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Versatile Reactivity of the Germene Mes$_2$Ge═CR$_2$ toward Esters and Related Carbonyl Derivatives

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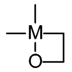
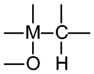
Dimesitylfluorenylidenegermane, Mes$_2$Ge═CR$_2$ (**1**; Mes = 2,4,6-trimethylphenyl, CR$_2$ = fluorenylidene), undergoes a [2 + 4] cycloaddition with the C═CC═O system of α-ethylenic esters such as methyl acrylate, dimethyl maleate and dimethyl fumarate, and diethyl fumarate, leading to the 1,2-oxagerma-5-cyclohexenes **2** and **3a**,**b**, respectively. With diethyl oxalate, maleic anhydride, and cyclopent-2-ene-1,3-dione [2 + 2] cycloadditions are observed between the Ge═C double bond and the carbonyl function, with formation of 1,2-oxagermetanes **4**−**6**, respectively. In the last case, a double [2 + 2] cycloaddition on both CO groups to form a tricyclic compound occurs with excess germene. Germene **1** reacts exclusively by an ene reaction with 2-methyl-1,3-pentadione to give the corresponding (germyloxy)cyclopentenone **8**.

Introduction

The isolation of compounds containing low-coordinate group 14 metal atoms, namely silicon, germanium, and tin analogues of olefins, has been a major breakthrough in recent organometallic chemistry. Unsaturated silicon, germanium, and tin compounds show a heightened reactivity and constitute valuable building blocks for the synthesis of unusual derivatives by means of addition or cycloaddition reactions onto a M═X double bond[1] (M = Si, Ge, Sn; X = C, M, N, P). Thus, the behavior of the silenes, germenes, and stannenes >M═C< toward carbonyl compounds such as saturated aldehydes and ketones, α-ethylenic aldehydes and ketones, and a quinone are well-known (for reviews on the reactivity of carbonyl compounds, see refs 1f−h (Si═C), 1i−k (Ge═C), 2 (with references cited therein), and 3). Saturated aldehydes and ketones normally undergo [2 + 2] reactions leading to four-membered heterocycles of type **A**, except those with a mobile hydrogen atom lead to ene reactions (type **B**) and α-unsaturated species give six-membered heterocycles **C** by [2 + 4] reactions.



A



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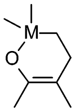

C

In contrast, the influence of another oxygen atom at the carbonyl carbon atom, as in esters, is still relatively poorly documented.[4]

Thus, we report in this paper the reactivity of dimesitylfluorenylidenegermane, Mes$_2$Ge═CR$_2$ (**1**;[5] Mes = 2,4,6-trimethylphenyl, CR$_2$ = fluorenylidene), toward various esters (α-ethylenic esters and γ-diesters) and closely related carbonyl derivatives such as anhydrides and a comparison with cyclic diketones which have a similar structure.

Results and Discussion

Methyl Acrylate, Dimethyl Maleate, Dimethyl Fumarate, and Diethyl Fumarate. These derivatives theoretically offer various possibilities of [2 + 2] or [2 + 4] cycloadditions with the Ge═C double bond of germenes: a [2 + 2] cycloaddition onto the C═O double bond, as with saturated aldehydes and ketones,[3a,b,d] or onto the C═C double bond. Although **1** does not react generally with alkenes, it could give a cycloadduct with the activated C═C double bond of methyl acrylate. For example, a [2 + 2] cycloaddition has been observed by Wiberg between the C═C double bond of methyl vinyl ether and the Ge═C double bond of the germene Me$_2$Ge═C(SiMe$_3$)$_2$, leading to a four-membered-ring heterocycle.[3b] A [2 + 4] cycloaddition onto the conjugated C═CC═O system could also occur, as in the case of α-ethylenic aldehydes and ketones.[3c,d] Such a [2 + 4] cycloaddition has been observed by Brook between a silene

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Scheme 1

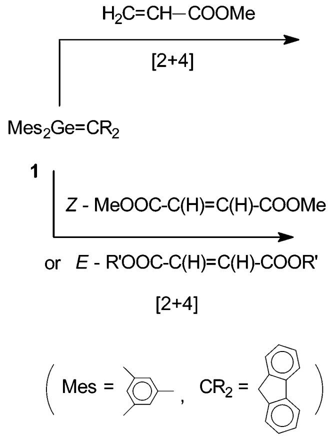
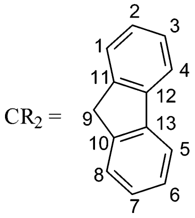


Chart 1



and various acrylates, maleates, and fumarates, leading to six-membered-ring derivatives with the oxygen bonded to the silicon atom.[4]

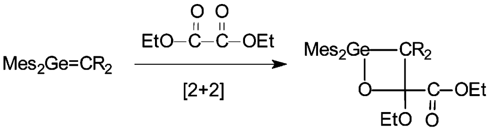
Among all of these possibilities of reactions, only the [2 + 4] cycloaddition between germene **1** and the conjugated system of methyl acrylate, dimethyl maleate, dimethyl fumarate, and diethyl fumarate was observed with the clean formation of 1,2-oxagerma-5-cyclohexenes **2** and **3a**,**b**, respectively (Scheme 1). The unique regiochemistry involving the oxygen atom bonded to the germanium atom probably arises from the anticipated polarities of the germene double bond and of the α,β-unsaturated system, as commmonly prevails in [2 + 4] cycloadditions. The reverse regiochemistry occurring from the Brook silene, which has two electropositive silicon atoms on the metal and an oxygen atom on the sp^2 carbon and, thus, is electronically very different from germene **1**, has been explained in terms of predominant frontier orbital interactions.[4]

