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Physical-chemical studies and reactivity of new divalent germanium species

S. Mazières *, H. Lavayssière, G. Dousse, J. Satgé

Labora;oire d'Hétérochimie Fondamentale et Appliquée. URA No. 477 CNRS, Université Paul Sabatier, 118 route de Narbonne, 31062 Toulouse Cedex, France

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Abstract

This work concerns the synthesis of five- and six-membered ring heterocyclic germylenes, derived from hydroxy or thiohydroxy acids and germanium spiranic corresponding structures. These compounds were prepared by the exchange reaction of dichlorogermylene or germanium tetrachloride with different germanium heterocycle compounds containing Ge(1V). Structural studies (IR, ¹³C NMR) of 11–17 revealed that these derivatives, which show a double or triple mass peak in mass spectroscopy, are intermoleculary associated by the carbonyl group to the metal $C=01 \rightarrow Ge$. However, different cycloaddition reactions with dienes, quinones and heterobutadienes showed these dimers or trimers had a germylene type reactivity. Oxidation reactions of germylenes 10 and 12 are also described.

Keywords: Heterocyclic germylenes

1. Introduction

Germylenes are known and have been studied for several years; numerous recent reviews have described the main synthetic paths and developed their reactivity [1–3]. Among the heterocycle germylenes, with five- or six-membered ring, and Ge-O, Ge-N, Ge-S or Ge-P bonds, previously described in the 'literature, part of them were synthesized by our group [4–7]. In particular, exchange reactions with germanium heterocyclic compounds and various germanium halides have constituted a large part of the synthetic methods to obtain new germylenes [6–9] and also the corresponding spiranic germanium structures.

We report here the synthesis of new germylenes, derived from five- or six-membered ring heterocyclic germanium compounds previously described [10,11] and their corresponding spiranic structures. This work has already provided a preliminary communication [10]. Reactivity of these new germylenes, with dienes, orthoquinones, α - β ethylenic ketones or oxidizing reagents was also described.

2. Results and discussion

2.1. Synthesis of spiranic germanium structures: spirogermanes

Germanium heterocyclic compounds react with germanium tetrachloride via a non-exothermic reaction, to lead to the expected spirogermanes, in good yields (~70%, Eq. (1)).



 $[\]begin{array}{l} S: X=O, R=H; 4: X=S, R=H; 5: X=O, R=4,5\text{-}C_4H_4; 6: X=O, R=6\text{-}Me\\ 7: X=O, R=5\text{-}Me; 8: X=O, R=6\text{-}OMe \end{array}$

These reactions seem to proceed, according to the literature [9,12,13], by a two-step concerted mechanism, via formation

^{*} Corresponding authors.

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of the intermediate dichloride derivative. In some cases, by proceeding at low temperature (4-5°C) and with diluted solutions, we could isolate such intermediates (Eq. (2)).



Dichloride derivatives are not so stable at room temperature, because of the balance with the spiranic form. At higher temperature (>100°C) the redistribution reaction (symmetrization) becomes more important and leads essentially to spirogermanes.

2.2. Synthesis of heterocyclic germylenes

New germylenes **9–17** (Fig. 1) were obtained by an exchange reaction with the corresponding germanium heterocycles [11] and dichlorogermylene (Eq. (3)):

These exchange reactions leaded to the expected heterocycle germylenes in good yields (60–85%). Experimental procedures are the same for all of these compounds (see Section 3). They are colored powders when X = S and white powders when X = O. Most of them are sensitive to moisture and infusible, but can be sublimed. Their characterization data (¹H, ¹³C NMR, mass spectroscopy and IR) are found in Fig. 1, Fig. 2 and Fig. 3.

2.3. Physical-chemical studies

While five-membered ring cyclic germylenes 9 and 10 appeared to be monomers by mass spectroscopy, six-membered ring cyclic germylenes 11, 14 and 16 showed a double or a triple mass peak (Fig. 2).

There could be several reasons for this observation: (i) metal-metal interaction with formation of a 'bent' bond or a π bond Ge=Ge (Scheme 1, type I) or (ii) germylenc-heteroelement (oxygen, sulfur) dative interaction could lead either via a type II association to cyclic dimers or trimers, or linear polygermanes with variable chain length (Scheme 1, type II).

