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Persistent Digermenes with Acyl and α-Chlorosilyl Functionalities

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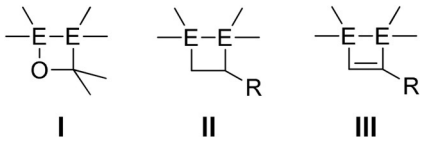
Abstract: We report the preparation of α-chlorosilyl- and acyl-substituted digermenes. Unlike the corresponding transient disilenes, these species with a Ge=Ge double bond show an unexpectedly low tendency for cyclization, but in turn are prone to thermal Ge=Ge bond cleavage. Triphenylsilyldigermene has been isolated as a crystalline model compound, and is the first fully characterized example of a neutral digermene with an A_2GeGeAB substitution pattern. Spectroscopic and computational evidence prove the constitution of 1-adamantoyldigermene as a first persistent species with a heavy double bond conjugated with a carbonyl moiety.

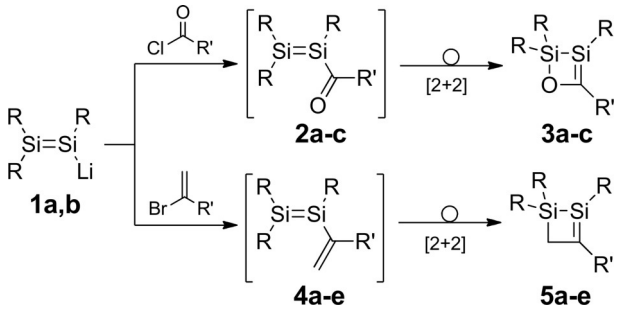
Introduction

The discovery of the first alkene analogue in 1976, Lappert's distannene,[1] led to a rapid growth in interest in the chemistry of multiple bonds between heavier Group 14 elements. This resulted in the isolation of stable doubly and eventually triply bonded species of both silicon and germanium,[2] which have since been proven to be useful synthons in preparative chemistry. For example, Si- and Ge-based ring systems are accessible by their cycloaddition to unsaturated organic substrates such as ketones (**I**),[3] alkenes (**II**),[4] and acetylenes (**III**)[3e,5] (Scheme 1).



Scheme 1. Small ring systems (E = Si, Ge) derived from [2+2] cycloadditions of disilenes or digermenes to ketones (**I**), alkenes (**II**), and acetylenes (**III**).

The synthetic application of disilenes gained further momentum with the advent of functionalized derivatives, most notably disilenides as analogues of vinyllithium.[6] The anionic, nucleophilic silicon center in these species enables targeted peripheral functionalization of the uncompromised Si=Si moiety, as documented by various examples.[7] In some cases, however, these functional disilenes rearrange to cyclic isomers, a process that is thermodynamically driven by replacement of the weak π bond by stronger bonds (Scheme 2). In particular, disilenides **1a**,**b** undergo quantitative reactions with carboxylic acid chlorides to afford cyclic Brook-type silenes **3a**–**c**.[8] The plausible



Scheme 2. Synthesis of cyclic silenes **3a**–**c** and **5a**–**e** (**1a**: R = Tip = 2,4,6-*i*Pr$_3$C$_6$H$_2$; **1b**: R = SiMe*t*Bu$_2$; **2a**, **3a**: R = Tip, R′ = *t*Bu; **2b**, **3b**: R = Tip, R′ = 1-adamantyl; **2c**, **3c**: R = SiMe*t*Bu$_2$, R′ = 1-adamantyl; **4a**, **5a**: R = Tip, R′ = Ph; **4b**, **5b**: R = Tip, R′ = SiMe$_3$; **4c**, **5c**: R = SiMe*t*Bu$_2$, R′ = H; **4d**, **5d**: R = SiMe*t*Bu$_2$, R′ = Ph; **4e**, **5e**: R = SiMe*t*Bu$_2$, R′ = SiMe$_3$).[8,9]

intermediates, acyl disilenes **2a**–**c**, could not be detected by NMR spectroscopy, even at low temperature. Documented examples of acyl-substituted species with double bonds between heavier main group elements are still unknown, both experimentally and theoretically. Likewise, disilenides **1a**,**b** react with various vinyl bromides to afford 1,2-disilacyclobut-2-enes **5a**–**e**, without spectroscopic evidence for the putative intermediates, vinyldisilenes **4a**–**e**.[9] The electronic structure of the latter has been investigated theoretically for the parent species.[10] Experimentally, however, 1,2-disilabutadienes are as yet unknown, except for the recently reported 1,2,3-trisilacyclopentadienes, in which cyclization is hindered by incorporation of the butadiene motif into the five-membered ring.[11]

Conversely, α-chlorosilyldisilenes **6a**,**b**, prepared from the reaction of **1a** with dichlorosilanes, have been isolated, although they readily rearrange to cyclotrisilanes **7a**,**b** (Scheme 3).[12]

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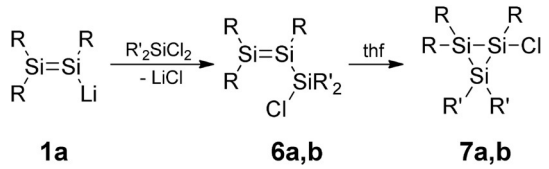
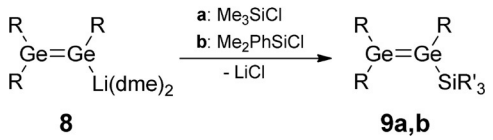


Scheme 3. Synthesis of α-chlorosilyldisilenes **6a**,**b** and cyclotrisilanes **7a**,**b** (R = Tip; **6a**, **7a**: R′ = Me; **6b**, **7b**: R′ = Ph).[12]

Specifically, the dimethyl-substituted trisilaallyl chloride **6a** spontaneously cyclizes to cyclotrisilane **7a**, even at room temperature in the absence of a donor solvent, whereas the corresponding diphenyl derivative **6b** is stable in a hydrocarbon solvent for several weeks and needs elevated temperature or the addition of THF to promote isomerization to **7b**.

Compared to the versatile syntheses, reactions, and applications of disilenes, the chemistry of digermenes is still in its infancy. We recently reported the isolation of the first lithium digermenide **8** as well as proof-of-principle experiments for its reactivity as a nucleophile in salt metathesis reactions with monochlorosilanes (Scheme 4).[13] Single-crystal X-ray diffraction data for the resulting unsymmetrically substituted digermenes **9a**,**b** could only be obtained for a partially hydrolyzed sample of **9b**, which were of limited value in terms of the determination of pertinent bonding parameters.



Scheme 4. Previously reported synthesis of unsymmetrically substituted digermenes **9a**,**b** (R = Tip = 2,4,6-*i*Pr$_3$C$_6$H$_2$; **9a**: SiR′$_3$ = SiMe$_3$; **9b**: SiR′$_3$ = SiMe$_2$Ph).[13]

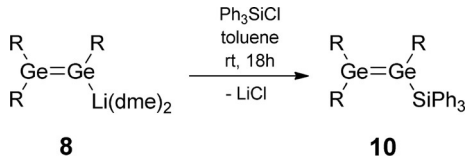
Considering the vast synthetic possibilities offered by the availability of disilenides and the lack of simple synthetic protocols for digermasilacyclopropanes[14] and cyclic Brook-type germenes, we investigated the reactivity of **8** towards dichlorosilanes and acyl chlorides in order to prepare the digerma analogues of previously reported silacycles **3** and **7**.

Results and Discussion

Triphenylsilyldigermene 10

Reaction of Ph$_3$SiCl with digermenide **8** in toluene at room temperature yielded triphenylsilyldigermene **10** of NMR spectroscopic purity. Crystallization from a concentrated solution in hexane afforded single crystals of **10** as yellow plates in 52% yield (Scheme 5).

