# *Articles*

# New Digermylalkenes and Digermylalkynes: [1,3]-Chlorine Shifts in Organogermanium Chemistry?

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Dimesitylfluoro(trichloromethyl)germane (**1**) has been synthesized from difluorodimesitylgermane, chloroform, and *n*-butyllithium. Addition of *n*-butyllithium to compound **1** gave the lithium carbenoid $Mes_2(F)Ge-C(Li)Cl_2$ (**2**), which behaves as a synthetic equivalent of the *C*-dichlorogermene $Mes_2Ge{=}CCl_2$ (**5**). Warming **2** to room temperature afforded the 1,2-digermylalkene $Mes_2(F)Ge-CCl{=}CCl-Ge(Cl)Mes_2$ (**6**) possibly by an unprecedented [1,3]-Cl shift from the transient germene $Mes_2(F)Ge-CCl_2-CCl{=}GeMes_2$ (**8**). Addition of *tert*-butyllithium to **6** gave bis(chlorogermyl)alkyne $Mes_2(Cl)Ge-C{\equiv}C-Ge(Cl)Mes_2$ (**9**) probably via a 3-chloro-1-germaallene/(chlorogermyl)alkyne rearrangement.

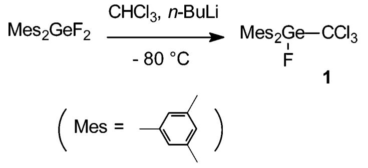
## Introduction

Doubly bonded compounds of heavier group 14 elements $>M{=}C<$ (M = Si, Ge, Sn) are important building blocks in organometallic chemistry due to the more pronounced reactivity of the $>M{=}C<$ double bonds, compared to the corresponding $>C{=}C<$ bonds of their alkene analogues.[1] The introduction of one or two halogen substituents on the sp$^2$ carbon atom should greatly increase the synthetic utility of such compounds. The *C*-dihalophosphaalkenes $Mes^*P{=}CX_2$[2] and arsaalkenes $Mes^*As{=}CX_2$[3] (Mes* = 2,4,6-tri-*tert*-butylphenyl, X = Br, Cl, I), for instance, have proven to be powerful starting materials for the synthesis of functionalized phospha(or arsa)alkenes,[4] phosphaalkynes,[5] and phospha(or arsa)allenes.[6] In contrast to their pnictogen counterparts, *C*-dihalometallaalkenes $>M{=}CX_2$ derivatives (M = Si, Ge, Sn) are still unknown.

Here we describe the preparation of the lithium compound $Mes_2(F)Ge-C(Li)Cl_2$, a potential synthetic equivalent of the *C*-dichloro compound $Mes_2Ge{=}CCl_2$, and its conversion on warming to room temperature into the digermylalkene $Mes_2(F)Ge-CCl{=}CCl-Ge(Cl)Mes_2$. The reaction of the latter with *tert*-butyllithium afforded the digermylalkyne $Mes_2(Cl)Ge-C{\equiv}C-Ge(Cl)Mes_2$. The mechanisms of these reactions and the rearrangements involved are supported by B3LYP/6-31G(d) calculations.

## Results and Discussion

Addition of *n*-butyllithium to a mixture of difluorodimesitylgermane[7] and chloroform afforded the air- and moisture-stable dimesitylfluoro(trichloromethyl)germane (**1**) (eq 1). The structure of **1** was proven by its NMR spectra. The high-field shift in the $^{19}F$ NMR spectrum ($\delta$ $^{19}F = -96.1$ ppm) lies in the expected range for a fluorine atom bonded to a $Mes_2Ge-CR_3$ moiety (for example −105.2 ppm in $Mes_2(F)Ge-CH_2CN$[8]). Moreover a $^{13}C$ NMR signal at 94.96 ppm was observed for the carbon atom bearing three chlorine atoms (comparable to $\delta$ $^{13}C = 77.7$ ppm for $CHCl_3$). The molecular peak was observed in the mass spectrum of **1** (chemical ionization with $NH_3$).



$$Mes_2GeF_2 \xrightarrow[-80\ °C]{CHCl_3,\ n\text{-}BuLi} Mes_2Ge(F)-CCl_3 \quad \mathbf{1} \qquad (1)$$

