

As stated in Section 1, the next step for the synthesis of a diazogermylene requires the halogenation of the germanium. For the synthesis of halogermylenes the disproportionation reaction between a symmetric disubstituted germlyene R₂Ge: and a dihalogermylene is commonly used and usually these reactions are nearly quantitative. In our case, reaction of one equivalent of **1a** and GeCl₂-dioxane led quantitatively to the chloromesityloxygermylene **9** as a stoichiometric complex with the tetramethylethylenediamine (Scheme 4).

Like **1**, **9** appears as a waxy material which can not be crystallized. Nevertheless it was obtained in a high degree of purity and unambiguously characterized by NMR spectroscopies and mass spectrometry. The synthesis of the dimesityloxy(trimethylsilyl)diazogermylene MesOGeC(N₂)-SiMe₃ from **9** and the study of its photolysis are now in progress.

3. Conclusion

The method reported allows the synthesis of monomeric mesityloxygermylenes complexed with amines. These germlyenes which are stabilized by complexation show an enhanced reactivity compared to most classic germlyenes: they react readily without activation with 2,3-dimethyl-1,3-butadiene and undergo addition to an acetylenic compound leading to a germirene derivative characterized by a quenching reaction with mesitol. Like in the case of silylenes [11] this high reactivity of our germlyenes is triggered

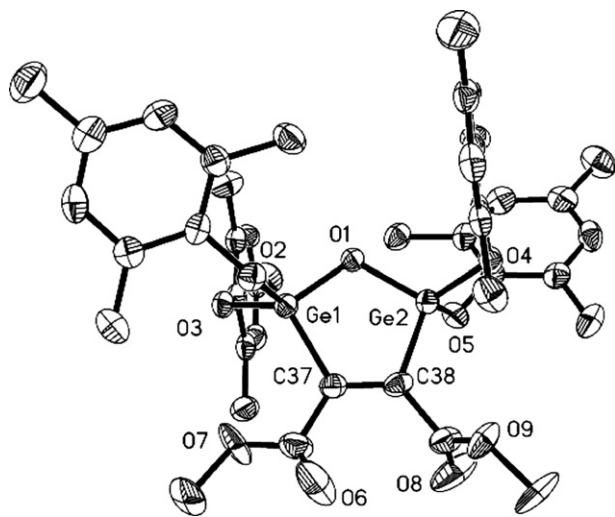
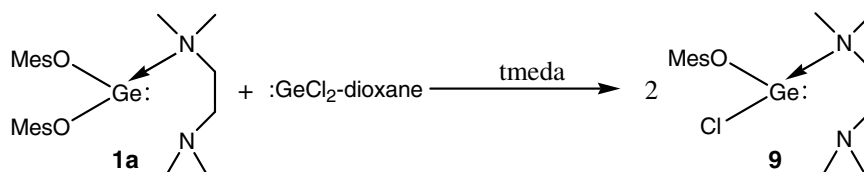


Fig. 3. Molecular structure of **8** in the solid state. Thermal ellipsoids are at the 50% probability level. Hydrogen atoms are omitted for clarity.



Scheme 4.

by the presence of Lewis bases (amines) and the back donation of oxygen atoms which decrease the electron deficiency of the germanium empty 4p orbital and increase the energy of the germanium lone pair.

4. Experimental

4.1. General

All experiments were carried out under an argon atmosphere using Schlenk and vacuum line techniques or a glove box. All the solvents were dried by appropriate procedures and freshly distilled before use. ^1H , ^{13}C , ^{29}Si NMR spectra were recorded on Bruker AC 200 and on Bruker Avance 300; 400 and 500 spectrometers, chemical shifts (δ , ppm) are relative to SiMe_4 (TMS). EI spectra were obtained at 70 eV on a Hewlett–Packard 5989 instrument and samples were contained in glass capillaries under argon. Melting points were determined on a digital melting point Electrothermal. Complex GeCl_2 -dioxane was prepared accordingly to the literature procedure.

4.2. Synthesis of the dimesityloxygermylene-amine complexes **1a–e**

To a stirred solution of dichlorogermylene-dioxane (2.32 g, 9.98 mmol) in 30 mL of toluene, was added 2 equiv. of 2,4,6-trimethylphenol (2.72 g, 19.96 mmol) in 20 mL of toluene, then four equivalents of the desired amine [**a**: tetramethylethylenediamine (tmeda); **b**: triethylamine; **c**: diethylamine; **d**: dicyclohexylamine; **e**: 1,4-diazabicyclo[2.2.2]octane (dabco)] was added dropwise (39.92 mmol). The reaction mixture was stirred for 16 h and the solid filtered off. The filtrate was evaporated to dryness to lead to a waxy material.

