

Reactivity of Germene $\text{Mes}_2\text{Ge}=\text{CR}_2$ with Cumulative Unsaturation-Containing Compounds: Synthesis of New Germanium Heterocycles

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Germene **1** reacts with the CO and CS double bonds respectively of phenylisocyanate and methylisothiocyanate by formal [2+2] cycloadditions, leading to four-membered ring derivatives **2** and **3**. With CS_2 , dithiagermolane **11** and dithiadigermetane **12** are obtained; the first step of this reaction is probably a formal [2+2] cycloaddition between the $\text{Ge}=\text{C}$ and $\text{C}=\text{S}$ double bonds. With nitromethane, oxazadigermolidine **19** and fluorenone are obtained, the first step likely being a [2+3] cycloaddition between the $\text{Ge}=\text{C}$ double bond and the NO_2 moiety. Compounds **11** and **19** were characterized by X-ray diffraction analysis.

Introduction

Metallaalkenes $>\text{M}=\text{C}<$ ($\text{M} = \text{Si}, \text{Ge}, \text{Sn}$)¹ are important building blocks in organometallic chemistry owing to the great reactivity of the $\text{M}=\text{C}$ double bond toward electrophiles and nucleophiles and in various types of cycloaddition with many unsaturated species. Among all the “heavy” alkenes synthesized so far, dimesitylfluorenylidene germane $\text{Mes}_2\text{Ge}=\text{CR}_2$ ($\text{Mes} = 2,4,6\text{-trimethylphenyl}$, $\text{CR}_2 = \text{fluorenylidene}$) **1**² presents additional interest due to the conjugation between the $\text{Ge}=\text{C}$ double bond and the fluorenylidene moiety: a rather unusual cycloaddition takes place between **1** and *tert*-butylphosphaacetylene^{3a} or phenylacetonitrile.^{3b} These reactions may begin with a formal [2+2] cycloaddition between the germene and the alkynes, with the germene acting as the 4π -component.

Although compounds containing cumulative unsaturations offer several possibilities for reaction with “heavy” low-coordinate species owing to the presence of

two adjacent double bonds, their behavior toward metallaalkenes is poorly documented.

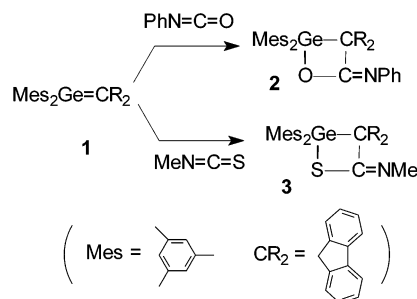
We present in this paper new investigations in this field by the study of the reactions of germene **1** with phenylisocyanate, methylisothiocyanate, carbon disulfide, and nitromethane.

Results and Discussion

(a) Reaction of **1** with PhNCO and MeNCS .

Addition of phenylisocyanate and methylisothiocyanate, at room temperature, to crude solutions of germene **1**,² prepared by dehydrofluorination of $\text{Mes}_2\text{Ge}(\text{F})\text{CHR}_2$ by *t*-BuLi in Et_2O , afforded the four-membered heterocycles oxagermetane **2** and thiagermetane **3** in nearly quantitative yields (Scheme 1). These reactions are regio- and chemoselective, involving formal [2+2] cycloadditions between the $\text{Ge}=\text{C}$ unsaturation and the $\text{C}=\text{O}$ and $\text{C}=\text{S}$ double bonds, respectively; no reaction of the $\text{C}=\text{N}$ unsaturation was observed: oxygen and sulfur are bonded to germanium as expected from the polarity of the $\text{C}=\text{O}$ and $\text{C}=\text{S}$ moieties and that of the $\text{Ge}=\text{C}$ double bond ($\text{Ge}^{\delta+}=\text{C}^{\delta-}$). The formation of strong $\text{Ge}-\text{O}$ and $\text{Ge}-\text{S}$ bonds is another driving force for the

Scheme 1



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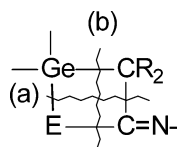
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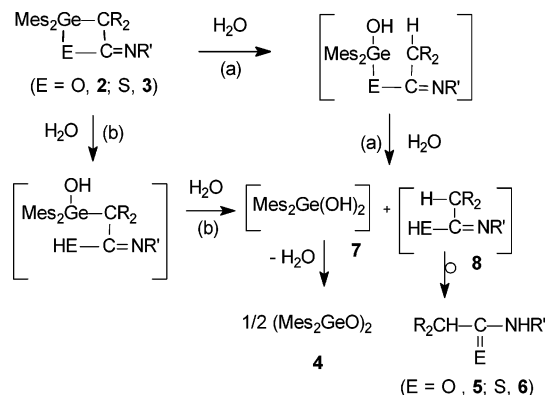
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Chart 1



Scheme 2



formation of such regioisomers. Thus, the first step in these reactions could be the nucleophilic attack of the heteroatom (O or S) onto the germanium followed by cyclization.