The structures of **2** and **3a**,**b** were determined by their physicochemical analysis such as ^{13}C NMR spectroscopy with characteristic chemical shifts for the $O_2C{=}CH$ pattern (159−160 and 68−70 ppm, respectively); the C9 carbon atom (see Chart 1 for the numbering scheme) of the CR_2 group resonates between 48 and 50 ppm, in the expected range for such a carbon atom of a fluorenylidene group bonded to a germanium and a carbon atom. In the case of the reverse regiochemistry, this C9 atom would be bonded to an oxygen atom and should display a chemical shift at lower field, between 80 and 100 ppm. In the mass spectrometry of **3**, the fragment at *m*/*z* 329 corresponds to $Mes_2GeO + 1$ and provides further support to the regiochemistry of the reaction, which has been unambiguously established by a X-ray structure determination. These data clearly confirm the expected regiochemistry of the addition, which is probably influenced by the well-known oxophilic character of germanium and the polarities of the reactants ($Ge^{\delta+}{=}C^{\delta-}$ and $C^{\delta+}{=}CC{=}O^{\delta-}$).

Although the Ge−O bond, and particularly the $GeOC{=}C$ moiety, are generally extremely sensitive to water, these derivatives are stable toward air and moisture, probably owing to the high steric hindrance.

Thus, germene **1** appears to be much more reactive toward α-ethylenic esters, such as methyl acrylate, dialkyl fumarates, and dialkyl maleates, than toward saturated esters since, under the same experimental conditions of solvent or temperature, no reaction was observed between **1** and diethyl malonate or PhCOOMe. Note that, even with an excess of germene, no further reaction was observed with the thus nonconjugated COOR moiety of **3**.

Diethyl Oxalate. Between **1** and diethyl oxalate, an α-diester with two conjugated CO groups ($O{=}CC{=}O$ instead of $O{=}CC{=}C$, as was used previously), two types of reactions could theoretically occur: a [2 + 4] cycloaddition of the Ge═C double bond with the $O{=}CC{=}O$ system, leading to a six-membered heterocycle, and a [2 + 2] cycloaddition between Ge═C and C═O, with one or both C═O units leading to four-membered-ring compounds. Only the reaction between one CO group and the unsaturated Ge═C bond occurred, leading to the oxagermetane **4**, substituted by a COOEt moiety (eq 1).



(1)

4

The ^{13}C NMR signal at 168.14 ppm indicates that one C═O moiety is still present. Even with an excess of germene, only the formation of the monoadduct **4** could be evidenced. Thus, when one ester function has reacted, the second one becomes inert toward the germene under the conditions of the reaction, as in the previous case of **3**, confirming again that the activation of the ester function, here by a vicinal carbonyl group, is necessary.

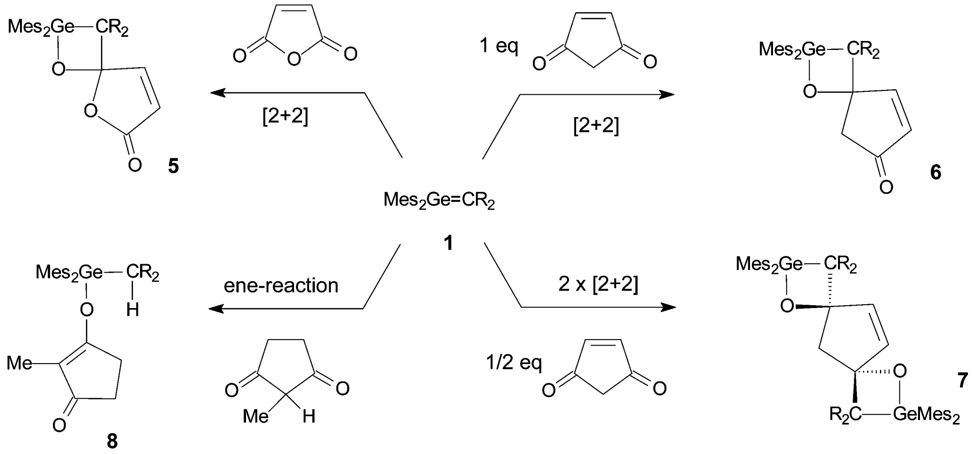
Maleic Anhydride, 4-Cyclopentene-1,3-dione, and 2-Methyl-1,3-cyclopentanedione. After α-ethylenic esters and α-diesters, we have examined the reactivity of anhydrides. It appeared interesting to us to compare the reactivity of this anhydride to that of closely related derivatives (same five-membered-ring structures with two CO groups in a β-position) which possess a ketonic function.

Unlike α-ethylenic esters such as acrylates, maleates, and fumarates, maleic anhydride and 4-cyclopentene-1,3-dione feature a rigid transoid $C{=}CC{=}O$ system, preventing a [2 + 4] cycloaddition with the Ge═C double bond. Thus, an exclusive [2 + 2] cycloaddition between the Ge═C and the C═O unsaturations occurred, leading to oxagermetanes **5** and **6** (Scheme 2).

The presence of the CH═CH moiety with nonequivalent ethylenic protons at 5.77/7.17 ppm ($J_{HH} = 5.5$ Hz) for **5** and 5.89/8.55 ppm ($^3J_{HH} = 6$ Hz) for **6** in the ^{1}H NMR spectra and of signals at 169.35 ppm for **5** (lactonic carbon atom) and 206.8 ppm for **6** (C═O group) in the ^{13}C NMR spectra shows that only one C═O group has reacted.

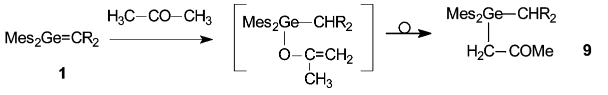
In contrast with the case of maleic anhydride, a double [2 + 2] cycloaddition occurs between the second C═O group of 4-cyclopentene-1,3-dione and the Ge═C double bond when the reaction is carried out with 2 equiv of germene **1**, leading to derivative **7**. Only one diastereoisomer was formed with the two oxagermetane rings in a trans position in relation to the cyclopentene mean plane, since the methylene protons appear to be equivalent in the ^{1}H NMR spectrum (singlet at 1.97 ppm).