1a: (92% yield); ^1H NMR (250.1 MHz, C_6D_6), δ (ppm): 2.05 [s, 12 H, CH_3 (tmeda)], 2.23 (s, 6H, *p*- CH_3), 2.37 [s, 4H, CH_2 (tmeda)], 2.40 (s, 12H, *o*- CH_3), 6.84 (s, 4H, *meta*-H); ^{13}C NMR (75.4 MHz, C_6D_6), δ (ppm): 19.81 (*o*- CH_3), 21.22 (*p*- CH_3), 44.98 [CH_3 (tmeda)], 55.74 [CH_2 (tmeda)], 128.41 (2,6-aryl-C), 130.19 (3,5-aryl-C), 138.32 (4-aryl-C), 154.80 (1-aryl-C); EI-MS (70 eV), m/z (%): 344 [(MesO) $_2\text{Ge}^+$, 20%], 209 [MesOGe $^+$, 31%], 119 [Mes $^+$, 100%]. **1b**: (57% yield); ^1H NMR (250.1 MHz, C_6D_6), δ (ppm): 0.69 [t, $^3J_{\text{H/H}} = 7.5$ Hz, 9H, $\text{CH}_3(\text{Et}_3\text{N})$], 2.20 (s, 6H, *p*- CH_3), 2.42 [q, $^3J_{\text{H/H}} = 7.5$ Hz, 6H, $\text{CH}_2(\text{Et}_3\text{N})$], 2.51 (s, 12H, *o*- CH_3), 6.82 (s, 4H, *meta*-H); ^{13}C NMR (75.4 MHz, C_6D_6), δ (ppm): 16.51 (CH_3 , Et_3N), 20.26(*o*- CH_3), 20.38 (*p*- CH_3), 23.07 (CH_2 , Et_3N), 128.59 (2,6-aryl-C), 129.18 (3,5-aryl-C), 132.01 (4-aryl-C), 152.93 (1-aryl-C); EI-MS (70 eV), m/z (%): 209 [MesOGe $^+$, 10%], 135 [MesO $^+$, 100%]. **1c**: (97%); ^1H NMR (250.1 MHz, C_6D_6), δ (ppm): 0.68 [t, $^3J_{\text{H/H}} = 7.3$ Hz, 6H, $\text{CH}_3(\text{Et}_2\text{NH})$], 2.21 (s, 6H, *p*- CH_3), 2.38 (s, 12H, *o*- CH_3), 2.57 [q, $^3J_{\text{H/H}} = 7.3$ Hz, 4H, $\text{CH}_2(\text{Et}_2\text{NH})$], 6.84 (s, 4H, *meta*-H); ^{13}C NMR (75.4 MHz, C_6D_6), δ (ppm): 8.24

[CH_3 , (Et_2NH)], 20.24(*o*- CH_3), 20.89 (*p*- CH_3), 45.42 [CH_2 , (Et_2NH)], 128.48 (2,6-aryl-C), 129.61 (3,5-aryl-C), 137.82 (4-aryl-C), 153.62 (1-aryl-C); EI-MS (70 eV), m/z (%): 344 [(MesO) $_2\text{Ge}^+$, 10%], 209 [MesOGe $^+$, 20%], 119 [Mes $^+$, 100%]. **1d**: 49% yield; ^1H NMR (250.1 MHz, C_6D_6), δ (ppm): 2.20 (s, 6H, *p*- CH_3), 2.37 (s, 12H, *o*- CH_3), 6.80 (s, 4H, *meta*-H), 1.18 (br, 8H, 3,5- CH_2 -cyclohexylamine), 1.72 (br, 4H, 4- CH_2 -cyclohexylamine), 2.60 (br, 10H, $\text{CH}_2/2,6\text{-CH}_2$ -cyclohexylamine); ^{13}C NMR (75.4 MHz, C_6D_6), δ (ppm): 16.94 (*o*- CH_3), 20.32 (*p*- CH_3), 25.10 (3,5- CH_2 -cyclohexylamine), 26.35 (4- CH_2 -cyclohexylamine), 34.39 (2,6- CH_2 -cyclohexylamine), 52.79 (1- CH -cyclohexylamine), 129.02 (3,5-aryl-C); 129.63 (2,6-aryl-C); 131.94 (4-aryl-C); 151.35 (1-aryl-C). EI-MS (70 eV), m/z (%): 344 [(MesO) $_2\text{Ge}^+$, 20%], 135 [MesO $^+$, 100%]. **1e**: (51% yield); ^1H NMR (250.1 MHz, C_6D_6), δ (ppm): 2.22 (s, 6H, *p*- CH_3), 2.28 (s, 12H, *o*- CH_3), 2.33 [s, 12H, CH_2 (dabco)], 6.82 (s, 4H, *meta*-H); ^{13}C NMR (75.4 MHz, C_6D_6), δ (ppm): 17.17 (*o*- CH_3), 20.33 (*p*- CH_3), 45.06 [CH_2 (dabco)], 129.31 (3,5-aryl-C), 129.47 (2,6-aryl-C), 131.07 (4-aryl-C), 150.85 (1-aryl-C). EI-MS (70 eV), m/z (%): 344 [(MesO) $_2\text{Ge}^+$, 13%], 135 [MesO $^+$, 100%].