The C=N moiety of **2** and **3** was evidenced by IR ($\nu_{\text{C=N}}$: 1690 cm^{-1}) and ^{13}C NMR ($\delta_{\text{C=N}}$ 171.55 ppm for **2** and 160.71 ppm for **3**) spectroscopies. Their structures were also elucidated from their mass spectra, which display, besides the molecular peak, the fragments corresponding to the two possible [4] $\rightarrow$ [2+2] decompositions; path (b) is favored, particularly when E = S (Chart 1).

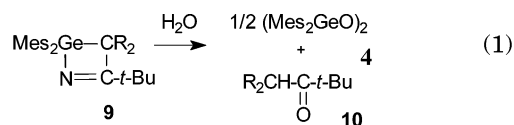
The structures of **2** and **3** were chemically confirmed by their hydrolysis, leading quantitatively to tetramesityldioxadigermetane **4**,⁴ to amide **5** (from **2**), and to thioamide **6** (from **3**) (Scheme 2). **4** was formed from dihydroxygermane **7**, which slowly loses H_2O in solution at room temperature as previously reported.⁵ Compounds **5** and **6** could not be isolated in completely pure form, but their structures were assigned by ^1H and ^{13}C NMR ($\delta_{\text{C=O}}$: 168.77 ppm, $\delta_{\text{C=S}}$: 201.96 ppm) and mass spectrometry.

The formation of **4**, **5**, and **6** can occur by route (a) (initial cleavage of the Ge–C bond) or route (b) (initial cleavage of the Ge–O or Ge–S bond). Standard Ge–C bonds are generally more resistant to hydrolysis than Ge–O or Ge–S bonds; however, they should be weakened in **2** and **3** due to the strain in the four-membered ring and their expected elongation caused by the steric repulsion between the Mes and CR_2 groups.

In the absence of isolation or characterization of the intermediates it is not possible to determine which of the hydrolysis routes (a) or (b) is occurring since both lead to **7** and **8** then to **4**, **5**, and **6**.

A cleavage of the Ge–C bond has recently been observed in the hydrolysis of a four-membered hetero-

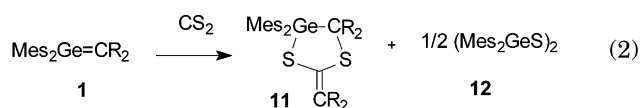
cycle, the 1-aza-2-germacyclobutene **9**,^{3b} leading to tetramesityldioxadigermetane **4** and fluorenyl(*tert*-butyl)-ketone **10** (eq 1).



Similar reactions involving exclusively the C=S double bond of phenylisothiocyanate have been observed with metallathiones and metallaselenones $>\text{M}=\text{X}$ (M = Si, X = S;⁶ M = Ge, X = S,⁷ Se⁸). Between germanimines $>\text{Ge}=\text{N}-$ and $\text{MeN}=\text{C}=\text{S}$ or $\text{PhN}=\text{C}=\text{S}$, the reactions are not chemoselective: additions onto both the C=N and C=S bonds have been observed.⁹ By contrast to **1**, germanimines $>\text{Ge}=\text{N}-$ react with the C=N double bond of PhNCO ⁹ to give the corresponding four-membered heterocycle. An unexpected reaction occurs between disilene $t\text{-Bu}_2\text{Si}=\text{Si}t\text{-Bu}_2$ and $t\text{-Bu}_3\text{SiN}=\text{C}=\text{O}$, the first step being a [3+2] cycloaddition between the Si=Si double bond and the NCO moiety.¹⁰

Thus, our results show a close similarity in chemical behavior between the Ge=C double bond of germene **1** and the Ge=S, Ge=Se, and Si=S double bonds of germathiones, germaselenones, and silathiones toward isocyanates and isothiocyanates. The more polar Ge=N double bond of germanimines shows different chemoselectivity.

(b) Reaction of 1 with CS_2 . When 1 equiv of carbon disulfide was added to a solution of germene **1** cooled to -78°C , a violet color appeared immediately. After 7 h of stirring at room temperature and usual workup, a fractional crystallization successively afforded the five-membered heterocycle 2-fluorenylidene-1,3,4-dithiagermolane **11** and 2,2,4,4-tetramesityl-1,3,2,4-dithiadigermetane **12**. Other experimental conditions (addition of germene **1** to CS_2 or the reaction performed at room temperature) led to the same result (eq 2).