In order to verify this kind of association, we carried out an IR and 13 C NMR study of these compounds. With sixmembered ring heterocyclic germylenes 11–17, a type II association could be considered, indeed chemical ionization mass spectroscopy (CH₄) showed MH⁺ and M+29 peaks from dimers or trimers ions which cannot come from frag-

Germylene	Yield %	m.p. °C (subl.)	¹ Η NMR δ ppm	¹³ C NMR* δ ppm
: C+ 9 CH, 9	83	380 (dec.)	(DMSO d ₆) CH ₃ = 1.24 (s)	(DMSO d ₆) C ₁ = 184.38 C ₂ = 74.49 CH ₃ = 29.45
Contraction CH, 10	78	> 200 (dec.)	(DMSO d ₆) CH = 3.77 (q) CH ₃ = 1.42 (d) ³ J(CH-CH ₃) = 7.15 Hz	(DMSO d ₆) C ₁ = 173.40 C ₂ = 40.93 CH ₃ = 23.14
:Ge(), , , , , , , , , , , , , , , , , , ,	60	273-5 (195)	(DMSO d ₆) 6.73-6.91 (m, 1H) 7.27-7.48 (m, 2H) 7.77-7.90 (m, 1H)	$\begin{array}{c} (DMSO \ d_6) \\ C_1 = 166.55 \\ C_2 = 117.74 \\ C_3 = 130.87 \\ C_4 = 120.02 \\ C_5 = 133.78 \\ C_6 = 118.09 \\ C_7 = 160.82 \end{array}$
: Get , Control (Control (Contro) (Contro) (Contro) (Contro) (Contro) (Contro) (Cont	75	300 (dec.)	(CDCl3) 7.33-7.58 (m, 1H) 6.61-6.82 (m, 2H) 6.26-6.36 (m, 1H)	$\begin{array}{l} (DMSO \ d_6) \\ C_1 = 165.66 \\ C_2 = 132.04 \\ C_3 = 131.17 \\ C_4 = 124.53 \\ C_5 = 132.91 \\ C_6 = 130.75 \\ C_7 = 138.04 \end{array}$
			(CDCl3)	(DMSO dg)
:	80	330 (dec) (290)		$c_1 = 104.10$ $C_2 = 121.55$ $C_3 = 157.29$ $C_4 = 113.60$ $C_5 = 125.51$ $C_6 = 122.97$ $C_8 = 128.82$ $C_9 = 132.44$ $C_{10} = 126.67$ $C_{11} = 136.65$
Ga 0-700+ 14 CH3	82	260 (dec) (225)	(DMSO d _d) CH ₃ = 2.17 (s) H ₄ = 7.69 (m, 1H) H ₃ ·H ₅ : 7.28 (m, 1H) 6.72 (m, 1H)	(DMSO dg) CH ₃ = 16.37 C ₁ = 164.10 C ₂ = 118.69 C ₃ = 128.72 C ₄ = 117.71 C ₅ = 134.06 C ₆ = 128.11 C ₇ = 158.88
: Ge , CH ₃	π	272-4 (240)	$\begin{array}{l} \text{(DMSO 4c)} \\ \text{(H}_3 = 2.25 \text{ (s)} \\ \text{H}_3 \text{+H}_4 &: \\ 7.72 \text{ (d, 1H)} \\ 6.65 \text{ (d, 1H)} \\ \text{H}_6 = 6.61 \text{ (s, 1H)} \\ \text{J}_3(\text{H}_3 \text{-H}_6) = 7 \text{ Hz} \end{array}$	$\begin{array}{l} (DMSO d_6) \\ (DMSO d_6) \\ CH_3 = 20.98 \\ C_1 = 163.94 \\ C_2 = 116.39 \\ C_3 = 130.94 \\ C_4 = 119.58 \\ C_5 = 143.64 \\ C_6 = 120.27 \\ C_7 = 160.63 \end{array}$
	72	< 200 (dec)	(CDCl) CH3 = 3.90 (s) H3-H5 : 7.13-6.59 (m, 2H) 6.71-6.51 (m, 1H)	$\begin{array}{c} (DMSO \ 4_6) \\ (DMSO \ 4_6) \\ CH_3 = 55.65 \\ C_1 = 163.88 \\ C_2 = 119.12 \\ C_3 = 117.24 \\ C_4 = 115.18 \\ C_5 = 122.21 \\ C_6 = 151.11 \\ C_7 = 150.08 \end{array}$
:Gr 17 4 3 17	65	> 200 (dec.)	(DMSO d ₆) H ₆ = 6.92 (d) H ₃ = 8.7 (d) H ₅ = 8.19 (dd) JH ₅ -H ₆ = 9.09 Hz 4 J(H ₃ -H ₆) = 3.08 Hz	$\begin{array}{l} \text{(DMSO d_6)} \\ \text{C}_1 = 167.05 \\ \text{C}_2 = 118.65 \\ \text{C}_3 = 127.52 \\ \text{C}_4 = 138.27 \\ \text{C}_5 = 128.34 \\ \text{C}_6 \approx 121.93 \end{array}$