Scheme 2



This reaction confirms again the greater reactivity of germene toward ketones than toward esters.

A completely different reaction occurs between germene **1** and 2-methyl-1,3-cyclopentanedione, leading exclusively to the (germyloxy)cyclopentenone **8**. In contrast to the case of maleic anhydride and 4-cyclopentene-1,3-dione, the [2 + 2] cycloaddition of the Ge═C double bond with the carbonyl group was not observed. Thus, the ene reaction is faster than the [2 + 2] cycloaddition between the Ge═C moiety and the carbonyl group; such a reaction is not surprising, since an ene reaction has previously been observed between **1** and acetone, leading after the Lutsenko rearrangement[6] to the germyl ketone **9**[3a] (eq 2).



$$\underset{\mathbf{1}}{Mes_2Ge{=}CR_2} \xrightarrow{H_3C-CO-CH_3} \left[\begin{array}{c} Mes_2Ge-CHR_2 \\ | \\ O-\underset{CH_3}{\underset{|}{C}}{=}CH_2 \end{array}\right] \xrightarrow{\curvearrowright} \begin{array}{c} Mes_2Ge-CHR_2 \\ | \\ H_2C-COMe \end{array} \quad \mathbf{9} \qquad (2)$$

Such a germanotropic rearrangement is not observed in the case of the (germyloxy)cyclopentenone **8**, due to both steric reasons and the presence of the conjugated O═CC═C moiety.

^1H and ^{13}C Spectroscopic Studies. Sharp signals for the ortho methyl groups of the equivalent mesityl groups are observed in the ^1H NMR spectrum of **8**, indicating that the germanium atom is not included in a cyclic structure.

In contrast, in the four- and six-membered-ring heterocycles **3**−**7**, extremely broad signals are observed for ortho methyl groups (half-width up to 120 Hz for **5**). As the two mesityl groups are nonequivalent, due to the presence of an asymmetric carbon atom, extremely different chemical shifts (0.91 and 2.61 ppm for the two ortho methyl groups of the same mesityl in **5**) are observed, due to their special positions in relation to different groups; this is due to a hindered rotation on the NMR time scale caused by the large steric hindrance. Whereas this hindered rotation is observed for all the mesityl groups of **3**, **6**, and **7**, it is not the case for derivatives **4** and **5**, in which one broad singlet was observed for the two ortho methyl groups of one Mes group and two broad singlets were observed for the ortho methyl groups of the other one, indicating a hindered rotation of only one mesityl on the NMR time scale (possibly the Mes in a cis position in relation to the COOEt group in **4** and to the OCO moiety in **5**). The two para methyl groups of the mesityl groups appear as sharp singlets, since they are not influenced by the slow or hindered rotation around the Ge−C(Mes) bond.

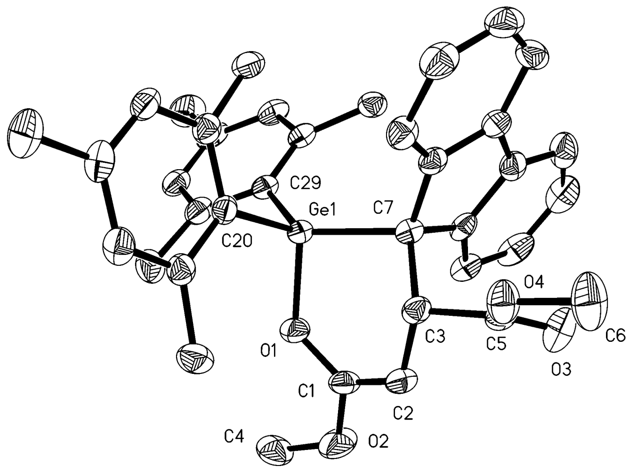


Figure 1. Molecular structure of **3a** (thermal ellipsoids at the 50% probability level). H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge−O1 = 1.843(2), C1−O1 = 1.323(4), C1−O2 = 1.367(3), C1−C2 = 1.328(4), C2−C3 = 1.502(4), C3−C7 = 1.586(4), Ge−C7 = 2.017(3), Ge−C20 = 1.960(3), Ge−C29 = 1.970(3), C3−C5 = 1.519(4); C7−Ge−O1 = 98.50(11), C1−O1−Ge = 123.7(2), O1−C1−C2 = 127.8(3), C1−C2−C3 = 122.0(3), C3−C7−Ge = 102.7(18).

Mass Spectrometry. The mass spectra of both four- and six-membered heterocycles by EI at 70 eV (or by DCI/NH_3 for **7**) showed some similarities: the molecular peak was observed (except for **3b**), and fragments corresponding to the germylene Mes_2Ge and to the starting germene $Mes_2Ge{=}CR_2$ were also found. In the case of **3b**, fragmentations leading to both $Mes_2Ge{=}CR_2$ and to $Mes_2Ge{=}O$ appeared. The only exception is **6**, in which only the $Mes_2Ge{=}O$ fragment was observed; such a [2 + 2] fragmentation leading to a germanone and to an alkene is classic in oxagermetane rings.[7]

X-ray Crystallographic Analyses. The structures of **3a**, **5**, and **8** have been determined by a X-ray study. The main feature is the lenghtening of the Ge−CR_2 and Ge−O bonds due to the large steric congestion: 1.997−2.0227 and 1.819−1.863 Å, respectively (standard Ge−C and Ge−O bond lengths lie generally in the ranges 1.94−1.98[8] and 1.73−1.79 Å, respectively).[8a] In the six-membered ring of oxagermacyclohexene **3a**