Formation of **12**¹¹ obviously arises from the dimerization of the transient dimesitylgermanethione **13**, but that of **11** deserves some comment (Scheme 3). Unfortunately, as no intermediate could be isolated or characterized, only hypotheses can be formulated. By comparison with the reaction of **1** with $\text{MeN}=\text{C}=\text{S}$, the first step of the reaction is possibly the formation of the four-membered ring derivative **14** by a [2+2] cycloaddition between the Ge=C and one of the C=S double bonds. This heterocycle could then undergo a [4] $\rightarrow$ [2+2] fragmentation, a well-known process in four-membered

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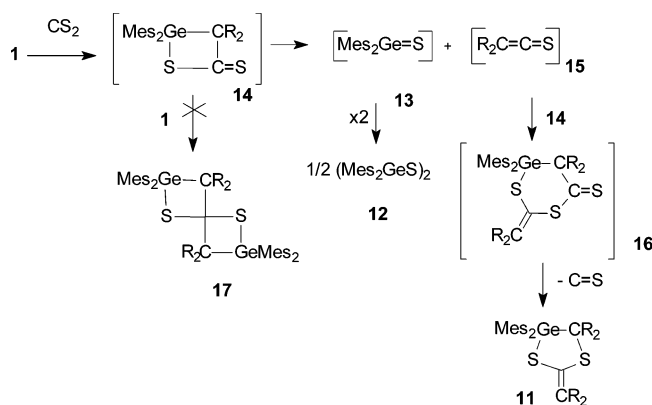
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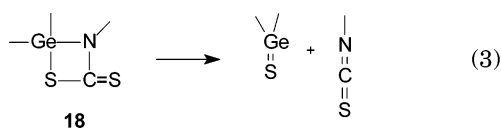
Scheme 3



organometallic heterocycles. An argument for this assumption is the observation in mass spectrometry of a facile decomposition in the similar four-membered ring compound **3** obtained from $\text{MeN}=\text{C}=\text{S}$ and **1**. The very reactive thioketene **15**¹² should then react with **14** by a regioselective insertion of the CS moiety into the $\text{Ge}-\text{S}$ bond, leading to intermediate **16**, which finally loses CS to form the dithiagermolane **11**. Such a loss of $\text{C}=\text{S}$ in organometallic heterocycles has previously been observed.¹³ The fact that the dithiadigermetane **12** is obtained in a much better yield (83%) than **11** (17%), whose formation needs an additional step, is also an argument for this mechanism.

Formation of **11** from spiro compound **17** (Scheme 3) by a rearrangement involving the loss of germylene Mes_2Ge can be ruled out since with 2 equiv of germene **1**, **17** is not formed: in this case 1 equiv of unreacted germene is recovered along with **11** and **12**.

Such a [2+2] cycloaddition between the GeN double bond of germanimines and CS_2 leading to transient four-membered ring heterocycles **18** followed by their [4] $\rightarrow$ [2+2] decomposition has been previously reported^{9,14} (eq 3).



Compound **11** has been characterized by mass spectrometry and ^1H NMR spectroscopy: the protons 1–8 of the CR_2 group bonded to the germanium atom (perpendicular to the five-membered ring plane) give rise to four signals (proton 1 equivalent to 8, 2 to 7, 3 to 6, and 4 to 5) (see numbering in Chart 3), giving two doublets and two triplets. By contrast, four doublets and four triplets are observed as expected for the proton of the other CR_2 group, since H1–8 are nonequivalent. The *o*-Me groups of mesityl groups display a very broad singlet due to their slow rotation.

11, unlike **2** and **3**, is stable toward air and moisture. Its structure was established by an X-ray analysis, which shows standard bond lengths except for the $\text{Ge}-$

Chart 2

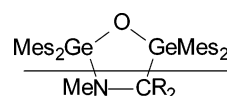
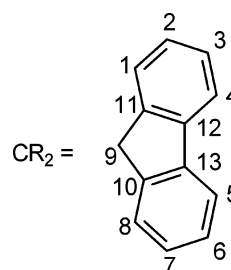


Chart 3



$\text{C}(\text{R}_2)$ bond, which is slightly elongated (2.014(4) Å) compared to the standard values (1.93–1.98 Å¹⁵) (Figure 1).