Fig. 1. * Experimental ¹³C NMR chemical shifts are in agreement with theoretical chemical shifts.

Germylene	Mass spectrum M+-	IR (cm ⁻¹)	
:Ge 0 1 CH ₃ 9 0 CH ₃	176 (monomer)	C=O: 1684 (KBr) C=O: 1570 (KBr) C=O: 1684 (DMSO)	
:Ge 5	450 (dimer)	C=O : 1560 (KBr) C=O : 1652 (DMSO)	
Ge	668 (trimer)	C=O : 1529 (KBr) C=O : 1652 (DMSO)	
: Ge , 0 , 15 , 15 , 15 , 15 , 15	668 (trimer)	C=O : 1568 (KBr) C=O : 1654 (DMSO)	
Ge 1 16	716 (trimer)	C=O : 1578 (KBr) C=O : 1655 (DMSO)	

Fig. 2.





ments. Moreover, by IR spectroscopy, the stretching frequency of > C=O for 14-16 (KBr pellet) fluctuates between 1530 and 1570 cm⁻¹, while in a polar solvent solution such as DMSO, this frequency is moved to 1650 cm⁻¹ (Fig. 2). This decrease of about 100 cm⁻¹ in the solid state is consistent with a type II association. Such metal-heteroelement interactions were frequently found in tin chemistry [14-17], and were also noticed in germanium chemistry [18].

Results from a 13 C NMR study of germylene 12, made in both solid solution and in DMSO, seem to confirm this hypothesis (Fig. 3). The type II intermolecular association hypothesis would predict an upfield shift of the C₁ carbon chemical shift because the lone pair would interact with the electrophilic Ge atom, deshielding the C atom. On the other hand, in DMSO, complexation of the solvent with the metal should prevent such an interaction. These results can be compared with the work of Brouwer and al. [19] about solvent effects in 13 C NMR for acrylic acid.

IR spectroscopy of five-membered ring heterocyclic germylenes showed simultaneous presence in solid solution (KBr) of ν C=O bands at 1684 and 1570 cm⁻¹. This observation could explain either a short chain length linear association (type III) or an equilibrium monomer/type II dimer.

2.4. Reactivity

Although these species can appear as cyclic or linear associated in form, they showed a germylene type reactivity.

2.4.1. Reaction with conjugated dienes

Functionalized germylenes 9, 11 and 12 are reactive with conjugated dienes giving only concerted 1,4-cycloaddition products, in contrast to dimethylgermylene which reacts with 1,3-dienes to give two types of adducts [1,2,20,21]. Thermal reaction (100°C, 10 min) of germylene 9 with dimethyl-butadiene gave the 1,4-adduct 18 in 60% yield (Eq. (4)).



The six-membered ring germylenes 11 and 12 required 4 h at 95°C to give the corresponding 1,4-adducts with only 50% yield. All products from cycloadditions were isolated and characterized by ¹H NMR and compared with the same adducts obtained by another synthetic route from 1,1-bis(diethylamino)-3,4-dimethyl-1-germacyclopent-3-ene according to Eq. (4).