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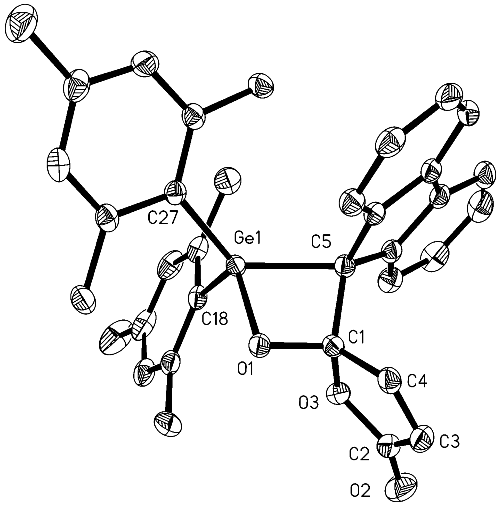

Figure 2. Molecular structure of **5** (thermal ellipsoids at the 50% probability level). H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge−C5 = 2.0227(17), Ge−O1 = 1.8631(12), O1−C1 = 1.400(2), C1−C5 = 1.561(2), Ge−C18 = 1.9548(17), Ge−C27 = 1.9519(17), C1−C4 = 1.508(2), C1−O3 = 1.461(2), C4−C3 = 1.318(3), C3−C2 = 1.478(3), C2−O3 = 1.365(2), C2−O2 = 1.199(2); Ge−C5−C1 = 83.17(10), Ge−O1−C1 = 93.81(9), O1−C1−C5 = 102.96(13), C5−Ge−O1 = 73.12(6), C18−Ge−C27 = 115.21(7), C5−Ge−C27 = 120.63(7), C5−Ge−C18 = 117.62(7), O1−Ge−C27 = 110.37(6), O1−Ge−C18 = 111.31(7).

(Figure 1), the five atoms Ge, O(1), C(1), C(2), and C(3) are approximately in a plane; the mean deviation in relation to this mean plane is 0.05 Å, and the maximum deviation is 0.08 Å for O(1). The angle between the mean plane GeO(1)C(1)C(2)C(3) and the plane GeC(7)C(3) is 50.2°. Derivative **5** (Figure 2) exhibits, as expected from the steric congestion of the four-membered ring, the longest intracyclic Ge−O and Ge−CR_2 bonds; in the distorted oxagermetane ring, the angle between the planes C(5)C(1)O(1)/C(5)Ge(1)O(1) and C(1)C(5)Ge(1)/Ge(1)O(1)C(1) are 28.4 and 27.7°, respectively. The folding is higher than in other oxagermetanes obtained from **1** and benzaldehyde or benzophenone (23 and 12°, respectively)[3a] and in an oxagermetane featuring an exocyclic P=C double bond obtained from the phosphagermaallene −P=C=Ge< and fluorenone (18.7 and 18.9°).[9] More acute bond angles are generally observed in oxasiletanes[10] or in symmetrical 1,3,2,4-dioxadigermetanes[11] and wider fold angles in 1,3-digermazanes (34−38°)[12] and in cyclobutanes. The angle between the four-membered and the planar five-membered rings at the C(1) carbon atom (planes C(5)C(1)O(1) and C(4)C(1)O(3)) is 88.4°, close to the ideal 90°. The small angle O(1)−Ge(1)−C(5) (73.12(6)°) at the germanium atom is in the range of similar angles reported in other four-membered heterocycles (74.1° in a 1,3,2,4-dioxadigermetane,[11] 75 and 75.6° in a 1,2-oxagermetane,[3a] and 75° in a 1,2-phosphagermetane).[13] In **8** (Figure 3), the main features are the near parallelism between the quasi-planar C(1)−C(5) five-membered ring and the fluorenyl group (angle between these two planes: 10°) and an acyclic Ge−O bond (1.819(4) Å) shorter than the intracyclic ones in **3** (1.843(2) Å) and **5** (1.863(1) Å).

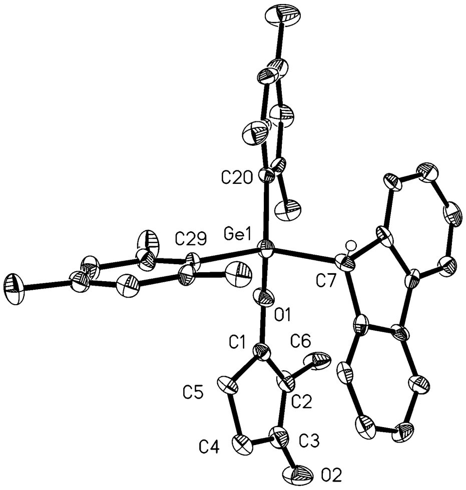

Figure 3. Molecular structure of **8** (thermal ellipsoids at the 50% probability level). H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge−O1 = 1.819(4), O1−C1 = 1.344(8), Ge−C7 = 2.017(7), Ge−C20 = 1.961(7), Ge−C29 = 1.975(6), C1−C2 = 1.334(8), C2−C3 = 1.433(10), C3−C4 = 1.532(9), C4−C5 = 1.529(9), C5−C1 = 1.515(8); Ge−O1−C1 = 128.2(4), C7−Ge−C20 = 106.9(2), C7−Ge−O1 = 101.3(2), C7−Ge−C29 = 124.8 (3), C20−Ge−C29 = 110.9(3), C20−Ge−O1 = 107.3(3), C29−Ge−O1 = 104.0(2).

In conclusion, dimesitylfluorenylidenegermane (**1**) behaves as an extremely reactive and versatile partner toward various carbonyl derivatives and constitutes a very useful building block in organogermanium chemistry. It reacts with esters activated by a C=C double bond or by a carbonyl group but is unreactive when they are not activated, in contrast to the case of closely related ketones which undergo a [2 + 2] cycloaddition or an ene reaction.