The ^{29}Si NMR spectrum of **10** features one singlet at δ = 1.89 ppm, in the expected range for a tetracoordinate silicon center, which compares well to the signals observed for **9a** (δ = 1.87 ppm) and **9b** (δ = 0.25 ppm).[13] The longest wavelength absorption in the UV/Vis spectrum is located in the typical region for heavier alkene homologues at λ_{max} = 426 nm (ε = 20845 L mol^{-1} cm^{-1}) and is thus slightly blue-shifted compared to the value reported for digermenide **8** (λ_{max} = 435 nm).[13] Single-crystal X-ray diffraction analysis confirmed the constitution of **10** as a silyl-substituted digermene (Figure 1). The



Scheme 5. Synthesis of triphenylsilyl digermene **10** (R = Tip = 2,4,6-*i*Pr$_3$C$_6$H$_2$).

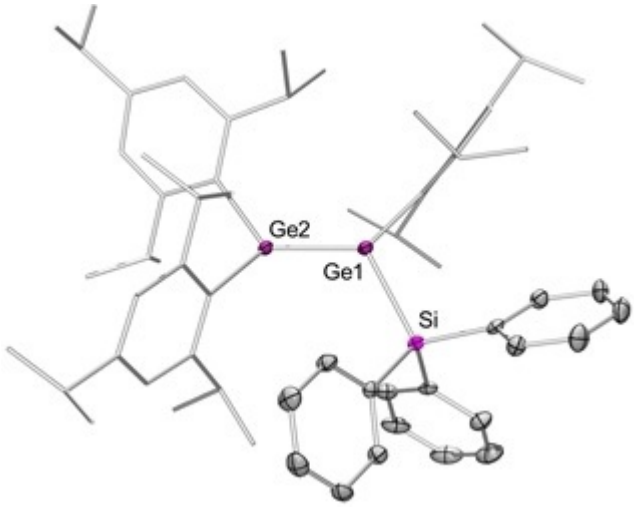


Figure 1. Molecular structure of triphenylsilyl digermene **10** in the solid state (hydrogen atoms omitted for clarity; thermal ellipsoids drawn at 50% probability). Selected bond lengths [Å] and angles [°]: Ge1–Ge2 2.3279(4), Ge1–Si 2.3984(8); Ge2–Ge1–Si 119.09(8), Σ°(Ge1) 346.53, Σ°(Ge2) 345.24, θ(Ge1) 23.7, θ(Ge2) 21.3, τ 13.6. Σ°(E) refers to the sum of angles around atom E.

trans-bent angles θ (defined as the angle between the R-E-R′ plane normal and the E-E bond vector) in **10** [θ(Ge1) = 23.7°; θ(Ge2) = 21.3°] are substantially larger than those in **8** [θ(GeTipLi) = 12.8°, θ(GeTip$_2$) = 7.1°] or the symmetrically substituted Tip$_2$Ge=GeTip$_2$ [θ(GeTip$_2$) = 12°]. In contrast, the twist angle τ (defined as the angle between the R-E-R′ plane normals) of **10** (τ = 13.6°) is similar to that in Tip$_2$Ge=GeTip$_2$ (τ = 14°) and thus smaller than that in **8** (τ = 19.9°).[13,15,16] In agreement with the increased *trans* bending, the Ge–Ge distance of 2.3279(4) Å is elongated compared to those in both **8** (2.284 Å) and Tip$_2$Ge=GeTip$_2$ (2.213 Å).[13,15,16] The Ge1–Si bond of 2.3984(8) Å is slightly shorter than those in persilyl-substituted digermenes (*i*Pr$_2$MeSi)$_2$Ge=Ge(SiMe*i*Pr$_2$)$_2$ (2.400 Å) and (*i*Pr$_3$Si)$_2$Ge=Ge(Si*i*Pr$_3$)$_2$ (2.427 Å).[17]

Reaction of digermenide 8 with dichlorosilanes

Treatment of **8** with 1.5 equivalents of Me$_2$SiCl$_2$ at −78 °C in toluene resulted in an immediate color change to bright-

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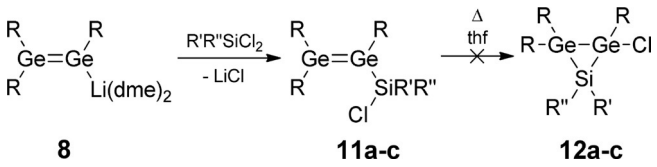
orange. The ^{1}H NMR spectrum of the reaction mixture showed full conversion to a single product, which was identified as silyl digermene **11 a** based on the following spectroscopic observations.

Three sharp singlets in the aryl region at $\delta = 7.12$, 7.09, and 7.01 ppm suggest the presence of three chemically inequivalent Tip groups that rotate rapidly on the NMR time scale and are therefore relatively unhindered. The singlet at $\delta = 0.58$ ppm with a relative intensity corresponding to six H atoms is assigned to the Si-bonded methyl groups. The identical chemical environment of the two methyl groups virtually excludes a three-membered Si_2Ge ring as the presence of the asymmetric Ge center in the hypothetical heavy cyclopropane **12 a** would cause diastereotopic splitting of the corresponding signals. Comparison with the NMR data of silyl disilene **6 a** and its isomeric cyclotrisilane **7 a** underpins this interpretation (Table 1).[11]

Table 1. NMR spectroscopic data for α-chlorosilyldigermenes **11 a–c** in comparison with those of α-chlorosilyldisilenes **6 a**,**b**, cyclotrisilanes **7 a**,**b**, and silyldigermenes **9 a**,**b** and **10**.

	δ ^{29}Si [ppm]	δ $^1H_{Tip\text{-}H}$ [ppm]	δ $^1H_{ortho\text{-}iPr\text{-}CH}$ [ppm]
11 a	31.5	7.12, 7.09, 7.02	3.89, 3.75, 3.59
11 b	23.7	7.12, 7.03, 7.03	3.92, 3.76, 3.62
11 c	15.2	masked by Ph signals	3.58, 3.54, 3.34
6 a	26.2	7.09, 7.06, 6.99	4.29, 4.00, 3.78
6 b	11.8	masked by Ph signals	4.15, 3.97, 3.74
7 a	−35.4	7.20, 7.18, 7.15, 7.02, 6.95	4.21, 4.09, 3.74, 3.61, 3.43
7 b	−54.8	masked by Ph signals	4.04, 3.96, 3.89, 3.55
9 a	1.87	7.11, 7.10, 7.02	3.84, 3.83, 3.65
9 b	0.25	7.09, 7.06, 7.05	3.85, 3.82, 3.67
10	1.89	7.06, 7.01, 6.95	3.86, 3.76, 3.72

Consistent evidence is provided by the ^{13}C NMR spectrum of **11 a**, with twelve signals between 153.1 and 122.0 ppm that satisfyingly match, in number and chemical shifts, the corresponding signals of silyl disilene **6 a**, while being in stark contrast to the eighteen signals in this range for cyclotrisilane **7 a**.[12] The ^{29}Si NMR signal at $\delta = 31.5$ ppm is typical of a terminal silyl group (**6 a**: $\delta = 26.2$ ppm, **9 a**: $\delta = 1.87$ ppm, **9 b**: $\delta = 0.25$ ppm), unambiguously excluding the presence of an endocyclic Si atom (**7 a**: $\delta = -35.4$ ppm).[12,13] The slightly lower field ^{29}Si NMR shift of **11 a** compared to **6 a** can be rationalized in terms of the higher electronegativity of germanium compared to silicon. The UV/Vis spectrum of a freshly prepared and filtered solution shows the longest-wavelength absorption at $\lambda_{max} = 435$ nm ($\varepsilon = 11\,110$ L mol^{-1} cm^{-1}), close to the values for silyldisilenes and digermenes (**7 b**: 427 nm,[12] **10**: 426 nm), strongly supporting the presence of an uncompromised Ge=Ge moiety. Based on the accumulated spectroscopic evidence, we are confident in assigning the connectivity of α-chlorosilyldigermene **11 a** to the main product of the reaction of digermenide **8** with Me_2SiCl_2 (Scheme 6). Despite various attempts at crystallization from concentrated solutions in hexane, pentane, benzene, toluene, mesitylene, fluorobenzene, or THF, single crystals of **11 a** could not be obtained.