(c) **Reaction of 1 with MeNO_2 .** Germene **1** reacts with nitromethane to give the air- and moisture-stable 1,3,2,5-oxazadigermolidine **19** and fluorenone **20** (Scheme 4). Irrespective of the reaction conditions, this reaction consumes 2 equiv of germene and 1 equiv of MeNO_2 .

The most likely mechanism involves the initial [2+3] cycloaddition between the $\text{Ge}=\text{C}$ double bond and nitromethane with formation of the heterocycle **21**, which undergoes a [5] $\rightarrow$ [3+2] decomposition leading to fluorenone and the oxazagermirane **22** followed by ring expansion of the latter by reaction with **1** (Scheme 4). Similar “two-atom insertion” of olefins into three-membered rings is a well-known process.

Such [2+3] cycloadditions between the NO_2 moiety of nitrobenzene and the $\text{Si}=\text{Si}$ double bond of disilenes¹⁶ or the $\text{C}=\text{C}$ double bond of an alkene¹⁷ have been previously reported.

The structure of **19** was evidenced by its NMR data. In ^1H NMR spectroscopy, four signals are observed as

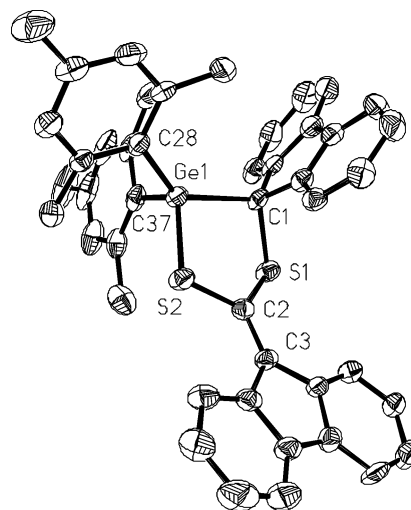


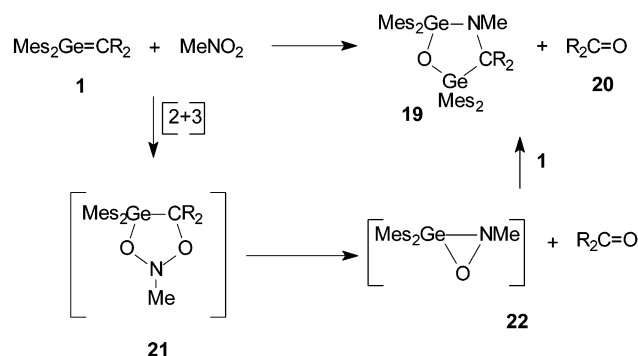
Figure 1. Molecular structure of **11** with ellipsoids drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg). H atoms are omitted for clarity. $\text{Ge}-\text{C1} = 2.014(4)$, $\text{Ge}-\text{C28} = 1.986(4)$, $\text{Ge}-\text{C37} = 1.983(4)$, $\text{Ge}-\text{S2} = 2.2549(11)$, $\text{S2}-\text{C2} = 1.773(4)$, $\text{S1}-\text{C2} = 1.762(4)$, $\text{S1}-\text{C1} = 1.832(4)$, $\text{C2}-\text{C3} = 1.348(5)$, $\text{S2}-\text{Ge}-\text{C1} = 93.05(11)$, $\text{Ge}-\text{C1}-\text{S1} = 102.75(18)$, $\text{C1}-\text{S1}-\text{C2} = 101.68(18)$, $\text{C2}-\text{S2}-\text{Ge} = 100.15(13)$, $\text{S2}-\text{C2}-\text{S1} = 115.6(2)$, $\text{S2}-\text{C2}-\text{C3} = 122.2(3)$, $\text{S1}-\text{C2}-\text{C3} = 122.2(3)$.

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Scheme 4



expected for the *o*- and *p*-Me of the mesityl groups, showing that the two mesityl groups on each Ge atom are equivalent due to a rapid inversion of nitrogen on the NMR time scale. The very broad signal at 1.71 ppm can be attributed to the *o*-Me groups of the Mes_2Ge bonded to the CR_2 group, the rotation of these mesityl groups probably being hindered for steric reasons. In mass spectrometry, besides the molecular peak, the main fragment was $\text{Mes}_2\text{GeOGeMes}_2$ resulting from a [5] $\rightarrow$ [3+2] fragmentation (Chart 2).