From reactions with germylated 1,3-dienes we obtained readily and in good yields difunctionalized polymetallated polycyclic structures (Fig. 4).



The difference in reactivity between these heterocyclic germylenes and diethylgermylene with dimethylbutadiene which was previously described [7], demonstrates the electrophilic character of our compounds [1,10]. This chelotropic [4+2] pericyclic reaction, which should proceed via an interaction of the LUMO of the germylene with the HOMO of the diene in the transition state [2], showed also the singlet state of these germylenes. Otherwise, higher reactivity observed with germylated 1,3-dienes may be due to their locked *cis*-conformation.

2.4.2. Reactions with o-quinones

Addition reactions of germylenes and stannylenes with σ -quinones, including the action of 3,5-di-t-butyl-orthoquinone with germylenes which has already been reported by our group [24], are well-known [2,22,23]. Summarized in Fig. 5 are the reactivities of germylenes 9, 10, 11 and 13 with 3,5-di-t-butyl-orthoquinone and phenanthraquinone. From these addition reactions, we did not always obtain the 1,4cycloadducts. In some cases only the symmetrization products were characterized, as shown in Eq. (5).



2.4.3. With trans-chalcone

E-1,3-Diphenyl-prop-2-enone (chalcone) was the only α -enone which reacted well with our germylenes, and in order to compare the germylene reactivity, we extended this study to dihalide germylenes GeX₂ (X = Cl, I) and 1,3-dithiolane-2-germylene [4] (Eq. (6)).

Quinone	Germylene	Cycloadduct	Products from symmetrization	
	Get CH 9	, , , , , , , , , , , , , , , , , , ,	^{co} _{cu} + ^{co} + ^{co} + ^{co} + ^{co} + ^a	
ب کٹر	:G√ CH, 10		",,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	
	:4 11		29 (50%) + 26 [*] (50%)	
	:c2		30 (50%) + 26 [*] (50%)	
Û. O	:G. CH ₃ 9	0 0 0 25 (43%)	ang Hark H ^{ang} 27 (28%) ang Park Hang 27 (28%) spiroquinone not characterized	



Two mechanisms could explain the results: either a [4+2] concerted 1,4-addition according to Refs. [2,25] leading exclusively to 3,5-diphenyl-2-germa-1-oxocyclopentenic structures, or a mechanism with a zwitterionic intermediate following the initial attack of the oxygen from the carbonyl on the electrophilic germanium atom (Eq. (7)).

$$\begin{array}{c} X & & & & \\ Y & & & \\ Y & & & \\ Y & & & \\ Ph & & & \\ \end{array} \begin{array}{c} Ph \\ Add. 1.4 \\ Y & & \\ Ph \end{array} \begin{array}{c} & & & \\ & & \\ Y & & \\ Ph \end{array} \begin{array}{c} & & & \\ & & \\ Ph \end{array} \begin{array}{c} & & & \\ & & \\ & & \\ & & \\ Ph \end{array} \begin{array}{c} & & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ Ph \end{array} \begin{array}{c} & & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ \end{array} \begin{array}{c} & & \\ &$$

Besides, yields (by ¹H NMR) fluctuate between 65 and 8%, depending upon the germylene used, as shown in Fig. 6. These results attest to the instability of such adducts which lead to the corresponding spirogermanium structures by redistributive symmetrization. An example with 1,3-dithiolane-2-germylene is shown in Eq. (8).



2.4.4. Oxidation with dimethyldisulfide

Disulfides react readily with divalent germanium [26] and tin [27] compounds to give the corresponding insertion adducts. At room temperature, we noticed an oxidative addition of dimethyldisulfide with germylene 12. The cycloadduct 37 was slowly obtained and a redistributive symmetrization took place to lead to spirogermane 4 and tetra(methylthio)germanium (Eq. (9)).



2.4.5. Oxidation with thiirane

Germylene 10 reacted with thiirane to lead to the spirogermanium derivative 38, in 89% yield, as shown in Eq. (10)).