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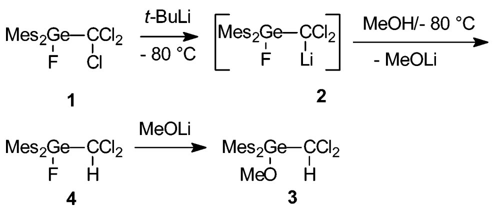
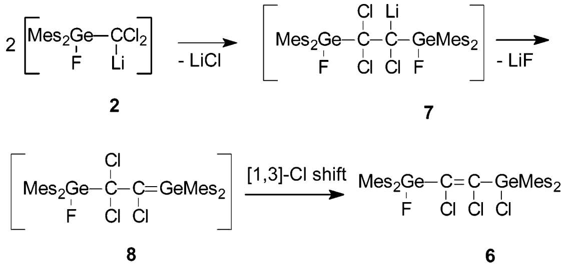
10.1021/om061188j CCC: $37.00

**Scheme 1**



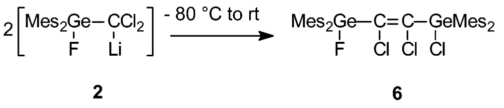
**Scheme 2**



Treatment of fluorogermane **1** with *tert*-butyllithium at low temperature afforded the lithium (fluorogermyl)carbenoid **2**. Quenching **2** with methanol gave the methoxygermane **3** by further reaction of the initially produced fluorogermane **4** with lithium methoxide (Scheme 1).

Formation of **3** by successive elimination of lithium fluoride from **2** to give $Mes_2Ge{=}CCl_2$ **5** followed by addition of methanol to the double bond of **5** can be ruled out since warming **2** to room temperature in the absence of methanol did not give either **5**, its dimer, or a rearrangement product (vide infra). However, since methoxygermane **3** is the anticipated product of the reaction of **5** with methanol, lithium carbenoid **2** can be considered as a synthetic equivalent of the still unknown *C*-dichlorogermene **5**.

**(Chloroalkyl)germene/(Chlorogermyl)alkene Rearrangement.** Warming lithium compound **2** to room temperature surprisingly afforded the 1,2-dichloro(chlorogermyl)(fluorogermyl)ethene **6** in nearly quantitative yield (eq 2). The formation of **6** can be reasonably explained by the selective $\beta$-elimination of LiF from **7**, leading to the transient germene $Mes_2(F)Ge-CCl_2-CCl{=}GeMes_2$ **8** (Scheme 2). Compound **7** could be formed by an "eliminative dimerization" of two molecules of carbenoid **2** (as $Cl_2(H)C-CCl(H)Li$ from $Cl_2(H)CLi$[9]) or by insertion of the carbene $Mes_2(F)Ge-CCl$ into the carbenoid **2**. Germene **8** then undergoes an unprecedented [1,3]-chlorine shift (Scheme 2).



(2)

Unfortunately, attempts to trap any intermediate by 2,3-dimethylbutadiene failed. This prompted us to gain insight into the reaction pathway by theoretical studies. The mechanism of the [1,3]-Cl shift from (chloroalkyl)germene **8** to (chlorogermyl)alkene **6** was investigated by means of DFT B3LYP/6-31G(d) calculations on the model systems **8H** and **6H**, in which the bulky substituents on germanium have been replaced by hydrogen atoms. The relative energies of **8H**, **6H**, and the transition state relating them are given in Figure 1. The barrier of this reaction (59 kJ mol$^{-1}$) is contrastingly lower than that calculated for the [1,3]-Cl shift in 3-chloro-1-propene (216 kJ mol$^{-1}$),[10] which suggests that this process might be facile in **8** as well. This chlorotropic migration affords finally the thermodynamically favorable *E*-dichlorodigermylalkene **6**.

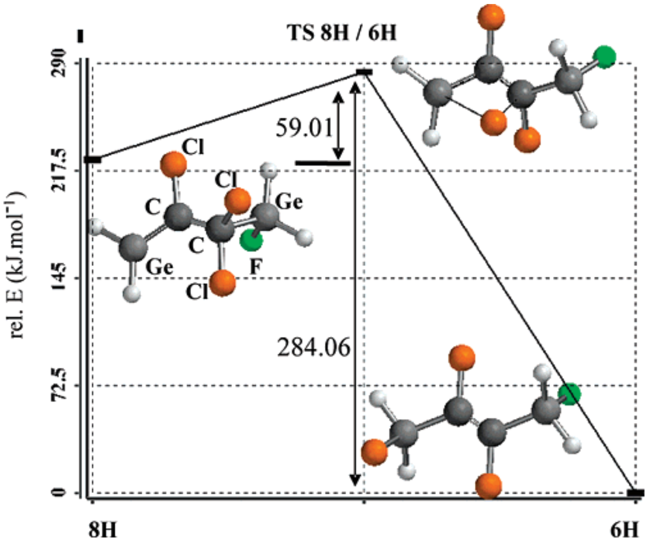
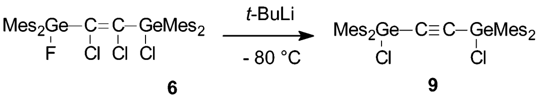