An X-ray-structure determination study unambiguously established the structure of **19** (Figure 2). A long $\text{Ge1}-\text{C}(\text{R}_2)$ bond (2.060(11) Å) was observed due to the large steric hindrance caused by the Mes and CR_2 groups. A rather surprising feature is the great difference in the $\text{Ge}-\text{C}(\text{Mes})$ bond lengths for the same GeMes_2 moiety: 2.001(9) and 1.960(11) Å for $\text{Ge}(1)\text{Mes}_2$, 2.016(10) and 1.933(11) Å for $\text{Ge}(2)\text{Mes}_2$.

Conclusion

This study confirms the high reactivity of germene **1** toward unsaturated compounds and its powerful potential in organometallic heterochemistry. Other aspects of the behavior of this building block are under active investigation.

Experimental Section

General Procedures. All reactions were carried out under N_2 or Ar using standard Schlenk techniques with solvents freshly distilled from sodium/benzophenone. ^1H and ^{13}C NMR spectra were recorded in CDCl_3 on Bruker AC 200, AC 250, and Avance 300 instruments at 200.13, 250.13, and 300.13 MHz (^1H) and 50.10, 62.89, and 75.47 MHz (^{13}C), respectively. Mass spectra were measured on a Hewlett-Packard 5989 A spectrometer by EI at 70 eV. Melting points were determined on a Leitz 250 microscope heating stage. IR spectra were recorded on a Perkin-Elmer 1600 FT-IR spectrometer. Elemental analyses were performed by the "Service de Microanalyse de l'Ecole de Chimie de Toulouse".

For the ^1H and ^{13}C NMR study, the carbon atoms of the fluorenyl group are numbered as shown in Chart 3.

Synthesis of Germene 1. Germene **1** was prepared as previously described² by addition of 1 molar equiv of *tert*-butyllithium (1.7 M in pentane) to a solution of the fluoro-germane $\text{Mes}_2\text{Ge}(\text{F})\text{CHR}_2$ (1.00 g, 2.02 mmol) in Et_2O (20 mL)

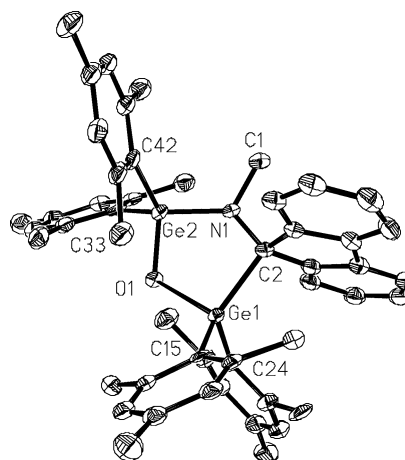


Figure 2. Molecular structure of **19** with ellipsoids drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg). H atoms are omitted for clarity. $\text{Ge1}-\text{O} = 1.806(6)$, $\text{Ge2}-\text{O} = 1.756(6)$, $\text{Ge2}-\text{N} = 1.841(9)$, $\text{Ge1}-\text{C2} = 2.060(11)$, $\text{N}-\text{C2} = 1.472(14)$, $\text{N}-\text{C1} = 1.481(13)$, $\text{Ge1}-\text{C24} = 2.016(10)$, $\text{Ge1}-\text{C15} = 1.933(11)$, $\text{Ge2}-\text{C33} = 1.960(11)$, $\text{Ge2}-\text{C42} = 2.001(9)$, $\text{O}-\text{Ge2}-\text{N} = 97.3(3)$, $\text{Ge2}-\text{N}-\text{C2} = 118.0(7)$, $\text{N}-\text{C2}-\text{Ge1} = 105.1(7)$, $\text{C2}-\text{Ge1}-\text{O} = 95.5(4)$, $\text{Ge1}-\text{O}-\text{Ge2} = 117.0(4)$, $\text{Ge2}-\text{N}-\text{C1} = 121.9(7)$, $\text{C1}-\text{N}-\text{C2} = 111.4(9)$, $\text{C33}-\text{Ge2}-\text{C42} = 110.7(4)$, $\text{C15}-\text{Ge1}-\text{C24} = 112.7(4)$.

at -78°C . Warming to room temperature afforded an orange solution of **1**, which is produced in nearly quantitative yield along with a precipitate of LiF . Crude solutions of **1** were used without further purification.

Reaction of 1 with PhNCO. To a crude solution of **1** (2.02 mmol) in 15 mL of Et_2O was slowly added by syringe at room temperature 1 equiv of PhNCO (0.22 mL, 2.01 mmol). The reaction mixture turned from orange to dark orange. After 1 h stirring at room temperature, the lithium salts were eliminated by filtration and the solvents were removed in vacuo. Crystallization of the residue from pentane afforded 0.77 g (65%) of white crystals of **2** (mp 225°C).