Experimental Section

General Procedures. All manipulations 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 250 and Avance 300 instruments at 250.13 and 300.13 MHz (^1H) and 75.47 MHz (^{13}C), respectively. Mass spectra were measured on a Hewlett-Packard 5989 A spectrometer by EI at 70 eV and on a Nermag R10-10 spectrometer by CI (NH_3). Melting points were determined on a Leitz microscope heating stage 250. 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 1.

Synthesis of Germene 1. Germene **1** was prepared as previously described[3] by addition of 1 mol equiv of *tert*-butyllithium (1.7 M in pentane) to a solution of the fluorogermane $Mes_2Ge(F)CHR_2$ (1.00 g, 2.02 mmol) in Et_2O (20 mL) cooled to −78 °C. Warming to room temperature afforded an orange solution of **1** with a precipitate of LiF. According to a ^1H NMR experiment, **1** is produced in a nearly quantitative yield. Thus, all reactions were performed on the crude reaction mixture containing LiF without isolation of **1**.

General Procedure for the Reactions of 1 with Carbonyl Compounds. To the reaction mixture of **1** and LiF cooled to −78 °C was added 1 equiv of the carbonyl reagent, neat (if liquid) or in

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solution in Et_2O or toluene (when solid) via syringe. After the end of the addition, the reaction mixture was slowly warmed to room temperature and stirred overnight, to lead to a yellow solution (except for other colors when indicated). A ^1H and ^{13}C NMR study of the crude solution showed in all cases the complete reaction of **1** and the unique formation of one type of adduct. The solvents were removed under reduced pressure, 30 mL of pentane was added, and LiF was removed by filtration. The yields in the cycloadducts were calculated from isolated crystals (after crystallization at −20 °C in pentane) from the starting $Mes_2Ge(F)CHR_2$.

Synthesis of 2 (1 and Methyl Acrylate). Yield: 1.01 g (85%) of white crystals of oxagermacyclohexene **2** (mp 220 °C). ^1H NMR (300.13 MHz): δ 1.30−3.20 (extremely broad m, 20H, Me of Mes and CH_2), 3.71 (s, 3H, OMe), 3.89 (t, $^3J_{HH} = 5.2$ Hz, 1H, CH=), 6.73 (very broad s (half-width 40 Hz), 4H, arom H of Mes), 7.12−7.44 (m, 6H, arom H of CR_2), 7.81 (d, $^3J_{HH} = 7.9$ Hz, 2H, H on C1,8 or C4,5 of CR_2). ^{13}C NMR (75.47 MHz): δ 20.99 (*p*-Me of Mes), 22.72 (*o*-Me of Mes), 34.31 (CH_2), 48.42 (CR_2), 54.60 (OMe), 68.72 (CH=), 119.72 (C4,5), 125.03, 126.67, 126.92, 129.28 (C1−3, C6−8, *m*-CH of Mes), 134.41, 139.38, 140.47, 148.38 (ipso-, *o*-, and *p*-C of Mes and C10−13), 160.23 (OC=). MS (EI, 70 eV, *m*/*z*): 562 (M, 3), 476 ($Mes_2Ge{=}CR_2$, 65), 311 ($Mes_2Ge - H$, 100). Anal. Calcd for $C_{35}H_{36}GeO_2$ (561.260): C, 74.90; H, 6.47. Found: C, 75.05; H, 6.60.

Synthesis of 3a (1 and (*Z*)- and (*E*)-MeOOCCH=CHCOOMe). (a) Dimethyl maleate: yield 0.87 g (70%) of white crystals of oxagermacyclohexane **3a** (mp 209 °C). (b) Dimethyl fumarate: yield 0.97 g (78%). ^1H NMR (300.13 MHz): δ 0.70 (broad s, 3H, *o*-Me of Mes), 1.40 (very broad s (half-width 45 Hz), 3H, *o*-Me of Mes), 2.04 and 2.27 (2 s, 2 × 3H, *p*-Me of Mes), 2.34 (broad s, 3H, *o*-Me of Mes), 2.70 (very broad s (half-width 40 Hz), 3H, *o*-Me of Mes), 2.83 and 3.67 (2 s, 2 × 3H, OMe), 3.84 and 4.34 (2 d, $^3J_{HH} = 2.4$ Hz, 2 × 1H, OC=CHCHCOOMe), 6.38 and 6.65 (2 broad s, 2 × 2H, arom H of Mes), 6.73, 7.55, 7.71, and 7.73 (4 d, $^3J_{HH} = 7.6$ Hz, 4 × 1H, H1,4,5,8 of CR_2), 7.01, 7.20, 7.26, and 7.33 (4 t, $^3J_{HH} = 7.6$ Hz, 4 × 1H, H2,3,6,7 of CR_2). ^{13}C NMR (75.47 MHz): δ 20.79 and 21.08 (*p*-Me of Mes), 22.74 (*o*-Me of Mes), 48.69, 51.08, and 54.77 ($CHCR_2$ and 2 OCH_3), 50.31 (CR_2), 69.16 (OC=CH), 119.36 and 119.53 (C4,5), 125.07, 125.87, 126.11, 126.29, 126.87, 127.02, 127.14, and 129.70 (C1−3, C6−8, and *m*-C of Mes), 133.30 and 134.24 (ipso-C of Mes), 139.27, 139.98, 141.13, 141.80, 143.85, and 145.60 (C10−13, *o*- and *p*-C of Mes), 160.16 (OC=CH), 171.72 (COOEt). MS (EI, 70 eV, *m*/*z*): 620 (M, 2), 606 (M − Me + H, 1), 589 (M − OMe, 2), 561 (M − COOMe, 1), 476 ($Mes_2Ge{=}CR_2$, 100), 311 ($Mes_2Ge - H$, 90), 165 (CHR_2, 30). Anal. Calcd for $C_{37}H_{38}GeO_4$ (619.296): C, 71.76; H, 6.18. Found: C, 71.92; H, 6.20.