Scheme 6. Synthesis of α-chlorosilyl digermenes **11 a–c** (R = Tip = 2,4,6-$iPr_3C_6H_2$; **11 a**, **12 a**: R′ = R″ = Me; **11 b**, **12 b**: R′ = Me, R″ = Ph; **11 c**, **12 c**: R′ = R″ = Ph).

In an analogous manner to Me_2SiCl_2, the sterically more demanding dichlorosilanes $MePhSiCl_2$ and Ph_2SiCl_2 reacted with digermenide **8** at −78 °C in toluene to afford the α-chlorosilyldigermenes **11 b** and **11 c**, which were characterized by multinuclear NMR spectroscopy, but again eluded crystallization. In principle, the same arguments for structure identification hold as in the case of **11 a** (Table 1): the ^{29}Si NMR signals of **11 b**,**c** (**11 b**: $\delta = 23.7$ ppm; **11 c**: $\delta = 15.2$ ppm) are detected at significantly lower field than expected for three-membered rings (**7 a**: $\delta = -35.4$ ppm; **7 b**: $\delta = -54.8$ ppm). Three chemically distinct Tip groups give rise to the minimum number of signals in the ^{1}H and ^{13}C NMR spectra, indicating free rotation about the Ge–C bond. Unfortunately, redox processes become competitive during the synthesis of **11 b** and **11 c**, resulting in increasing amounts of the intensely green 1,3-tetragermabutadiene $Tip_2Ge{=}Ge(Tip)–(Tip)Ge{=}GeTip_2$[18] as a side product (**11 b**: < 0.5 %; **11 c**: 2 %, as determined by ^{1}H NMR). Presumably, the increasing number of electron-withdrawing phenyl groups renders the dichlorosilane reagents more prone to reduction by digermenide **8**, which is oxidatively coupled to the tetragermabutadiene in the process.

As reported previously, isomerization of the related disilenes **6 a**,**b** to the corresponding cyclotrisilanes is induced by heating or the addition of THF as a donor solvent. At higher temperatures or upon addition of THF, however, all silyldigermenes eventually decompose to product mixtures dominated by the homoleptic $Tip_2Ge{=}GeTip_2$[15] as the only identifiable product. Digermenes in general are known to be readily cleaved into their constituent germylene fragments. Thermally induced dissociation of the Ge=Ge double bond of **10** and **11 a–c** and subsequent dimerization of the resulting Tip_2Ge: fragments plausibly explains the formation of Tip_4Ge_2. The concomitantly formed $Tip(R_2ClSi)Ge$: fragments seem to be highly unstable and presumably decompose via various pathways to a variety of unknown products.

Accordingly, α-chlorosilyldigermenes **11 a–c** are much less prone to cyclization to heavy cyclopropanes **12 a–c** compared to the disilene congeners **6 a**,**b**, but rather dissociate into their germylene fragments under thermal treatment or in the presence of *n*-donating solvents.

Reactions of digermenide 8 with acyl chlorides

In the light of the above observations, we anticipated that the use of acyl chlorides as substrates for the reaction with **8** might allow the isolation of the first stable compounds with acyl-substituted heavier double bonds. Upon addition of

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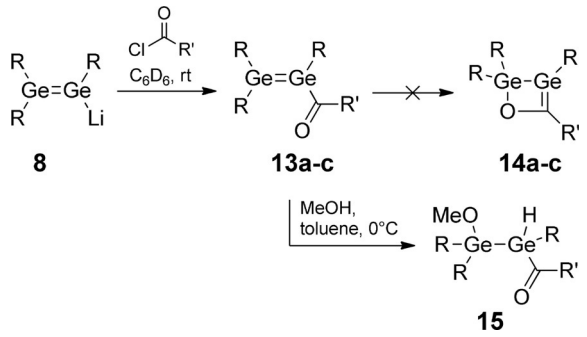
1 equivalent of either pivaloyl chloride, 2,2-dimethylbutyryl chloride, or 1-adamantoyl chloride to digermenide **8** at room temperature in C_6D_6, the reaction mixture instantly turned dark-red and precipitation of a white solid was observed (Scheme 7).



Scheme 7. Synthesis of acyl digermenes **13a–c** and trapping with methanol to afford **15** (R = Tip = 2,4,6-*i*Pr$_3$C$_6$H$_2$; **13a**, **14a**: R′ = *t*Bu; **13b**, **14b**: R′ = 2-methylbutan-2-yl; **13c**, **14c**, **15**: R′ = 1-adamantyl).

The ^{1}H NMR spectra of the crude products after five minutes indicated very clean conversion to single products in all cases. During the reported reactions of disilenide **1** with carboxylic acid chlorides, an initially occurring red color[8] might be attributed to transient yet undetected acyl disilenes. In the present case, the red color persisted at room temperature for up to several hours (**13a**,**b**) or days (**13c**). The ^{1}H and ^{13}C NMR signals of **13a–c** (see the Supporting Information) are of limited diagnostic value in distinguishing them from hypothetical cyclic germenes **14a–c** as the cyclic Brook silenes **3a**,**b** have been reported to show rapid inversion at the Si=C silicon atom at room temperature, leading to apparent C_s symmetry in solution and hence a lower number of signals for the Tip substituents than might otherwise be expected.[8]

Monitoring samples of **13a–c** by ^{1}H NMR revealed that conversion to homoleptic Tip$_2$Ge=GeTip$_2$ and various unidentified side products takes place even at room temperature, in analogy to what was observed for α-chlorosilyldigermenes **11a–c**. Whereas the reaction mixtures obtained from digermenide **8** and pivaloyl chloride or 2,2-dimethylbutyryl chloride largely decomposed in the course of one night, the 1-adamantoyl-substituted **13c** persisted to about 95% even after 18 h in reaction mixtures at the original concentration. The decomposition rate, however, increased at higher concentrations, which prevented the removal of 1,2-dimethoxyethane (liberated from **8**) from the reaction mixture as well as crystallization attempts from concentrated solutions. The similarity to the decomposition behavior of digermenes **11a–c**, however, suggests that the reaction products may indeed be the unprecedented acyldigermenes **13a–c**. Due to its superior stability in solution, we limit the following discussion to the 1-adamantoyl derivative **13c** (see the Supporting Information for spectra of **13a**,**b**).