4.3. Reaction of **1a** with 2,3-dimethyl-1,3-butadiene

To a stirred solution of **1a** (0.21 g, 0.46 mmol) in 2 mL of toluene, was added 15 equiv. of 2,3-dimethyl-1,3-butadiene (1.50 mL, 6.90 mmol). The reaction mixture was stirred for 2 h. Solvents were removed in vacuum and **2** was obtained as a white powder (17% yield); ^1H NMR (250.1 MHz, C_6D_6), δ (ppm): 1.37 (s, 6H, C- CH_3), 1.61 (s, 4H, CH_2), 2.17 (s, 6H, *p*- CH_3), 2.32 (s, 12H, *o*- CH_3), 6.79 (s, 4H, *meta*-H); ^{13}C NMR (75.4 MHz, C_6D_6), δ (ppm): 15.43 (C- CH_3), 16.99 (*o*- CH_3), 20.21 (*p*- CH_3), 23.08 (CH_2), 122.55 (C- CH_2), 128.83 (2,6-aryl-C), 129.14 (3,5-aryl-C), 130.40 (4-aryl-C), 150.26 (1-aryl-C). EI-MS (70 eV), m/z (%): 426 [M^+ , 2], 344 [(ArO) $_2\text{Ge}$, 6], 209 [ArOGe, 20], 119 [Mes, 100].

4.4. Reaction of **1a** with dimethyl disulfide

To a stirred solution of **1a** (1.50 g, 3.59 mmol) in 12.8 mL of toluene, was added dropwise one equivalent of dimethyl disulfide (0.32 mL, 3.59 mmol) at room temperature. The reaction mixture was stirred for 16 h. Solvents were removed in vacuum, and **3** as a white solid was recrystallized in diethyl ether. **3**: (32% yield); mp: 132° C; ^1H NMR (400.1 MHz, C_6D_6), δ (ppm): 1.72 (s, 6H, S- CH_3), 2.14 (s, 6H, *p*- CH_3), 2.43 (s, 12H, *o*- CH_3), 6.75 (s, 4H, *meta*-H); ^{13}C NMR (100.6 MHz, C_6D_6), δ (ppm): 9.35 (S- CH_3), 17.85 (*o*- CH_3), 20.73 (*p*- CH_3), 129.71 (3,5-aryl-C), 129.76 (2,6-aryl-C), 131.77 (4-aryl-C), 152.5 (1-aryl-C); EI-MS (70 eV), m/z (%): 438 [M^+ , 50], 303 [M^+ -ArO, 50], 135 [ArO, 100] $^+$. Single crystals suitable for X-ray analysis were obtained from diethyl ether at -6 °C.

4.5. Reaction of **1a** with bis(trimethylsilyl)peroxide

To a solution of **1a** (1.27 g, 2.90 mmol) in 10 mL of toluene, was added dropwise at $-78\text{ }^{\circ}\text{C}$ a solution of bis(trimethylsilyl)peroxide (1.62 g, 2.76 mmol) in 5 mL of pentane. The reaction mixture was allowed to warm up to room temperature and was stirred for 1 h more. Compound **4** was obtained as a waxy material (78% yield); ^1H NMR (500.13 MHz, C_6D_6), δ (ppm): 0.06 (s, 18H, SiMe_3), 2.10 (s, 6H, *p*- CH_3), 2.32 (s, 12H, *o*- CH_3), 6.71 (s, 4H, *meta*-H); ^{13}C NMR (100.61 MHz, C_6D_6), δ (ppm): 2.09 (OSiMe_3), 17.60 (*o*- CH_3), 20.85 (*p*- CH_3), 129.23 (3,5-aryl-C), 129.47 (2,6-aryl-C), 131.65 (4-aryl-C), 150.51 (1-aryl-C); ^{29}Si NMR (59.63 MHz, C_6D_6), δ (ppm): 15.93 (SiMe_3); EI-MS (70 eV), m/z (%): 522 [M^+ , 100], 386 [$\text{M}-\text{ArO}$, 90], 298 [$\text{M}-2\text{ArO}-\text{OSiMe}_3$, 50].