Germylene	Product	Yield B	¹ Η NMR δppm	13 _{C NMR} δppm		
GeCl2.C4H8O2	Cl ₄ Ge Ph Ph	65	$(C_{6}D_{6})$ CH = 5.42 (d, 1H) CH = 3.82 (d, 1H) CH = 7.68-6.97 (m, 10H) $^{3}J_{CH-CH} = 3.3 Hz$	(C ₆ D ₆) CH = 98.67 CH = 46.32 CH = 129.28; 125.02 C = 157.01; 142.02; 134.34		
:Gel2	L ₂ Ge Ph Ph 32	8	(DMSO d ₆) CH = 5.74 (d,1H) CH = 3.47 (d,1H) CH = 8.20-7.41 (m,10H) ³ J _{CH-CH} = 2.8 Hz			
:G¢S	$ \begin{array}{c} \begin{pmatrix} S \\ S \\ S \\ P \\$	45	$\begin{array}{l} (C_{4}D_{5})\\ CH=5.59~(d,1H)\\ CH=3.91~(d,1H)\\ CH_{2}=2.50~(m,4H)\\ CH=7.82-7.03~(m,10H)\\ 3^{1}C_{1}C_{1}C_{1}H=3.25~Hz\\ CH=5.50~(d,2H)\\ CH=3.76~(d,2H)\\ CH=3.76~(d,2H)\\ CH=3.76~(d,2H)\\ CH=3.76~(d,2H)\\ CH=2.50~(s,8H)\\ \end{array}$	$\begin{array}{c} (C_{Q}D_{Q})\\ CH=99.74\\ CH=42.70\\ CH_{2}=37.15\\ C=160.12\\ 129.60; 129.12\\ CH=1\\ 130.43; 122.49\\ CH=97.14\\ CH=97.14\\ CH=41.77\\ C=151.85;\\ 142.06; 152.66\\ CH=\\ 129.51; 122.50\\ \end{array}$		
9	0_0_0_Ph	31	(DMSO dg) CH = 5.65 (d, 1H) CH = 3.61 (d, 1H) CH = 8.227.18 (m, 10H) ³ J _{CH-CH} = 3.1 Hz	(DMSO 46) CH = 96.14 CH = 37.61 CH ₃ = 27.96 C = 155.62; 140.7; 132.9 C=0 = 204.89 CH = 128.57; 124.61		
11		31	(DMSO d6) CH = 5.54 (d, 1H) CH = 3.38 (d, 1H) CH = 2.17 (s, 3H) CH = 7.88-7.06 (m, 13H) 3J _{CH-CH} = 2.65 Hz			
Fig. 6.						

We postulated two mechanisms, in which formation of a germathione is advanced (Scheme 2): either by β -decomposition of the germathietane previously formed by insertion of germylene in the σ C-S bond of the thiirane according to Ref. [28], shown in Scheme 2 as process A; or by direct sulfuration of germylene by the thiirane [29,30], described



through process B. The thiirane should react as a sulfuration agent according to a biphilic process between the sulfur from thiirane and germylene. Such a mechanism was already described to explain a P^{nL} -thiirane interaction [30].

3. Experimental

3.1. General procedures

All reactions were performed under an argon atmosphere. Air sensitive compounds were handled by using standard Schlenk and high vacuum-line techniques. All solvents were distilled from appropriate drying agents. ¹H NMR spectra were recorded on a Bruker AC 80 spectrometer operating at 80 MHz (chemical shifts are reported in parts per million relative to internal Me₄Si as reference) and ¹³C NMR spectra on an AC 200 MHz spectrometer. Gas-phase chromatography was carried out on an HP 5890 series II apparatus using nitrogen as the carrier gas. IR spectra were recorded on a Perkin-Elmer IRFT series 1600. Mass spectra were recorded on a Nermag R10.10 H spectrometer operating in the chemical ionization mode (CH₄) and on a Hewlett Packard 5989 spectrometer in the electron impact mode (70 eV). In all cases the complex envelope of peaks obtained for polygermanes agreed with the expected isotopic distribution based on the number of isotopes of germanium.