The ^{13}C NMR spectrum of **13c** at 300 K features two signals at $\delta = 232.4$ and 238.7 ppm, in the typical range for carbonyl C atoms, which we attribute to the s-*cis* and s-*trans* isomers of the Ge=Ge–C=O system. Theoretical calculations on their relative thermodynamic stabilities at the M06-2X(D3)/def2-TZVPP//BP86(D3)def2-SVP level of theory predicted the s-*cis* isomer (dihedral angle $\phi = 51.64°$) to be 10.9 kcal mol^{-1} more stable than the s-*trans* form ($\phi = -149.13°$). The IR band at 1649 cm^{-1} validates the presence of a C=O bond attached to germanium in **13c**, and is in acceptable agreement with the calculated value of 1690 cm^{-1} for the s-*cis* isomer. A shift of around 70 cm^{-1} to lower wavenumbers compared to fully organic ketones is well known for acylsilanes and -germanes, and has been rationalized in terms of lowering of the C–O bond order due to the σ donating character of the tetryl moiety.[19] In the UV/Vis spectrum of **13c**, two bands at $\lambda_{max} = 476$ nm and $\lambda = 386$ nm further support the proposed open-chain structure: the longest-wavelength absorption maximum falls within the typical absorption range of digermenes and shows a substantial bathochromic shift compared to the bands observed for **8** ($\lambda_{max} = 435$ nm), **9b** ($\lambda_{max} = 424$ nm), and **10** ($\lambda_{max} = 426$ nm), presumably due to strong polarization of the Ge=Ge moiety by the attached C–O double bond.[13] In contrast, the longest-wavelength absorptions of the cyclic Brook germenes **3a–c** ($\lambda_{max} = 351$, 355, and 354 nm) have been reported to be significantly blue-shifted compared to the corresponding peaks for disilenide **1**.[8] Even the second absorption of **13c** at $\lambda_{max} = 386$ nm is red-shifted compared to the bands of **3a–c**. The excellent agreement with λ_{max} of reported germyl-substituted ketones Et$_3$GeCOMe ($\lambda_{max} = 380$ nm) and Ph$_3$GeCOMe ($\lambda_{max} = 380$ nm) corroborates the presence of a C=O double bond in **13c**.[19b] The bathochromic shift observed in comparison to all-organic ketones (which typically absorb in the UV region) can be explained in terms of mixing of the oxygen-centered lone pair with the Ge–C bond.[19b,e,f,20]

Further support for the assignment was sought by performing time-dependent DFT calculations on **13c** at the M06-2X(D3)/def2-SVP level of theory. The predicted longest-wavelength absorption at $\lambda_{Ge=Ge,calc.} = 468$ nm is in excellent agreement with the experimental value $\lambda_{Ge=Ge,exp.} = 476$ nm and is mainly due to the HOMO→LUMO transition. The second-longest absorption wavelength $\lambda_{C=O,calc.} = 401$ nm also exhibits satisfactory agreement with the experimental value $\lambda_{C=O,exp.} = 386$ nm and stems from a complex transition with HOMO−1→LUMO as its main component. The HOMO−1 resembles the π-symmetric nonbonding orbital of an isolated carbonyl group, whereas the HOMO is the π orbital of the Ge=Ge double bond (Figure 2).[21] The two orbitals are only marginally intermixed, providing little evidence of conjugation. In contrast, the LUMO

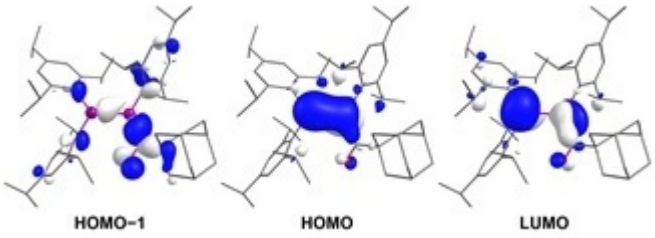


Figure 2. Selected Kohn–Sham orbitals of **13c** at the M06-2X(D3)/def2-SVP level of theory.

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is clearly a shared π* orbital of the conjugated Ge=Ge–C=O system resulting from substantial antibonding contributions of both the Ge=Ge double bond and the carbonyl group. Overestimation of this mixing between HOMO−1 and HOMO accounts for both the blue-shift of $\lambda_{Ge=Ge}$ and the red-shift of $\lambda_{C=O}$ in the calculated UV/Vis spectrum. The tendency of DFT methods to overvalue conjugation is well known.[22]

The strongest evidence for the existence of a persistent acyldigermene **13c** was finally provided by quenching with methanol. It should be noted that the cyclic adamantyl-substituted Brook silene **3b** has been reported to be inert towards MeOH in the absence of a base. The cyclic structure is retained, however, after base-catalyzed addition of MeOH to the Si=C moiety of **3b**.[8] In contrast, the reaction of **13c** with MeOH in toluene proceeds even at 0 °C and results in the formation of acyldigermane **15**, which can be isolated as pale-yellow crystals in 60% yield from a filtered and concentrated solution in hexane.

Single-crystal X-ray diffraction analysis confirmed the constitution of **15** as the 1,2-addition product of methanol to the Ge=Ge bond of **13c** (Figure 3). The Ge1–Ge2 distance of 2.4694(5) Å is in the expected range for Ge–Ge single bonds. The CO double-bond length of 1.215(3) Å is also unremarkable. The IR spectrum of **15** shows the expected bands for the Ge–H (2037 cm^{-1}) and C=O (1647 cm^{-1}) stretching modes, and the carbonyl moiety gives rise to a signal at $\delta = 238.6$ ppm in the ^{13}C NMR spectrum, similar to that of the acyldigermene starting material **13c**. The similarity of the ^{13}C NMR shifts and IR bands of α,β-unsaturated **13c** and saturated **15** confirms that π-conjugation between the Ge=Ge moiety and the carbonyl group in acyldigermene **13c** is insignificant and that solely the inductive effect of the digermanium moiety accounts for the observed differences to organic ketones. Conversely, the electron-withdrawing carbonyl moiety induces strong polarization of the Ge–Ge double bond towards the acyl-substituted terminus, as is evident from the regioselective addition of methanol.

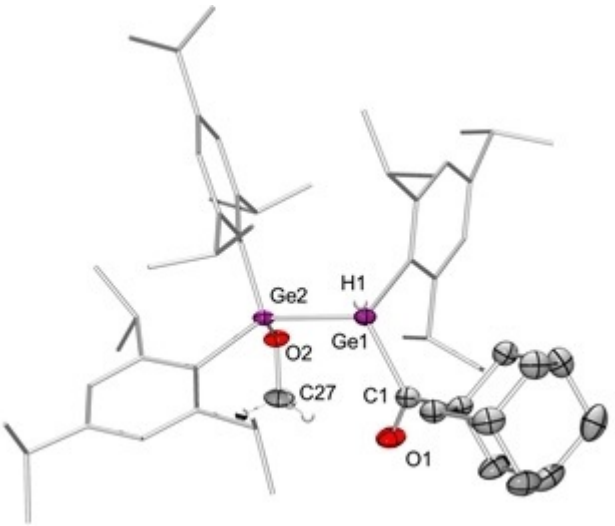
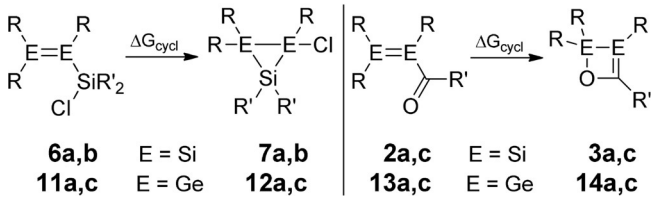


Figure 3. Molecular structure of acyldigermane **15** in the solid state (carbon-bonded hydrogen atoms omitted for clarity; thermal ellipsoids drawn at 50% probability). Selected bond lengths (Å) and angles (°): Ge1–Ge2 2.4694(5), Ge1–C1 2.041(3), C1–O1 1.215(3), Ge2–O2 1.8189(17); Ge1–C1–O1 118.7(2).

The sum of available evidence leaves no doubt that we have prepared the first persistent acyldigermenes **13a–c**, which, unlike the acyldisilenes (only proposed as intermediates), show no tendency for cyclization at room temperature but instead readily decompose by facile dissociation of the Ge=Ge bond. As similar conclusions apply to α-silyldigermenes **11a–c** (see above), the electronic structures and thermodynamic properties vary substantially between functionalized disilenes and digermenes. We therefore sought to shed some light on the underlying reasons by performing DFT calculations.