Anal. Found: C, 76.46; H, 6.11; N, 2.20. Calcd for $\text{C}_{38}\text{H}_{35}\text{GeNO}$: C, 76.80; H, 5.94; N, 2.36. ^1H NMR (C_6D_6): 1.99 (s, 18H, *o*- and *p*-Me of Mes), 6.56 (s, 4H, ar H of Mes), 6.92 (td, $^3J_{\text{HH}} = 7.4$ Hz, $^4J_{\text{HH}} = 1.2$ Hz, 2H, H2H7 or H3H6) and 7.01–7.23 (m, 5H, *m*- and *p*-H of Ph, H2H7 or H3H6), 7.42, 7.60, and 7.78 (3d, $^3J_{\text{HH}} = 7.4$ Hz, $3 \times 2\text{H}$, *o*-H of Ph, H1H8 and H4H5). ^{13}C NMR (C_6D_6): δ 20.57 (*p*-Me), 23.62 (*o*-Me), 72.58 (C9), 120.17, 123.69, 125.42, 125.82, 126.92, 128.47 and 128.91 (CH of Ph and CR_2), 132.90, 134.32, 140.26, 140.75, 142.63, and 144.04 (C10–13, *ipso*-C of Ph, *ipso*-, *o*-, and *p*-C of Mes), 171.55 (C=N). IR (NaCl film): 1690 cm^{-1} ($\nu\text{C}=\text{N}$). MS (EI, m/z , %): 595 (M^+ , 32), 492 ($\text{M} - \text{PhNC}$, 3), 476 ($\text{Mes}_2\text{Ge}=\text{CR}_2$, 12), 327 ($\text{Mes}_2\text{GeO} - 1$, 12), 311 ($\text{Mes}_2\text{Ge} - 1$, 82), 267 ($\text{R}_2\text{C}=\text{C}=\text{NPh}$, 67), 190 ($\text{R}_2\text{C}=\text{CN}$, 60), 164 (CR_2 , 100).

Hydrolysis of 2. Water (large excess) was added to a solution of **2** (0.50 g, 0.84 mmol) in THF. An NMR analysis showed the complete disappearance of the starting cycloadduct. The new signals observed in the ^1H and ^{13}C NMR spectra were assigned to dioxadigermetane **4**⁴ (by comparison with an authentic sample) and to amide **5**. Fractional crystallization afforded 0.18 g (75%) of **5** in 90% purity.

5: ^1H NMR (C_6D_6): δ 4.98 (s, 1H, CHR_2), 6.85 (br s, 1H, NH), 7.03 (t, $^3J_{\text{HH}} = 7.3$ Hz, 1H, *p*-H of Ph), 7.24, 7.40, and 7.49 (3t, $^3J_{\text{HH}} = 7.3$ Hz, $3 \times 2\text{H}$, *m*-H of Ph, H3H6 and H2H7), 7.33, 7.77, and 7.84 (3d, $^3J_{\text{HH}} = 7.3$ Hz, $3 \times 2\text{H}$, *o*-H of Ph, H4H5 and H1H8). ^{13}C NMR (C_6D_6): δ 57.10 (C9), 119.94, 120.34, 124.51, 125.45, 128.03, 128.68, and 128.87 (CH of Ph and CR_2), 137.38, 141.01, and 141.47 (*ipso*-C of Ph and C10–13), 168.77 (C=O).

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Reaction of 1 with MeN=C=S. To a crude solution of **1** (2.02 mmol) in Et₂O (30 mL) cooled at 0 °C was slowly added by syringe 0.15 mL of MeN=C=S (2.01 mmol). The reaction mixture progressively turned brown then orange after 2 h stirring at room temperature. Solvents were eliminated in vacuo and replaced by pentane (20 mL). After filtration to eliminate lithium salts, crystallization at -20 °C afforded 0.77 g (70%) of orange crystals of **3** (mp 185 °C).