4.6. Reaction of **1a** with iodomethane

To a stirred solution of **1a** (0.21 g, 0.45 mmol) in 4 mL of toluene, was added dropwise 1 equivalent of iodomethane (0.03 mL, 0.45 mmol). The reaction mixture was stirred for 1.5 h. Solvents were removed in vacuum leading to **5** (82% yield); ^1H NMR (300.1 MHz, C_6D_6), δ (ppm): 0.52 (s, 3H, CH_3), 2.13 (s, 6H, *p*- CH_3), 2.23 (s, 12H, *o*- CH_3), 6.73 (s, 4H, *meta*-H); ^{13}C NMR (75.4 MHz, C_6D_6), δ (ppm): 15.43 (Me), 17.05(*o*- CH_3), 20.32 (*p*- CH_3), 128.93 (2,6-aryl-C), 129.32 (3,5-aryl-C), 131.05 (4-aryl-C), 151.10 (1-aryl-C); EI-MS (70 eV), m/z (%): 358 [$\text{M}-\text{I}$], 223 [$\text{M}-\text{I}-\text{ArO}$].

4.7. Reaction of **1a** with dimethyl acetylenedicarboxylate

To a stirred solution of **1a** (0.82 g, 1.78 mmol) in 5 mL of toluene, was added dropwise at $-78\text{ }^{\circ}\text{C}$ 1 equivalent of dimethyl acetylenedicarboxylate (0.25 mL, 1.78 mmol). Then a solution of 2,4,6-trimethylphenol (0.24 g, 1.78 mmol) in 5 mL of toluene was added at $-60\text{ }^{\circ}\text{C}$. The reaction mixture returned slowly to room temperature. Solvents were removed in vacuum, the compound **7** (*Z* isomer) was obtained by selective recrystallizations in *n*-pentane from the mixture of *Z* and *E* isomers. **7** (*Z* isomer): (21% yield); mp: $160\text{ }^{\circ}\text{C}$; ^1H NMR (300.13 MHz, C_6D_6), δ (ppm): 2.11 (s, 9H, *p*- CH_3), 2.38 (s, 18H, *o*- CH_3), 2.87 (s, 3H, COOMe), 3.32 (s, 3H, COOMe), 6.46 (s, 1H, $\text{CH}=\text{C}$), 6.70 (s, 6H, *meta*); ^{13}C NMR (75.4 MHz, C_6D_6), δ (ppm): 17.40 (*o*- CH_3), 20.33 (*p*- CH_3), 52.17 (COOMe), 52.58 (COOMe), 129.06 (3,5-aryl-C), 129.49 (2,6-aryl-C), 130.58 (4-aryl-C), 136.80 ($\text{C}=\text{CH}$), 146.00 (1-aryl-C), 151.99 ($\text{C}=\text{CH}$), 166.22 (COOMe), 166.62 (COOMe); EI-MS (70 eV), m/z (%): 622 [M^+ , 15], 487 [$\text{M}-\text{ArO}$, 100]; CI-MS (NH_3): 623 [MH^+]; 640 [$\text{M} + \text{NH}_4^+$]. Single crystals suitable for X-ray analysis were obtained from *n*-pentane at $-22\text{ }^{\circ}\text{C}$. **7** (*E* isomer): (12% yield); ^1H NMR (300.13 MHz, C_6D_6), δ (ppm): 2.06 (s, 9H, *p*- CH_3), 2.27 (s, 18H, *o*- CH_3), 3.00 (s,

3H, COOMe), 3.26 (s, 3H, COOMe), 6.64 (s, 6H, *meta*), 7.25 (s, 1H, $\text{CH}=\text{C}$); ^{13}C NMR (75.4 MHz, C_6D_6), δ (ppm): 17.15 (*o*- CH_3), 20.26 (*p*- CH_3), 51.51 (COOMe), 51.67 (COOMe), 129.31 (3,5-aryl-C), 129.03 (2,6-aryl-C), 131.47 (4-aryl-C), 143.25 ($\text{C}=\text{CH}$), 137.50 (1-aryl-C), 150.82 ($\text{C}=\text{CH}$), 163.61 (COOMe), 163.93 (COOMe).