Theoretical results

In order to rationalize the strongly differing inclinations of digermenes **11a–c** and **13a–c** towards cyclization compared to their lighter silicon analogues **2a–c** and **6a,b**, we took a closer look at the thermodynamics of these rearrangements (Scheme 8). To enable comparison, we restricted our investigations to those systems for which both the disilene and digermene are now known. In the case of the adamantyl-substituted acyldigermene **13c**, the s-*cis* conformer is thermodynamically favored over the s-*trans* conformer (see the Supporting Information) and we generalized these findings for the remaining acylmetallenes without further verification. The calculated free enthalpies of cyclization ΔG_{cycl} at the M06-2X(D3)/def2-TZVPP//BP86(D3)/def2-SVP level of theory for α-chlorosilyldigermenes **11a,c**, the corresponding disilenes **6a,b**, the s-*cis* acyldigermenes **13a,c**, and their silicon analogues **2a,c** show a clear trend (Table 2).



Scheme 8. Theoretically investigated cyclizations of α-chlorosilyldimetallenes **6a,b** and **11a,c** as well as acyldimetallenes **2a,c** and **13a,c** (R = Tip = 2,4,6-*i*$Pr_3C_6H_2$; **6a**, **7a**: E = Si, R′ = Me; **6b**, **7b**: E = Si, R′ = Ph; **11a**, **12a**: E = Ge, R′ = Me; **11c**, **12c**: E = Ge, R′ = Ph; **2a**, **3a**: E = Si, R′ = *t*Bu; **2c**, **3c**: E = Si, R′ = 1-adamantyl; **13a**, **14a**: E = Ge, R′ = *t*Bu; **13c**, **14c**: E = Ge, R′ = 1-adamantyl).

While the acyclic digermenes **11a,c** and **13a,c** show slightly endergonic or exergonic ΔG_{cycl} values near 0 kcal mol^{-1}, the corresponding disilenes **6a,b** and **2a,c** exhibit far more negative cyclization enthalpies ranging from −5.1 to −17.9 kcal mol^{-1}, in line with the observed trend for the formation of small rings **7a,b** and **3a,c**. Geometric ring parameters of cyclic silicon systems and their germanium analogues do not differ significantly (see the Supporting Information), and so differences in ring strain are unlikely to be a destabilizing factor. Therefore, to a first approximation, ΔG_{cycl} can be taken as a measure of the bond dissociation energy (BDE) balance of the cycliza-

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Table 2. Calculated free reaction enthalpies ΔG_{cycl} at the M06-2X(D3)/def2-TZVPP//BP86(D3)/def2-SVP level of theory.

	E	R′	ΔG_{cycl} [kcal mol^{-1}]
11 a/12 a	Ge	Me	+2.6
11 c/12 c	Ge	Ph	+0.02
6 a/7 a	Si	Me	−7.6
6 b/7 b	Si	Ph	−5.1
13 a/14 a	Ge	*t*Bu	−2.5
13 c/14 c	Ge	1-Ad	−3.1
2 a/3 a	Si	*t*Bu	−17.9
2 c/3 c	Si	1-Ad	−16.9

tion. While an Si–Cl bond appears in both the starting material and the product during the formation of cyclotrisilanes **7 a**,**b** and hence is unlikely to exert a pronounced influence on ΔG_{cycl}, the difference in BDEs of Si–Cl (ca. 100 kcal mol^{-1})[23] and Ge–Cl (ca. 93 kcal mol^{-1})[23] of about 7 kcal mol^{-1} is apparently responsible for the higher ΔG_{cycl} values of **12 a**,**c**. Similarly, the much more negative ΔG_{cycl} values of acyldisilenes compared to digermenes can be rationalized in terms of the higher BDE of Si–O bonds (ca. 191 kcal mol^{-1}) compared to Ge–O bonds (ca. 158 kcal mol^{-1}).[23]

Conclusions

Functionalized digermenes, namely α-chlorosilyldigermenes **11 a**–**c** and acyldigermenes **13 a**–**c**, have been synthesized and their stability has been studied. The rich cyclization chemistry of the corresponding functional disilenes appears not to be reflected by the analogous germanium systems. None of the systems shows a detectable tendency towards cyclization; instead, they slowly decompose under ambient conditions to the homoleptic $Tip_2Ge{=}GeTip_2$ and unidentified side products. Chlorosilyldisilenes **13 a**–**c** have been identified by detailed comparison of their NMR spectra with those of their silicon analogues. In addition, the newly synthesized triphenylsilyldigermene **10** has been fully characterized as the first neutral digermene with an $A_2Ge{=}GeAB$ substitution pattern. IR and UV/Vis spectra of **13 c** as well as trapping with methanol to yield digermane **15** provide evidence for the synthesis of acyldigermenes **13 a**–**c**, which, to the best of our knowledge, are the first isolated examples of acyldimetallenes of any heavier main group element. Considering the wide scope of reactions that α,β-unsaturated ketones are known for in organic chemistry, our current focus is on exploring the synthetic potential of **13 a**–**c**.

Experimental Section

All reactions were carried out under a protective argon atmosphere using the Schlenk technique or gloveboxes. Pentane was heated to reflux with sodium/benzophenone and distilled prior to use. Hexane and toluene were taken directly from a solvent purification system (Innovative Technology PureSolv MD7). Deuterated benzene was heated to reflux over potassium and distilled prior to use. NMR spectra were recorded at 300 K on a Bruker Avance III 300 (^{1}H: 300.13 MHz, ^{7}Li: 116.59 MHz, ^{29}Si: 59.6 MHz) or Bruker Avance III HD 400 instrument (^{1}H: 400.13 MHz, ^{13}C: 100.61 MHz, ^{29}Si: 79.5 MHz). Chemical shifts are reported relative to $SiMe_4$. UV/Vis spectra were measured on a Shimadzu UV-2600 spectrometer from solutions in quartz cells with a path length of 1 mm. Fourier-transform IR spectra were acquired on a Bruker Vertex 70 spectrometer in attenuated total reflectance (ATR) mode. Elemental analyses were carried out on an Elementar Vario Micro Cube and show slightly suppressed carbon and hydrogen contents for digermenes **10**, **11 a**, and **13 a**–**c** as a result of their extraordinary sensitivity towards oxygen. Methanol, dichlorodimethylsilane, dichloromethylphenylsilane, dichlorodiphenylsilane, pivaloyl chloride, and 2,2-dimethylbutyryl chloride were boiled over magnesium and distilled prior to use. 1-Adamantoyl chloride was recrystallized from hexane prior to use. Chlorotriphenylsilane was dried in vacuo and stored under argon prior to use. Digermenide **8** was prepared according to our published procedure.[13] For theoretical data, crystallographic details, and plots of spectra, see the Supporting Information. CCDC 1920322 (**10**) and 1920323 (**15**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Center.