Anal. Found: C, 72.42; H, 6.17; N, 2.40. Calcd for C₃₃H₃₃GeNS: C, 72.29; H, 6.07; N, 2.55. ¹H NMR (C₆D₆): δ 2.00 (s, 6H, *p*-Me), 2.11 (s, 12H, *o*-Me), 3.18 (s, 3H, MeN), 6.57 (s, 4H, ar H of Mes), 6.95 and 7.13 (2 td, ³J_{HH} = 7.4 Hz, ⁴J_{HH} = 1.2 Hz, 2 × 2H, H2H7 and H3H6), 7.58 and 7.72 (2 d, ³J_{HH} = 7.4 Hz, 2 × 2H, H1H8 and H4H5). ¹³C NMR (C₆D₆): δ 20.50 (*p*-Me), 23.68 (*o*-Me), 41.41 (MeN), 82.15 (C9), 119.81 (C4C5), 124.29, 126.95, and 127.02 (C1–3, C6–8), 129.59 (*m*-C of Mes), 132.80 (*ipso*-C of Mes), 139.59, 139.66, 143.06, and 145.47 (C10–13, *o*- and *p*-C of Mes), 160.71 (C=N). IR (NaCl film): 1690 cm⁻¹ (νC=N). MS (EI, *m/z*, %): 549 (M⁺, 3), 343 (Mes₂Ge=S - 1, 5), 311 (Mes₂Ge - 1, 3), 205 (R₂C=C=NMe, 67), 190 (R₂C=C=N, 100).

Hydrolysis of 3. Hydrolysis of **3** slowly occurred when it was left at room temperature in an NMR tube in wet solutions of CDCl₃. After 3 days, the signals of **3** disappeared and new signals assigned to dioxadigermetane **4**⁴ and thioamide **6** were observed in the ¹H and ¹³C NMR spectra.

6: ¹H NMR (C₆D₆): δ 2.27 (d, ³J_{HH} = 4.8 Hz, 3H, Me), 5.47 (s, 1H, CHR₂), 7.05 and 7.16 (2t, ³J_{HH} = 7.4 Hz, 2 × 2H, H3H6 and H2H7), 7.50 and 7.66 (2d, ³J_{HH} = 7.4 Hz, 2 × 2H, H4H5 and H1H8). NH was not clearly observed. ¹³C NMR (C₆D₆): δ 32.13 (MeN), 64.24 (C9), 119.92 (C4C5), 125.56, 127.81 and 128.41 (C1–3, C6–8), 141.15 and 142.66 (C10–13), 201.96 (C=S). MS (EI, *m/z*, %): 239 (M⁺, 80), 208 (R₂CC=S, 5), 165 (R₂CH, 100), 74 (MeNHC=S, 78).

Reaction of 1 with CS₂. To a crude solution of **1** (3.96 mmol) in Et₂O (20 mL) cooled at -78 °C was slowly added CS₂ (0.22 g, 3.95 mmol). A violet coloration appeared immediately. After 7 h stirring at room temperature, the lithium salts were filtered off and the solvents removed in vacuo. Fractional crystallization in pentane/Et₂O (80/20) gave two products: **12** (1.13 g, white crystals, 83%¹¹) and **11** (0.48 g, white crystals, 17%, mp 320 °C (dec)). Anal. Found: C, 75.42; H, 5.19. Calcd for C₄₅H₃₈GeS₂: C, 75.54; H, 5.35.

11: ¹H NMR (C₆D₆): δ 1.98 (s, 6H, *p*-Me), 2.16 (vbr s, 12H, *o*-Me), 6.56 (s, 4H, arom H of Mes), H1–8: CR₂ bonded to CS₂; H1'–H8': CR₂ bonded to Ge; 6.84 and 6.87 (2 td, ³J_{HH} = 7.7 Hz, ⁴J_{HH} = 1.2 Hz, 2 × 1H, H2H7 or H3H6); 6.86 (d, ³J_{HH} = 7.7 Hz, 2H, H1'H8' or H4'H5'), 7.02 and 7.11 (2 td, ³J_{HH} = 7.7 Hz, ⁴J_{HH} = 1.2 Hz, 2 × 2H, H2'H7' or H3'H6'), 7.21 and 7.33 (2 td, ³J_{HH} = 7.7 Hz, ⁴J_{HH} = 1.2 Hz, 2 × 1H, H3H6 or H2H7), 7.58 (d, ³J_{HH} = 7.7 Hz, 2H, H4'H5' or H1'H8'), 7.53, 7.60, 8.44, and 9.33 (4d, ³J_{HH} = 7.7 Hz, 4 × 1H, H1H4 and H5H8). ¹³C NMR (C₆D₆): δ 20.51 (*p*-Me), 23.38 (*o*-Me), 60.78 (GeCR₂), 119.26 and 119.50 (C4C5), 120.11 (C4'C5'), 125.08, 125.90, 126.06, 126.56, 126.96, 128.10, and 129.78 (CH of Mes and CR₂), 132.76, 138.51, 139.12, 139.26, 139.52, 139.97, 140.30, and 141.54 (S–C=C, C of Mes and C10–13). IR (KBr): ν(C=C) = 1615 cm⁻¹. MS (EI, *m/z*, %): 716 (M, 70), 520 (M - R₂C - S, 5), 508 (M - R₂C=C-S, 40), 372 (R₂C=C-S-CR₂, 40), 345 (Mes₂Ge=S + 1, 80), 311 (Mes₂Ge - 1, 100).