Synthesis of 3b (1 and Diethyl Fumarate, (*Z*)-EtOOCCH=CHCOOEt). Yield: 0.97 g (71%) of white crystals of **3b** (mp 170 °C). ^1H NMR (300.13 MHz): δ 0.40 (t, $^3J_{HH} = 7.2$ Hz, 3H, OCH_2CH_3), 0.68 and 1.18 (2 broad s, 2 × 3H, *o*-Me of Mes), 1.26 (t, $^3J_{HH} = 7.2$ Hz, 3H, OCH_2CH_3), 2.01 and 2.24 (2 s, 2 × 3H, *p*-Me of Mes), 2.31 (broad s, 3H, *o*-Me of Mes), 2.72 very broad s, *o*-Me of Mes), 3.28 (AB q, $^2J_{HH} = 9.0$ Hz, $^3J_{HH} = 7.2$ Hz, 1H, $OCH_AH_BCH_3$), 3.29 (AB q, $^2J_{HH} = 9.0$ Hz, $^3J_{HH} = 7.2$ Hz, 1H, $OCH_AH_BCH_3$), 3.89 and 4.31 (2 d, $^3J_{HH} = 2.4$ Hz, 2 × 1H, OC=CHCHCOOEt), 3.92 (q, $^3J_{HH} = 7.2$ Hz, 2H, OCH_2CH_3), 6.33 and 6.60 (2 broad s, 2 × 2H, arom H of Mes), 6.73, 7.59, 7.68, and 7.69 (4 d, $^3J_{HH} = 7.6$ Hz, 4 × 1H, H1,4,5,8 of CR_2), 6.97, 7.16, 7.23, and 7.30 (4 t, $^3J_{HH} = 7.6$ Hz, 4 × 1H, H2,3,6,7 of CR_2). ^{13}C NMR (75.47 MHz): δ 13.31 and 14.96 (OCH_2CH_3), 21.08 and 21.11 (*p*-Me of Mes), 22.74 and 22.88 (*o*-Me of Mes), 48.73 ($CHCR_2$), 50.44 (CR_2), 59.90 and 62.84 (OCH_2CH_3), 70.61 (OC=CH), 119.31 and 119.48 (C4,5), 125.29, 126.26, 126.31, 126.81, 127.04, and 127.15 (C1−3, C6−8), 128.55 and 129.71 (*m*-C of Mes), 133.54 and 134.57 (ipso-C of Mes), 139.23, 139.92, 141.26, 142.56, 144.03, and 145.86 (C10−13, *o*- and *p*-C of Mes), 159.05 (OC=CH), 171.34 (COOEt). MS (EI, 70 eV, *m*/*z*): 477 ($Mes_2Ge{=}CR_2 + H$, 2), 329 ($Mes_2GeO + H$, 5), 313 ($Mes_2Ge + H$, 10), 165 (CHR_2, 100). IR: ν(CO), 1742.4 cm^{-1}; ν(C=C), 1605.3 cm^{-1}. Anal. Calcd for $C_{39}H_{42}GeO_4$ (647.350): C, 72.36; H, 6.54. Found: C, 71.82; H, 6.30.

Synthesis of 4 (1 and Diethyl Oxalate). Yield: 1.04 g (79%) of white crystals of oxagermetane **4** (mp 180 °C). ^1H NMR (250.13 MHz): δ 0.39 (t, $^3J_{HH} = 7.2$ Hz, 3H, OCH_2CH_3), 0.88 (broad s, 3H, *o*-Me of Mes), 1.21 (t, $^3J_{HH} = 7.2$ Hz, 3H, OCH_2CH_3), 2.19 (s, 3H, *p*-Me of Mes), 2.24 (broad s, 6H, *o*-Me of Mes), 2.31 (s, 3H, *p*-Me of Mes), 2.70 (broad s, 3H, *o*-Me of Mes), 3.25 and 4.17 (2 dq, $^2J_{HH} = 7.2$ Hz, $^3J_{HH} = 7.2$ Hz, 2 × 1H, $CHH'CH_3$ and $CHH'CH_3$ for one Et group), 3.46 and 3.80 (2 dq, $^2J_{HH} = 10.7$ Hz, $^3J_{HH} = 7.3$ Hz, 2 × 1H, $CHH'CH_3$ and $CHH'CH_3$ for the other Et group), 6.35−6.80 (very broad s, 2H, arom H of Mes), 6.83 (s, 2H, arom H of Mes), 7.05 (1H), 7.16 (1H), and 7.36 (2H) (3 t, $^3J_{HH} = 7.6$ Hz, H2,3,6,7 of CR_2), 7.28, 7.43, 7.24, and 7.99 (4 d, $^3J_{HH} = 7.6$ Hz, 4 × 1H, H1,4,5,8 of CR_2). ^{13}C NMR (75.47 MHz): δ 13.13 and 14.78 (OCH_2CH_3), 21.01 and 21.13 (*p*-Me of Mes), 22.84 (*o*-Me of Mes), 59.51 and 60.32 (OCH_2CH_3), 70.20 (CR_2), 106.14 (OCO), 119.24 and 119.31 (C4,5), 124.05, 126.52, 126.56, 126.67, 126.81, and 128.20 (C1−3, C6−8 of CR_2), 128.60 (broad s) and 129.18 (*m*-C of Mes), 131.33 and 131.72 (ipso-C of Mes), 139.85, 139.89, 140.01, 140.22, 141.15, 143.19, and 144.13 (C10−13, *o*- and *p*-C of Mes), 168.14 (CO). MS (EI, 70 eV, *m*/*z*): 622 (M, 3), 577 (M − OEt, 5), 476 ($Mes_2Ge{=}CR_2$, 10), 357 ($MesGe{=}CR_2$, 20), 311 ($Mes_2Ge - H$, 60), 220 ($R_2CCOEt - H$, 25), 165 (CHR_2, 100). IR: ν(CO), 1725.4 cm^{-1}. Anal. Calcd for $C_{37}H_{40}GeO_4$ (621.312): C, 71.53; H, 6.49. Found: C, 71.52; H, 6.20.