Synthesis and characterization

$Tip_2Ge{=}Ge(Tip)SiPh_3$ (10): Digermenide **8** (600 mg, 0.58 mmol) and chlorotriphenylsilane (171 mg, 0.58 mmol, 1 equiv.) were mixed as solids in a Schlenk flask and toluene (6 mL) was added by means of a syringe. The reaction mixture was stirred overnight at room temperature, whereupon a white precipitate was formed. After removal of the solvent in vacuo, hexane (10 mL) was added, and the mixture was filtered through a cannula to remove insoluble material. Reducing the volume to approximately 1.5 mL gave a dark-red solution, from which 308 mg (52%) of digermene **10** was obtained as crystalline yellow plates (m.p. 177 °C; dec.). ^{1}H NMR (400 MHz, C_6D_6, 300 K, TMS): δ = 7.75 (d, ^3J = 6.88 Hz, 6 H; *m*-Ph-*H*), 7.06 (s, 2 H; Tip-*H*), 7.05 (br, 3 H; *p*-Ph-*H*), 7.01 (s, 2 H; Tip-*H*), 6.99 (s, 3 H; *o*-Ph-*H*), 6.97 (s, 3 H; *o*-Ph-*H*), 6.95 (s, 2 H; Tip-*H*), 3.85 (sept, ^3J = 6.61 Hz, 2 H; *i*Pr-C*H*), 3.80–3.69 (m, 4 H; *i*Pr-C*H*), 2.73 (sept, ^3J = 6.90 Hz, 3 H; *i*Pr-C*H*), 1.26 (br d, 6 H; *i*Pr-CH_3), 1.20, 1.17, 1.14 (each d, ^3J = 6.94 Hz, 6 H each; *i*Pr-CH_3), 1.10–0.84 (d & v br, ^3J = 6.54 Hz, altogether 24 H; *i*Pr-CH_3), 0.74 ppm (br d, 6 H; *i*Pr-CH_3); ^{13}C NMR (100.61 MHz, C_6D_6, 300 K, TMS): δ = 153.2, 152.9, 151.9, 149.8, 149.4, 149.2, 146.4, 143.9, 139.7 (each s; Tip-*C*), 136.9, 136.0, 129.1, 127.5 (each s; Ph-*C*), 122.3, 122.0, 121.4 (each s; Tip-*C*), 38.3, 37.1, 37.0, 34.3, 34.2, 34.1 (each s; *i*Pr-CH), 24.8, 24.4, 24.1, 23.9, 23.9, 23.7 ppm (each s, *i*Pr-CH_3); ^{29}Si{^{1}H} NMR (79.5 MHz, C_6D_6, 300 K, TMS): δ = 1.9 ppm; UV/Vis (hexane): λ_{max} = 425 nm (ε = 20843 L mol^{-1} cm^{-1}); elemental analysis calcd (%) for $C_{63}H_{84}Ge_2Si$ (1014.71): C 74.57, H 8.34; found: C 73.26, H 8.02.

$Tip_2Ge{=}Ge(Tip)SiMe_2Cl$ (11 a): Digermenide **8** (212 mg, 0.2 mmol) was dissolved in toluene (8 mL) and the solution was cooled to −60 °C. Dropwise addition to a solution of dichlorodimethylsilane (53 mg, 50 μL, 0.41 mmol, 2 equiv.) in toluene (2 mL) at −60 °C led to an immediate color change to bright-orange. The reaction mixture was stirred overnight and allowed to reach room temperature. After removal of the solvent and volatiles in vacuo, hexane (6 mL) was added and the mixture was filtered. Although formation of **11 a** and the purity of the orange-red filtrate were confirmed by NMR spectroscopy, no crystals could be obtained under any conditions. ^{1}H NMR (400.13 MHz, C_6D_6, 300 K, TMS): δ = 7.12, 7.09, 7.02 (each s, 2 H each, altogether 6 H; Tip-*H*), 3.89, 3.75, 3.59 (each sept, ^3J = 6.75 Hz, 2 H each, altogether 6 H; Tip-Pr-C*H*), 2.85–2.63 (m, 3 H; Tip-Pr-C*H*), 1.33 (d, ^3J = 6.47 Hz, 12 H; Tip-Pr-CH_3), 1.27 (br d, ^3J = 6.07 Hz, 9 H; Tip-Pr-CH_3), 1.21, 1.18 (each d, ^3J = 6.85 Hz, 9 H each;

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Tip-Pr-CH_3), 1.11 (d, ^3J=6.85 Hz, 6H; Tip-Pr-CH_3), 0.99 (d, ^3J=6.85 Hz, 9H; Tip-Pr-CH_3), 0.58 ppm (s, 6H; Si-CH_3); ^{13}C NMR (100.61 MHz, C_6D_6, 300 K, TMS): δ=153.1, 153.4, 152.5, 150.9, 150.1, 149.8, 145.8, 143.7, 139.3, 122.6, 122.4, 122.0 (Tip-Ar-*C*), 38.7, 37.6, 37.5, 34.8, 34.7, 34.4 (Tip-Pr-*C*H), 25.3, 25.0, 24.6, 24.3, 24.2, 24.0 (Tip-Pr-CH_3), 7.4 ppm (Si-CH_3); ^{29}Si{^{1}H} NMR (79.5 MHz, 300 K, C_6D_6, TMS): δ=31.5 ppm; UV/Vis (hexane): λ_{max}=435 nm (ε=11 080 L mol^{-1} cm^{-1}); elemental analysis calcd (%) for $C_{47}H_{75}ClGe_2Si$ (848.91): C 66.50, H 8.91; found: C 65.60, H 8.55.

Tip$_2$Ge=Ge(Tip)SiMePhCl (11 b): Digermenide **8** (265 mg, 0.26 mmol) was dissolved in toluene (8 mL) and the solution was cooled to −60 °C. Dropwise addition to a solution of dichloromethylphenylsilane (59 mg, 50 µL, 0.31 mmol, 1.2 equiv.) in toluene (2 mL) at −60 °C led to an immediate color change to bright-orange. The reaction mixture was allowed to reach room temperature, whereupon it turned yellow-green due to the formation of a small amount of tetragermabutadiene (not detectable in the ^{1}H NMR spectrum). After removal of the solvent and volatiles in vacuo at 60 °C, hexane (8 mL) was added and the mixture was filtered. Although formation of **11 b** and the purity of the product solution were confirmed by NMR spectroscopy, no crystals could be obtained under any conditions. ^{1}H NMR (400.13 MHz, C_6D_6, 300 K, TMS): δ=7.74 (d, J=6.58 Hz, 2H; Si-Ph-*H*), 7.12 (s, 2H; Tip-*H*), 7.03 (s, 2H; Tip-*H*), 7.03 (s, 2H; Tip-*H*), 7.00–6.90 (m, 3H, overlapping with $MePhSiCl_2$; Si-Ph-*H*), 3.92 (sept, ^3J=7.05 Hz, 2H; Tip-*i*Pr-C*H*), 3.76 (sept, ^3J=7.05 Hz, 2H; Tip-*i*Pr-C*H*), 3.62 (sept, ^3J=6.35 Hz, 2H; Tip-*i*Pr-C*H*), 2.79–2.63 (m, 3H; Tip-*i*Pr-C*H*), 1.28 (d, ^3J=6.30 Hz, 12H; Tip-*i*Pr-CH_3), 1.20, 1.17 (each d, ^3J=7.16 Hz, altogether 18H; Tip-*i*Pr-CH_3), 1.11 (d, ^3J=6.77 Hz, 12H; Tip-*i*Pr-CH_3), 1.04 (d, ^3J=6.77 Hz, 6H; Tip-*i*Pr-CH_3), 0.96 (d, ^3J=6.37 Hz, 6H; Tip-*i*Pr-CH_3), 0.81 ppm (s, 3H, Si-CH_3); ^{13}C NMR (100.61 MHz, C_6D_6, 300 K, TMS): δ=154.2, 154.2, 152.5, 150.9, 150.2, 149.9, 146.0, 144.0, 138.0 (Tip-Ar-*C*), 134.7 (Si-Ph-*C*), 133.7 (Cl_2MeSiPh-*C*), 133.5 (Si-Ph-*C*), 133.4, 131.7 (Cl_2MeSiPh-*C*), 131.2, 130.2 (Si-Ph-*C*), 128.6 (Cl_2MeSiPh-*C*), 122.7, 122.4, 122.1 (Tip-Ar-*C*), 37.7, 37.6, 34.7, 34.7, 34.4 (Tip-*i*Pr-*C*H), 24.9, 24.6, 24.6, 24.2, 24.2, 24.0, 24.0 (Tip-*i*Pr-CH_3), 6.8 (Si-CH_3), 5.1 ppm (Cl_2PhSi-CH_3); ^{29}Si{^{1}H} NMR (79.5 MHz, 300 K, C_6D_6, TMS): δ=23.7 ppm.