3.2. General procedure for spirogermanes 1-8

A two-necked round-bottom flask was filtred with an argon inlet and a dropping funnel. Two equivalents of germanium heterocycle, in solution in the solvent, were added to the flask. One equivalent of germanium tetrachloride, in solution in the same solvent, was added dropwise, via the dropping funnel, at room temperature. The formation of El₂GeCl₂ was monitored by gas chromatography. The reaction mixture was magnetically stirred for 1 h. After removal of most of the solvent, the product was precipitated by addition of two volumes of pentane. After filtration, the product was dried under vacuum. Usually, these spiranic derivatives are not very soluble in organic solvents.

1: solvent: dichloromethane; recrystallization solve..t:pentane; 25% yield. M.p. > 300°C dec. 'H NMR (CDCl_3): δ 1.25 (s). CIMS (CH₄): m/z 279 (MH⁺, 11.5). 2: solvent: benzene (reflux for 3 h); 93% yield. M.p.> 300°C dec. (200°C sublim.). 'H NMR (DMSO-d_6): δ 1.44 (d, 6H), 3.73 (q, 2H), 1.43 (d, 6H), 3.72 (q, 2H), diasteroisomers in the ratio 1:1. CIMS (CH₄): m/z 283 (MH⁺, 100), 255 (M-CO, 25), 239 (M-CO₂, 2.9), 179 (M-CO₂CH-(CH₃)S, 3.1). 3: solvent: benzene; 76% yield. M.p.> 300°C dec. 'H NMR (CDCl₃): δ 6.82-7.92 (m, 8H). ¹³C NMR (DMSO-d₆): δ 166.56 (C₁), 117.73 (C₂), 131.15 (C₃), 120.02 (C₄), 133.82 (C₅), 118.09 (C₆), 160.40 (C₇). MS: m/z 346 (M⁺, 5), 210 (M-CO₂C₆H₄O, 1), 194 (GeCO₂C₆H₄, 5), 166 (GeOC₆H₄, 3), 92 (C₆H₄O, 10). 4: solvent: benzene; recrystallization: chloroform/pentane; 69% vield. M.p. 151-154°C. ¹H NMR (DMSO-d₆): δ8.01-7.91 (m, 4H), 7.47-7.13 (m, 4H). ¹³C NMR (DMSO-d₆): δ 167.55 (C₁), 131.90 (C₂), 131.40 (C₃), 124.80 (C₄), 132.36 (C₅), 131.16 (C₆), 138.87 (C₇). MS: m/z 378 (M⁺⁺, 2), 258 $(M - C_6H_4CO_2, 1)$, 226 $(M - CO_2C_6H_4S, 18)$, 182 (GeSC₆H₄, 20), 5: solvent: benzene; recrystallization: THF/ pentane: 86% yield. M.p. 330°C dec. ¹H NMR (DMSO-d₆, 200 MHz): δ 8.55 (s, 2H), 7.98 (d, 2H, ³J = 8.2 Hz), 7.78 (d, 2H, ${}^{3}J = 8.4$ Hz), 7.55 (dd, 2H, ${}^{3}J = 8.4$ and 8.0 Hz), 7.36 (dd, 2H, ${}^{3}J = 8.2$ and 8.0 Hz), 7.33 (s, 2H). CIMS $(CH_4): m/z 447 (MH^+, 15.1), 261 (M - CO_2C_{10}H_6O, 4.7).$ 6: solvent: benzene: 75% vield. M.p. 150°C dec. ¹H NMR $(DMSO-d_{\epsilon})$: δ 7.64 (dd, 2H, J = 7.6 and 1.3 Hz), 7.42 (dd, 2H, J = 7.6 and 1.3 Hz), 6.82 (t, 2H, ${}^{3}J = 7.6$ Hz), 2.19 (s, 6H). 7; solvent: benzene; 65% yield. M.p. 300°C dec. ¹H NMR (DMSO-d₆): δ 7.68 (d, 2H, ³J = 7.9 Hz), 6.74 (d, 2H, ${}^{3}J=7.9$ Hz), 6.79 (s, 2H), 2.24 (s, 6H). CIMS (CH₄): m/z 375 (MH⁺, 4.7). 8: solvent: benzene; 53% yield. M.p. 170°C dec. ¹H NMR (DMSO-d₆): δ 7.50 (dd, 2H, J=8.0 and 1.6 Hz), 7.09 (dd, 2H, J=8.0 and 1.6 Hz), 6.84 (m, 2H), 3.79 (s, 6H).