4.8. Synthesis of the chloromesityloxygermylene-amine complex **9**

To a stirred solution of dichlorogermylene-dioxane (0.58 g, 2.50 mmol) in 10 mL of THF, was added 1 equivalent of **1a** (1.15 g, 2.50 mmol) in 10 mL of THF. The reaction mixture was stirred for 2 h. Solvents were removed in vacuum, and **9** was isolated as a waxy compound (91% yield); ^1H NMR (250.1 MHz, C_6D_6), δ (ppm): 2.20 (s, 3H, *p*- CH_3), 2.20 [s, 12H, CH_3 (tmeda)], 2.38 (s, 6H, *o*- CH_3), 2.87 [s, 4H, CH_2 (tmeda)], 6.80 (s, 2H, *meta*-H); ^{13}C NMR (75.4 MHz, C_6D_6), δ (ppm): 18.70 (*o*- CH_3), 20.36 (*p*- CH_3), 44.52 [CH_3 (tmeda)], 55.12 [CH_2 (tmeda)], 128.96 (2,6-aryl-C), 129.46 (3,5-aryl-C), 131.77 (4-aryl-C), 153.08 (1-aryl-C); EI-MS (70 eV), m/z (%): 244 [MesO-GeCl^+ , 15%], 135 [MesO^+ , 100%].

5. Crystal data for **3**, **7** and **8**

3: $\text{C}_{20}\text{H}_{28}\text{GeO}_2\text{S}_2$, $M = 437.13$, monoclinic, $P2_1/n$, $a = 6.95(2)\text{ \AA}$, $b = 15.75(4)\text{ \AA}$, $c = 19.26(5)\text{ \AA}$, $\beta = 92.35(6)^\circ$, $V = 2106(10)\text{ \AA}^3$, $Z = 4$, $T = 133(2)\text{ K}$. 11 552 reflections (4338 independent, $R_{\text{int}} = 0.0602$) were collected. Largest electron density residue: 0.650 e \AA^{-3} , R_1 (for $I > 2\sigma(I)$) = 0.0316 and $wR_2 = 0.0852$ (all data) with $R_1 = \sum |F_o| - |F_c| / \sum |F_o|$ and $wR_2 = (\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2)^{0.5}$.

7: $\text{C}_{33}\text{H}_{40}\text{GeO}_7$, $M = 621.24$, triclinic, $P\bar{1}$, $a = 11.258(4)\text{ \AA}$, $b = 11.634(4)\text{ \AA}$, $c = 13.549(4)\text{ \AA}$, $\alpha = 83.046(7)^\circ$, $\beta = 80.076(7)^\circ$, $\gamma = 63.381(7)^\circ$, $V = 1560.9(9)\text{ \AA}^3$, $Z = 2$, $T = 173(2)\text{ K}$. 5470 reflections (3204 independent, $R_{\text{int}} = 0.1514$) were collected. Largest electron density residue: 0.504 e \AA^{-3} , R_1 (for $I > 2\sigma(I)$) = 0.0666 and $wR_2 = 0.1269$ (all data).

8: $\text{C}_{42}\text{H}_{50}\text{Ge}_2\text{O}_9$, $M = 844.00$, monoclinic, $P2_1/n$, $a = 10.525(1)\text{ \AA}$, $b = 18.167(2)\text{ \AA}$, $c = 21.396(2)\text{ \AA}$, $\beta = 97.962(2)^\circ$, $V = 4051.6(8)\text{ \AA}^3$, $Z = 4$, $T = 173(2)\text{ K}$. 23421 reflections (8259 independent, $R_{\text{int}} = 0.0857$) were collected. Largest electron density residue: 0.471 e \AA^{-3} , R_1 (for $I > 2\sigma(I)$) = 0.0494 and $wR_2 = 0.0981$ (all data) with $R_1 = \sum |F_o| - |F_c| / \sum |F_o|$ and $wR_2 = (\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2)^{0.5}$.

All data for all structures represented in this paper were collected at low temperatures using an oil-coated shock-cooled crystal on a Bruker-AXS CCD 1000 diffractometer with Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$). The structure was solved by direct methods [15] and all non-hydrogen atoms were refined anisotropically using the least-squares method on F^2 [16].

Appendix A. Supplementary material

CCDC 616157, 616158 and 616159 contain the supplementary crystallographic data for **3**, **7** and **8**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorgchem.2006.09.009](https://doi.org/10.1016/j.jorgchem.2006.09.009).

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