Tip$_2$Ge=Ge(Tip)SiPh$_2$Cl (11 c): Digermenide **8** (246 mg, 0.24 mmol) was dissolved in toluene (5 mL) and the solution was cooled to −70 °C. Dropwise addition to a solution of dichlorodiphenylsilane (60.4 mg, 50 µL, 0.24 mmol, 1 equiv.) in toluene (2 mL) at −70 °C led to an immediate color change to dark-red-orange. The reaction mixture was allowed to reach room temperature, whereupon it turned deep-green due to the formation of tetragermabutadiene (ca. 2%, as determined by ^{1}H NMR spectroscopy). After removal of the solvent and volatiles in vacuo, hexane (8 mL) was added, the mixture was filtered, and the filtrate was concentrated to a volume of 1 mL. At −26 °C, traces of tetragermabutadiene crystallized, which could be filtered off from the orange mother liquor. Although the formation of **11 c** was confirmed by NMR spectroscopy, no crystals could be obtained under any conditions due to the presence of side products. ^{1}H NMR (400.13 MHz, C_6D_6, 300 K, TMS): *Due to strong overlap with the signals of Tip$_4$-digermene, tetragermabutadiene, toluene, and remaining Ph$_2$SiCl$_2$, detailed assignment and integration of the signals was only possible to a limited extent.* δ=7.65 (dd, ^3J=7.91 Hz, ^4J=1.53 Hz, 4H; Ph-*H*), 7.07–6.97 (m, 8H; Tip-*H* & Ph-*H*, masked by signals of side products), 6.90 (t, ^3J=7.51 Hz, 4H; Ph-*H*), 3.87–3.73 (m, 4H; Tip-*i*Pr-C*H*), 3.59 (sept, ^3J=6.44 Hz, 2H; Tip-*i*Pr-C*H*), 2.77–2.65 (m, 3H; Tip-*i*Pr-C*H*, overlapping with signals of side products), 1.21–1.17 (m, 18H; Tip-*i*Pr-CH_3, overlapping with signals of side products), 1.13–1.08 (m, 24H; Tip-*i*Pr-CH_3, overlapping with signals of side products), 0.99 ppm (d, ^3J=6.54 Hz, 12H; Tip-*i*Pr-CH_3); ^{13}C NMR (100.61 MHz, C_6D_6, 300 K, TMS): δ=154.0, 153.3, 152.2, 150.7, 150.1, 149.8, 146.4, 144.2, 138.7 (Tip-Ar-*C*), 137.8 (Tol-Ar-*C*), 136.5, 135.9, 134.5, 134.4, 132.2, 131.8, 130.3 (Ph-Ar-*C*), 129.2, 128.5 (Tol-Ar-*C*), 128.5 (Ph-Ar-*C*), 125.6 (Tol-Ar-*C*), 122.7, 122.3, 121.8 (Tip-Ar-*C*), 38.8, 38.0, 37.3, 34.6, 34.5, 34.3 (Tip-*i*Pr-*C*H), 24.9, 24.5, 24.2, 24.1, 24.0, 23.9 (Tip-*i*Pr-CH_3), 7.4 ppm (toluene-CH_3); ^{29}Si{^{1}H} NMR (79.5 MHz, 300 K, C_6D_6, TMS): δ=15.2 ppm.

Tip$_2$Ge=Ge(Tip)-CO-*t*Bu (13 a): Pivaloyl chloride (4.0 µL, 0.032 mmol, 1 equiv.) was added at room temperature to a solution of digermenide **8** (30 mg, 0.032 mmol) in C_6D_6 (0.5 mL). The solution instantly turned dark-red and ^{1}H NMR confirmed the selective formation of acyldigermene **13 a**. In an attempted crystallization, digermenide **8** (402 mg, 0.389 mmol) was suspended in pentane (8 mL) and pivaloyl chloride (48 µL, 0.389 mmol, 1 equiv.) was added, which again afforded a dark-red solution. Insoluble material was filtered off after stirring for 15 min at room temperature, and the filtrate was concentrated. Crystals of **13 a** could not be obtained. ^{1}H NMR (300 MHz, C_6D_6, 300 K, TMS): δ=7.10 (s, 2H; Tip-*H*), 7.07 (s, 4H; Tip-*H*), 3.97 (sept, ^3J=6.74 Hz, 2H; Tip-*i*Pr-C*H*), 3.70 (sept, ^3J=6.78 Hz, 4H; Tip-*i*Pr-C*H*), 3.33, 3.13 (each s, altogether 20H; dme), 2.77–2.68 (m, 3H; Tip-*i*Pr-C*H*), 1.24–1.15 ppm (m, 63H; Tip-*i*Pr-CH_3, *t*Bu-CH_3); ^{13}C NMR (75 MHz, C_6D_6, 300 K, TMS): δ=154.3, 153.4, 150.4, 150.3, 142.4, 141.6, 122.5, 122.0 (Tip-Ar-*C*), 72.2 (dme), 58.7 (dme), 38.4, 36.2, 34.7, 34.6 (Tip-*i*Pr-*C*H), 28.0, 25.2, 25.0 (Tip-*i*Pr-CH_3), 24.5 (*t*Bu-*C*), 24.2 (Tip-*i*Pr-CH_3), 24.1 ppm (*t*Bu-CH_3); UV/Vis (hexane): λ_{max}=472 (4770), 383 nm (2750 L mol^{-1} cm^{-1}); IR (powder): ν(CO)=1652 cm^{-1}; elemental analysis calcd (%) for $C_{50}H_{78}Ge_2O$ (840.43): C 71.46, H 9.36; found: C 70.61, H 9.03.

Tip$_2$Ge=Ge(Tip)-CO-*t*Pent (13 b): 2,2-Dimethylbutyryl chloride (4.0 µL, 0.029 mmol) was added at room temperature to a solution of digermenide **8** (30 mg, 0.029 mmol) in C_6D_6 (0.5 mL). The solution instantly turned dark-red and ^{1}H NMR confirmed the selective formation of acyldigermene **13 b**. In an attempted crystallization, digermenide **8** (383 mg, 0.406 mmol) was suspended in pentane (6.5 mL) and 2,2-dimethylbutyryl chloride (56 µL, 0.406 mmol, 1 equiv.) was added, which again afforded a dark-red solution. After stirring for 15 min at room temperature, insoluble material was filtered off, and the filtrate was concentrated. A second crystallization attempt was made from hexane instead of pentane, but in neither case were crystals of **13 b** obtained. ^{1}H NMR (300 MHz, C_6D_6, 300 K, TMS): δ=7.13 (s, 2H; Tip-*H*), 7.09 (s, 4H; Tip-*H*), 4.03 (sept, ^3J=7.30 Hz, 2H; Tip-*i*Pr-C*H*), 3.75 (sept, ^3J=7.30 Hz, 4H; Tip-*i*Pr-C*H*), 3.34, 3.13 (each s, altogether 30H; dme), 2.75–2.73 (m, 3H; Tip-*i*Pr-C*H*), 1.65 (quart, ^3J=7.63 Hz, 2H; *t*pentyl-CH_2), 1.24, 1.23 (each d, ^3J=6.80 Hz, altogether 36H; Tip-*i*Pr-CH_3), 1.18–1.15 (m, 24H; Tip-*i*Pr-CH_3, *t*pentyl-CH_3), 0.79 ppm (t, ^3J=7.30 Hz, 3H; *t*pentyl-CH_2-CH_3); ^{13}C NMR (75 MHz, C_6D_6, 300 K, TMS): δ=154.4, 153.5, 150.4, 150.3, 142.6, 122.5, 121.9 (Tip-Ar-*C*), 72.3 (dme), 58.7 (dme), 38.4, 35.8, 34.7, 34.6 (Tip-*i*Pr-*C*H), 25.3, 25.0 (Tip-*i*Pr-CH_3), 24.9 ($C_{quart.}$), 24.1, 24.1 (*i*Pr-CH_3, *t*pentyl-CH_3), 8.9 ppm (*t*pentyl-CH_3); UV/Vis (hexane): λ_{max}=474 (4820), 382 nm (2780 L mol^{-1} cm^{-1}); IR (powder): ν(CO)=1653 cm^{-1}; elemental analysis calcd (%) for $C_{51}H_{80}Ge_2O$ (854.46): C 71.69, H 9.44; found: C 70.94, H 9.08.