Synthesis of 5 (1 and Maleic Anhydride). The carbonyl compound was dissolved in Et_2O, and the reaction mixture turned green and then turquoise blue. Yield: 0.87 g (75%) of white crystals of oxagermetane **5** (mp 243 °C). ^1H NMR (250.13 MHz): δ 0.91 (broad s, 3H, *o*-Me of Mes), 2.20 (extremely broad s (half-width 120 Hz), 6H, *o*-Me of Mes), 2.23 and 2.32 (2 s, 2 × 3H, *p*-Me of Mes), 2.61 (broad s, 3H, *o*-Me of Mes), 5.77 (d, $^3J_{HH} = 5.5$ Hz, 1H, =CHC=O), 6.58 (broad s, 1H, arom H of Mes), 6.87 (broad s, 3H, arom H of Mes), 7.17 (d, $^3J_{HH} = 5.5$ Hz, 1H, OCCH=), 7.16, 7.23, 7.34, and 7.39 (4 t, $^3J_{HH} = 7.6$ Hz, 4 × 1H, H2,3,6,7 of CR_2), 7.46, 7.66, 7.77, and 7.80 (4 d, $^3J_{HH} = 7.6$ Hz, 4 × 1H, H1,4,5,8 of CR_2). ^{13}C NMR (75.47 MHz): δ 21.04, 21.09, 22.16, 22.61, and 22.93 (*o*- and *p*-Me of Mes), 70.95 (CR_2), 116.12 (CO_2), 119.46 and 120.16 (C4,5 of CR_2), 122.90, 124.26, 127.12, 127.49, and 127.70 (C1−3, C6−8 of CR_2, O=CCH=), 128.55 and 129.05 (2 broad s, *m*-CH of Mes), 130.53 and 131.20 (ipso-C of Mes), 139.10, 139.68, 140.31, 140.43, 140.62, 142.25, 143.04, and 143.60 (C10−13 of CR_2, *o*- and *p*-C of Mes), 152.14 (O−CCH=), 169.35 (C=O). MS (EI, 70 eV, *m*/*z*): 574 (M, 5), 476 ($Mes_2Ge{=}CR_2$, 10), 411 ($M - Mes - CO_2$, 7), 311 ($Mes_2Ge - H$, 20), 246 ($M - Mes_2GeO$, 45), 218 ($M - Mes_2GeO - CO$, 50), 193 (MesGe, 50), 189 ($M - Mes_2Ge - CO_2 - CO - H$, 100), 165 ($CHR_2$, 60), 44 ($CO_2$, 65). IR: ν(CO), 1695.0 cm^{-1}. Anal. Calcd for $C_{35}H_{32}GeO_3$ (573.227): C, 73.34; H, 5.63. Found: C, 73.52; H, 5.86.

Synthesis of 6 (1 and 4-Cyclopentene-1,3-dione, 1:1 Molar Ratio). The carbonyl compound was dissolved in toluene. Yield: 0.92 g (80%) of white crystals of oxagermetane **6** (mp 205 °C). ^1H NMR (300.13 MHz): δ 0.94 and 1.48 (2 broad s, 2 × 3H, *o*-Me of Mes), 2.14 (d, $^2J_{HH} = 18.6$ Hz, 1H, CHH′), 2.16 and 2.27 (2 s, 2 × 3H, *p*-Me of Mes), 2.58 (broad s, 3H, *o*-Me of Mes), 2.60 (d, $^2J_{HH} = 18.6$ Hz, 1H, CHH′), 2.85 (broad s, 3H, *o*-Me of Mes), 5.89 (d, $^3J_{HH} = 6.0$ Hz, 1H, O=CCH=), 5.90, 6.51, 6.65, and 6.81 (4 broad s, 4 × 1H, arom H of Mes), 7.00−7.13 (m, 2H, arom H of CR_2), 7.25−7.32 (m, 3H, arom H of CR_2), 7.54, 7.71, and 7.74 (3 d, $^3J_{HH} = 7.8$ Hz, 3 × 1H, H on C1, C4, C5, or C8), 8.15 (d, $^3J_{HH} = 6.0$ Hz, 1H, OCCH=). ^{13}C NMR (75.47 MHz): δ 21.00 and 21.08 (*p*-Me of Mes), 22.38, 22.71, and 23.32 (*o*-Me of Mes),

Table 1. Crystal Data for 3a, 5, and 8

	3a	**5**	**8**
empirical formula	$C_{37}H_{38}GeO_4$	$C_{35}H_{32}GeO_3$	$C_{37}H_{38}GeO_2$
formula wt	619.26	573.20	587.26
temp (K)	173(2)	133(2)	173(2)
cryst syst	monoclinic	monoclinic	triclinic
space group	*Pn*	$P2_1/n$	$P\bar{1}$
a (Å)	11.3333(13)	11.4843(7)	9.861(2)
b (Å)	9.0086(10)	21.4191(13)	10.976(2)
c (Å)	15.1704(18)	11.6183(7)	15.163(3)
α (deg)			108.034(4)
β (deg)	101.477(2)	103.8080(10)	91.282(5)
γ (deg)			108.565(5)
V (Å^3)	1517.9(3)	2775.3(3)	1466.0(6)
Z	2	4	2
abs coef (mm^{-1})	1.049	1.139	1.077
no. of rflns collected	8700	16 315	4579
no. of indep rflns	4251 (R(int) = 0.0246)	5715 (R(int) = 0.0208)	4580 (R(int) = 0.0000)
abs cor	semiempirical	semiempirical	semiempirical
min/max transmissn	0.786 204	0.678 852	0.567 423
no. of data/restraints/params	4251/2/387	5715/0/357	4580/0/371
goodness of fit on F^2	1.043	1.039	1.004
final R indices ($I > 2\sigma(I)$)	R1 = 0.0283, wR2 = 0.0700	R1 = 0.0284, wR2 = 0.0712	R1 = 0.0584, wR2 = 0.1118
R indices (all data)	R1 = 0.0301, wR2 = 0.0712	R1 = 0.0338, wR2 = 0.0738	R1 = 0.0886, wR2 = 0.1241
largest diff peak, hole (e Å^{-3})	0.678, −0.342	0.609, −0.274	1.066, −1.025