Reaction of 1 with MeNO₂. To a solution of germene **1** (2.01 mmol) in Et₂O (20 mL) cooled at -78 °C was slowly added by syringe 0.13 g (2.01 mmol) of MeNO₂. The reaction mixture progressively turned from orange to light yellow by warming to room temperature. After 4 h stirring, 50 mL of pentane was added. Lithium salts were filtered off, and solvents were removed in vacuo. ¹H and ¹³C NMR analysis showed the formation of **19** and of fluorenone R₂C=O; the latter was identified by comparison with an authentic sample. Crystallization from Et₂O (20 mL) at -20 °C afforded 0.72 g (65%) of white crystals of **19** (mp 170 °C). Anal. Found: C, 72.38; H, 6.52; N, 1.75. Calcd for C₅₀H₅₅Ge₂NO: C, 72.25; H, 6.67; N, 1.69.

19: ¹H NMR (CDCl₃): δ 1.71 (br s, 12H, *o*-Me of Mes₂Ge bound to CR₂), 2.02 (s, 3H, CH₃-N), 2.14 and 2.27 (2s, 2 × 6H, *p*-Me), 2.44 (s, 12H, *o*-Me of Mes₂GeN), 6.51 and 6.79 (2s, 2 × 4H, arom H of Mes), 6.88 (td, ³J_{HH} = 7.6 Hz, ⁴J_{HH} = 1.2 Hz, 2H, H2H7 or H3H6), 6.93 (d, ³J_{HH} = 7.4 Hz, 2H, H4H5 or H1H8), 7.23 (td, ³J_{HH} = 7.6 Hz, ⁴J_{HH} = 1.2 Hz, 2H, H3H6 or H2H7), 7.69 (d, ³J_{HH} = 7.4 Hz, 2H, H1H8 or H4H5). ¹³C NMR (CDCl₃): δ 20.79 and 21.04 (*p*-Me of Mes), 22.84 and 22.94 (*o*-Me of Mes), 31.82 (MeN), 78.34 (C9), 119.44 (C4C5), 124.51, 125.53 and 126.55 (C1–3, C6–8), 128.54 and 129.34 (*m*-CH of Mes), 137.17, 137.38, 138.03, 138.61, 140.55, 142.59, 143.30 and 149.20 (*ipso*-, *o*- and *p*-C of Mes, C10–13). MS (EI, *m/z*, %): 831 (M⁺, 10), 711 (M - Mes - H, 1), 639 (Mes₂GeOGeMes₂ + 1, 35), 519 (Mes₂GeOGeMes, 15), 399 (MesGeOGeMes - 1, 40), 329 (Mes₂Ge=O + 1, 15), 311 (Mes₂Ge - 1, 100), 193 (MesGe and R₂CNMe, 90).

Crystal Data for 11 and 19. **11:** C₄₅H₃₈GeS₂, *M* = 715.46, orthorhombic, *P*2₁2₁2₁, *a* = 9.484(1) Å, *b* = 17.929(2) Å, *c* = 20.993(2) Å, *V* = 3569.4(6) Å³, *Z* = 4, *T* = 193(2) K; 18 284 reflections (6014 independent, *R*_{int} = 0.0624) were collected. Largest electron density residue: 0.416 e Å⁻³, *R*₁ (for *I* > 2σ(*I*)) = 0.0440 and *wR*₂ = 0.0812 (all data) with *R*₁ = Σ||*F*_o| - |*F*_c|| / Σ|*F*_o| and *wR*₂ = (Σ*w*(*F*_o² - *F*_c²)² / Σ*w*(*F*_o²)²)^{0.5}.

19: C₅₀H₅₅Ge₂NO, *M* = 831.14, triclinic, *P*1̄, *a* = 9.059(5) Å, *b* = 11.760(6) Å, *c* = 19.624(9) Å, α = 95.90(2)°, β = 97.58(1)°, γ = 91.71(1)°, *V* = 2059.3(17) Å³, *Z* = 2, *T* = 193(2) K; 6949 reflections were collected. Largest electron density residue: 1.429 e Å⁻³, *R*₁ (for *I* > 2σ(*I*)) = 0.0783 and *wR*₂ = 0.2884 (all data).

All data for both 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 Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods,¹⁸ and all non-hydrogen atoms were refined anisotropically using the least-squares method on *F*².¹⁹

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Supporting Information Available: CIF files for **11** and **19**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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