Tip$_2$Ge=Ge(Tip)-CO-1-Ad (13 c): 1-Adamantoyl chloride (6.4 mg, 0.032 mmol, 1.0 equiv.) in C_6D_6 (0.25 mL) was added at room temperature to a solution of digermenide **8** (30 mg, 0.032 mmol) in C_6D_6 (0.25 mL). The solution instantly turned dark-red and ^{1}H NMR confirmed the selective formation of acyldigermene **13 c**. In an attempted crystallization, pentane (5 mL) was added to a mixture of digermenide **8** (300 mg, 0.318 mmol) and 1-adamantoyl chloride (63 mg, 0.318 mmol, 1.0 equiv.), which again afforded a dark-red solution. After stirring for 15 min at room temperature, insoluble material was filtered off, and the filtrate was concentrated. A

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second crystallization attempt was made using hexane instead of pentane, but in neither case were crystals of **13c** obtained. ^{1}H NMR (300 MHz, C_6D_6, 300 K, TMS): $\delta = 7.13$ (s, 2H; Tip-*H*), 7.09 (s, 4H; Tip-*H*), 4.04 (sept, $^3J = 7.11$ Hz, 2H; Tip-*i*Pr-C*H*), 3.76 (br sept, $^3J = 6.56$ Hz, 4H; Tip-*i*Pr-C*H*), 3.34, 3.13 (each s, altogether 20H; dme), 2.74 (sept, $^3J = 6.85$ Hz, 3H; Tip-*i*Pr-C*H*), 2.01 (s, 6H; Ad-α-CH_2), 1.79 (s, 3H; Ad-β-C*H*), 1.50 (s, 6H; Ad-γ-CH_2), 1.28–1.23 (m, 36H; Tip-*i*Pr-CH_3), 1.18–1.15 ppm (m, 18H; Tip-*i*Pr-CH_3); ^{13}C NMR (100.61 MHz, C_6D_6, 300 K, TMS): $\delta = 232.4$ (C=O), 154.4, 153.4, 150.4, 150.2, 142.5, 141.4 (Tip-Ar-*C*), 127.9 (Tip-Ar-*C*, masked by solvent), 122.5, 121.9 (Tip-Ar-*C*), 72.3, 58.7 (dme), 51.5 (br; Ad-C_{quart}), 40.5 (br; Ad-α-CH_2), 38.5, 37.0 (Tip-*i*Pr-CH), 36.0 (br; Ad-γ-CH_2), 34.6 (Tip-*i*Pr-CH), 28.7 (Ad-β-CH), 25.3, 25.1, 24.1 ppm (Tip-*i*Pr-CH_3); UV/Vis (hexane): $\lambda_{max} = 476$ (4140), 385 nm (2240 L mol^{-1} cm^{-1}); IR (powder): ν(CO) = 1649 cm^{-1}; elemental analysis calcd (%) for $C_{55}H_{82}Ge_2O$ (918.55): C 73.23, H 9.22; found: C 72.22, H 9.15.

Tip$_2$(OMe)Ge–GeH(Tip)-CO-1-Ad (15): 1-Adamantoyl chloride (50.7 mg, 0.26 mmol, 1.0 equiv.) and digermenide **8** (240 mg, 0.26 mmol) were combined in a flask and toluene (5 mL) was added. The reaction mixture immediately turned dark-orange and was then cooled to −60 °C. Neat MeOH (12 μL, 9.8 mg, 0.31 mmol, 1.2 equiv.) was added to the cold reaction mixture and the cooling bath was removed. After reaching room temperature, all volatiles were removed from the green solution in vacuo and the remaining solid was redissolved in hexane (10 mL). The solution was filtered through a cannula. The green filtrate was concentrated to about 1 mL and stored at room temperature overnight, whereupon digermane **15** crystallized as 146 mg (60%) of pale-yellow needles. ^{1}H NMR (400.13 MHz, C_6D_6, 300 K, TMS): *The crystalline sample of* **15** *contained approximately 10% of the regioisomer* Tip$_2$HGe–Ge(OMe)(Tip)-CO-1-Ad **15′**, *which could not be removed by purification methods due to the chemical similarity between* **15** *and* **15′**. *Hence, integrals are overestimated in the spectrum.* $\delta = 7.22$ (d, 1H; Tip-*H*), 7.16 (br, masked by signal of C_6D_5H, 1H; Tip-*H*), 7.08 (d, 1H; Tip-*H*), 7.02 (d, 1H; Tip-*H*), 6.98 (d, 1H; Tip-*H*), 6.89 (d, 1H; Tip-*H*), 6.46 (s, 1H; Ge-*H*), 3.90 (s, 3H; OCH_3), 3.80 (sept, 1H; Tip-*i*Pr-C*H*), 3.61 (sept, 1H; Tip-*i*Pr-C*H*), 3.50 (sept, 1H; Tip-*i*Pr-C*H*), 3.38 (sept, 1H; Tip-*i*Pr-C*H*), 3.24 (sept, 1H; Tip-*i*Pr-C*H*), 2.94 (sept, 1H; Tip-*i*Pr-C*H*), 2.83–2.64 (m, 3H; Tip-*i*Pr-C*H*), 2.08 (br d, 3H; Ad-α-CH_2), 1.90 (br d, 3H; Ad-α-CH_2), 1.76 (br, 3H; Ad-β-C*H*), 1.63 (d, 3H; Tip-*i*Pr-CH_3), 1.55, 1.53 (each d, altogether 6H; Tip-*i*Pr-CH_3), 1.43 (br, 6H; Ad-γ-CH_2), 1.41 (d, 3H; Tip-*i*Pr-CH_3), 1.35 (d, 6H; Tip-*i*Pr-CH_3), 1.31 (d, 3H; Tip-*i*Pr-CH_3), 1.22 (d, 3H; Tip-*i*Pr-CH_3), 1.20 (d, 3H; Tip-*i*Pr-CH_3), 1.18–1.12 (m, 15H; Tip-*i*Pr-CH_3), 0.47 (d, 6H; Tip-*i*Pr-CH_3), 0.39 (d, 3H; Tip-*i*Pr-CH_3), 0.33 ppm (d, 3H; Tip-*i*Pr-CH_3); ^{13}C NMR (100.61 MHz, C_6D_6, 300 K, TMS): $\delta = 238.6$ (C=O), 155.8, 155.3, 155.1, 153.6, 153.5, 152.1, 150.7, 150.4, 150.0, 137.2, 136.8, 132.5, 123.3, 123.1, 122.8, 122.6, 122.2, 121.9 (Tip-Ar-*C*), 55.4 (Ad-C_{quat}), 53.9 (O-CH_3), 38.4, 36.8, 36.3, 35.6, 35.5, 34.6, 33.1, 32.4 (Tip-*i*Pr-CH, Ad-CH, and Ad-CH_2), 28.3, 27.5, 26.9, 25.7, 25.1, 24.9, 24.9, 24.6, 24.3, 24.2, 24.2, 24.1, 24.0, 24.0, 23.9, 23.4, 23.1, 22.9 ppm (Ad-CH_2 and Tip-*i*Pr-CH_3); IR (powder): $\nu = 1647$ (CO), 2037 cm^{-1} (Ge–H); m.p. > 220 °C; elemental analysis calcd (%) for $C_{57}H_{88}Ge_2O_2$ (950.59): C 72.02, H 9.33; found: C 72.17, H 8.99.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: cycloaddition · digermenes · double bonds · germanium · isomerization

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