49.61 (CR_2), 70.16 (CH_2), 90.40 (GeOC), 119.73 and 120.02 (C4,5), 124.51, 125.53, 126.65, 126.86, 126.94, 127.11, 128.49, 129.16, and 131.60 (C1−3, C6−8, *m*-CH of Mes and ═CHC═O), 130.94, 132.71, 139.73, 140.02, 140.11, 140.24, 140.43, and 145.86 (ipso-, *o*- and *p*-C of Mes, C10−13), 164.60 (═CHCOGe), 206.80 (C═O). MS (EI, 70 eV, *m*/*z*): 572 (M, 1), 329 (Mes_2GeO + H, 18), 311 (Mes_2Ge − H, 10), 244 (M − Mes_2GeO, 45), 119 (Mes, 90), 96 (M − $Mes_2Ge{=}CR_2$, 100). Anal. Calcd for $C_{36}H_{34}GeO_2$ (571.255): C, 75.69; H, 6.00. Found: C, 75.52; H, 5.81.

Synthesis of 7 (1 and 4-Cyclopentene-1,3-dione. 2:1 Molar Ratio). The carbonyl compound was dissolved in toluene. Yield: 0.90 g (82%) of white crystals of bis(oxagermetane) **7** (mp 171 °C). ^{1}H NMR (300.13 MHz): δ 0.92 and 1.33 (2 broad s, 2 × 6H, *o*-Me of Mes), 1.97 (s, 2H, CH_2), 2.11 (broad s, 12H, *o*- and *p*-Me of Mes), 2.17 (s, 6H, *p*-Me of Mes), 2.27 (broad s, 6H, *o*-Me of Mes), 6.20 (s, 2H, CH═), 6.40, 6.51, 6.64, and 6.75 (4 broad s, 4 × 2H, arom H of Mes), 6.96−7.06 (m, 5H, arom H of CR_2), 7.20−7.27 (m, 7H, arom H of CR_2), 7.68−7.71 (m, 4H, arom H of CR_2). ^{13}C NMR (75.47 MHz): δ 20.96 and 20.98 (*p*-Me of Mes), 22.24, 22.36, and 23.32 (*o*-Me of Mes), 53.05 (CR_2), 70.69 (CH_2), 93.25 (CO), 118.96 and 119.16 (C4,5), 125.86, 125.91, 125.96, 126.01, 126.10, 127.78, 127.96, 128.87, 129.33, 129.78, and 130.28 (C1−3, C6−8, *m*-CH of Mes), 136.81 (CH═), 131.95, 132.97, 139.32, 139.49, 140.01, 140.24, 142.15, 142.83, 143.64, 144.56, and 145.75 (ipso-, *o*- and *p*-C of Mes, C10−13). MS (DCI/NH_3, *m*/*z*): 1064 (M + 18, 20), 1047 (M + 1, 50), 720 (M − Mes_2GeO + H, 100). Anal. Calcd for $C_{67}H_{64}Ge_2O_2$ (1046.424): C, 76.90; H, 6.16. Found: C, 77.12; H, 6.20.

Synthesis of 8 (1 and 2-Methyl-1,3-cyclopentanedione). The carbonyl compound was dissolved in toluene. Yield: 0.97 g (78%) of yellow crystals of germyloxycylopentenone **8** (mp 216 °C). ^{1}H NMR (300.13 MHz): δ 1.53−1.58 (m, 2H, CH_2), 1.94−1.98 (m, 2H, CH_2), 2.10 (s, 12H, *o*-Me of Mes), 2.12 (s, 3H, ═CMe), 2.22 (s, 6H, *p*-Me of Mes), 4.88 (s, 1H, C*H*R_2), 6.75 (s, 4H, arom H of Mes), 7.03 and 7.27 (2 t, $^3J_{HH}$ = 7.8 Hz, 2 × 1H, H2,3,6,7 of CR_2), 7.16 and 7.73 (2 d, $^3J_{HH}$ = 7.8 Hz, 2 × 1H, H1,4,5,8 of CR_2). ^{13}C NMR (75.47 MHz): δ 21.04 (*p*-Me of Mes), 23.31 (*o*-Me of Mes), 23.52 (═C*Me*), 29.30 and 33.96 (CH_2CH_2), 45.74 (*C*HR_2), 119.78 (C4,5), 124.50, 126.09 and 126.58 (C1−3, C6−8), 129.25 (*m*-C of Mes), 135.46, 139.28, 140.23, 141.23, 142.59, 142.89, and 143.79 (C10−13, ipso-, *o*-, and *p*-C of Mes and C═C), 205.97 (CO). Anal. Calcd for $C_{37}H_{38}GeO_2$ (587.298): C, 75.67; H, 6.52. Found: C, 75.82; H, 6.20.

Crystal Data for 3a, 5, and 8. Crystallographic data for all structures are presented in Table 1. All data were collected at low temperatures using an oil-coated shock-cooled crystal on a Bruker-AXS CCD 1000 diffractometer with Mo Kα radiation (λ = 0.710 73 Å). The structures were solved by direct methods,[14] and all non-hydrogen atoms were refined anisotropically using the least-squares method on F^2.[15]

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Supporting Information Available: CIF files for **3a**, **5**, and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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