3.3. General procedure for synthesis of dichloride derivatives 2' and 7'

A round-bottom flask was charged with germanium heterocycle (1 equiv.) in a solution of benzene. A benzenic solution of one equivalent of germanium heterocycle was added dropwise, at room temperature. The reaction mixture was allowed to stir for 2 h. Formation of El₂GeCl₂ was monitored by GC. Solid product was obtained by filtration.

2': 86% yield. ¹H NMR (DMSO-d₆): δ 3.74 (q, 1H, ³*J*=7.14 Hz), 1.44 (d, 3H, ³*J*=7.14 Hz). CIMS (CH₄): *m/z* 249 (*MH*⁺, 29.4), 221 (*M* - CO, 21.4), 167 (*M* - CISCH₃, 100). 7': 84% yield. ¹H NMR (DMSO-d₆: δ 2.24 (s, 3H), 6.61 (m, 1H), 7.68 (m, 2H). CIMS (CH₄): *m/z* 295 (*MH*⁺, 6.4).

3.4. General procedure for synthesis of germylenes 9-17

At room temperature, germanium heterocycle in solution (or in suspension) in dioxane was placed in a round-bottom flask. An equimolar quantity of dichlorogermylene partially dissolved in dioxane was added slowly, via a dropping funnel. Et₂GeCl₂ formation was monitored by GC. Germylene precipitation was carried out by addition of pentane. The product was isolated by filtration and washed with pentane, then dried under vacuum (10^{-2} mm Hg). The main characterization data (¹H, ¹³C NMR, MS, IR) are found in Figs. 1 and 2.

3.5. Reactivity of germylenes 9, 11 and 12 with 2,3dimethyl-1,3-butadiene

The reaction was carried out in a sealed tube. One equivalent of germylene in suspension in anhydrous benzene was mixed with two equivalents of DMB. The tube was placed in an oven, at approximately 100°C, until there was no germylene left. The solvent was removed, and the product characterized.

18: 61% yield; ¹H NMR (C_6D_6): δ 1.61 (m, 12H), 1.85 (m, 4H). **19:** 47% yield. ¹H NMR (CDCl₃): δ 1.82 (m, 6H), 2.02 (m, 4H), 7.30 (m, 4H). MS: m/z 292 (M^{-+} , 74), 265 ($M - CH_3C$, 8), 210 (M - DMB, 99), 166 ($M - CO_2$, DMB, 80). **20:** 53% yield. ¹H NMR (CDCl₃): δ 1.70 (m, 6H), 2.0 (m, 4H).

3.6. General procedure for the reactivity with silicon and germanium 1,3-dienes

A two-necked round-bottom flask was charged with one equivalent of germylene, in suspension in dried benzene. One equivalent of organometallic diene in DMF (1 ml) was added slowly, via a dropping funnel. The reaction mixture was stirred at room temperature for 10 h. After removal of the solvent, the product was crystallized, and then analyzed.

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21: 87% yield. M.p. 145°C dec. ¹H NMR (CDCl₃): δ 1.50 (s, 6H), 2.08 (s, 8H), 7.43 (m, 10H). MS: m/z 482 (M^{++} , 10), 380 (M – OCOCMe₂O, 10), 231 (M – 251, 43), 228 (Ph₂Ge, 44), 151 (PhGe, 100). **22**: 28% yield. M.p. 90–95°C dec. ¹H NMR (CDCl₃): δ 2.15 (m, 8H), 7.38 (m, 16H). CIMS (CH₄): m/z 567 (MH^+ , 3.2), 489 (M – Ph, 1).

23: 67% yield. ¹H NMR (CDCl₃): δ 0.16 (s, 6H), 0.22 (s, 6H), 1.29 (s, 6H), 1.68 (m, 8H).

3.7. General procedure for the reactivity of germylenes with orthoquinones (see Fig. 5)

In a two-necked round-bottom flask was placed one equivalent of germylene in DMF. One equivalent of *o*-quinone in dioxane was then added dropwise. When the reaction mixture was bleached, the reaction was completed. The side products from the redistributive symmetrization reaction remained in solution. The product precipitated and was isolated by filtration.

24: ¹H NMR (DMSO-d₆, 200 MHz): δ 1.24 (s, 6H), 1.29 (s, 9H), 1.37 (s, 9H), 6.50 (d, 1H, J = 2.2 Hz), 6.58 (d, 1H, J = 2.2 Hz). MS: m/2 396 (M^{++}). **26**: ¹H NMR (DMSO-d₆): δ 1.24 (s, 18H), 1.41 (s, 18H), 6.49 (m, 2H), 6.62 (m, 2H). MS: m/2 718 (M^{++}). **27**: ¹H NMR (DMSO-d₆): δ 1.23 (s, 12H). MS: m/2 728 (M^{++}). **28**: ¹H NMR (DMSO-d₆): δ 1.42 (d, 6H), 1.44 (d, 6H), 3.72 (q, 2H), 3.73 (q, 2H),

³J=7.14 Hz. **29**: ¹H NMR (DMSO-d₆): δ 6.86–7.83 (m, 8H). MS: m/z 346 (M^{++}). **30**: ¹H NMR (DMSO-d₆, 200 MHz): δ 7.32 (s, 2H), 7.37 (dd, 2H, J=8.0 and 8.4 Hz), 7.55 (dd, 2H, J=8.2 and 8.4 Hz), 7.78 (d, 2H, J=8.2 Hz), 7.98 (d, 2H, J=8.0 Hz). MS: m/z 446 (M^{++}). **25**: ¹H NMR (DMSO-d₆): δ 1.38 (s, 6H), 7.51 (m, 4H), 8.12 (m, 2H), 8.68 (m, 2H).

3.8. General procedure for the reactivity of germylenes with E-1,3-diphenyl-2-propen-1-one

All these experiments were carried out in NMR tubes, at room temperature. An equimolar mixture of germylene and *trans*-chalcone was placed in the tube under Ar atmosphere. The solvents were C_6H_6 or DMSO-d₆. The reaction was monitored by ¹H and ¹³C NMR. Yields and spectroscopic data of compounds **31–36** are given in Fig. 6.

3.9. Oxidation reaction of 12 with dimethyldisulfide

A two-necked flask fitted with a reflux condenser was charged with 0.19 g (0.85×10^{-3} mol) of germylene 12 and 2 ml (d = 1.06 g/ml) of dimethyldisulfide. The reaction is exothermic. The reaction mixture was stirred for 2 h. Formation of Ge(SMe)₄ was monitored by GC. After removal of the excess dimethyldisulfide, a solid mixture precipitated, which contained 37 and spirogermane 4.

37: MS: *m*/*z* 320 (*M*⁺⁺, 20), 274 (*M*H-CH₃S, 13), 227 (*M*H-MeSSMe, 23). 4: MS: *m*/*z* 378 (*M*⁺⁺). Ge(SMe)₄: MS: *m*/*z* 262 (*M*⁺⁺, 11), 215 (*M*-CH₃S, 28), 121 (CH₃Ge, 30).

3.10. Oxidation reaction of germylene 10 with dimethylenesulfide (thiirane)

The experiment was carried out in a quartz reactor, equipped with a UV immersion lamp ($\lambda = 254$ nm). Nitrogen was bubbled through the reaction mixture to remove thylene which was subsequently trapped with Br₂/CCl₄. The reactor was charged with 0.1 g (0.56×10^{-3} mol) of 10 in THF (70 ml) and 0.07 g (1.12×10^{-3} mol) of thiirane. After, irradiating for 50 min, 10 ml of the Br₂/CCl₄ solution were bleached (89% yield). Following removal of the solvent, a white powder was obtained. Mass spectroscopic analyses showed a mixture of 4, 38 and 39.

38: 89% yield. ¹H NMR (DMSO-d₆): δ 1.43 (d, 3H, J=7.09 Hz), 2.51 (s, 4H), 3.65 (q, 1H, J=7.09 Hz).

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