**Figure 1.** B3LYP/6-31G(d)-calculated energies along the [1,3]-Cl shift reaction path in $H_2Ge{=}CCl-CCl_2-GeH_2F$, **8H**.

That alkene **6** is favored over germene **8** could also be expected by consideration of the bond energies involved: the C═C $\pi$-bond energy (250 kJ mol$^{-1}$) is greater than the Ge═C $\pi$-bond (about 130 kJ mol$^{-1}$),[11] whereas CCl and GeCl bond energies are not very different in magnitude (326 and 339 kJ mol$^{-1}$).

The structure of **6** in solution was deduced from its mass and NMR spectra: two sets of signals were observed in the $^1$H NMR spectrum for the nonequivalent $Mes_2Ge(Cl)$ and $Mes_2Ge(F)$ groups and one singlet and one doublet (coupling with fluorine) at 147.53 and 146.34 ppm ($^2J_{CF} = 57$ Hz), respectively, for the ethylenic carbon atoms in the $^{13}$C NMR spectrum. The structure of **6** in the solid state was unambiguously established by a single-crystal X-ray diffraction study (Figure 2), which showed it to be the *trans* isomer (Ge1C1C2Ge2 = 160.94(19)°, Cl3C1C2Cl4 = 174.23(18)°), a finding that is again supported by the calculated path of reaction shown in Figure 1. The bond lengths and bond angles in **6** lie in the normal range expected for such systems.[12]

**Germaallene/Germylalkyne Rearrangement.** The reaction of *tert*-butyllithium with compound **6** afforded bis(chlorodimesitylgermyl)alkyne (**9**) as the sole product. The NMR spectroscopic data are indicative of a symmetrical structure (two singlets for the *o*- and *p*-Me groups of equivalent mesityl groups and a single signal for the acetylenic carbon atoms at $\delta$ $^{13}$C = 114.12 ppm), as well as the absence of a fluorine atom (eq 3).



(3)

The preference for the lithium/chlorine exchange reaction to take place at the carbon atom bearing the $Mes_2Ge(F)$ moiety has been assessed by the B3LYP/6-31G(d) calculations on the enthalpy changes of the isodesmic reactions in eq 4:

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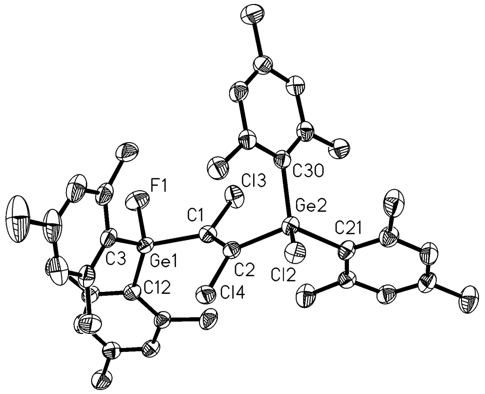


**Figure 2.** Molecular structure of **6** (thermal ellipsoids are shown at 50% probability level). Selected bond distances (Å), bond angles (°), and dihedral angles (°): Ge1C1 = 1.988(3), Ge2C2 = 1.987(3), C1C2 = 1.335(5), C1Cl3 = 1.749(3), C2Cl4 = 1.756(3), Ge1F1 = 1.778(9), Ge2Cl2 = 2.141(3), Ge1C3 = 1.955(4), Ge1C12 = 1.961(3), Ge2C21 = 1.957(3), Ge2C30 = 1.931(3), Ge1C1C2 = 127.9(3), Cl3C1C2 = 115.3(3), Ge1C1Cl3 = 116.6(2), Ge2C2Cl4 = 116.3(2), GeC2C1 = 127.9(3), Ge1C1C2Ge2 = 160.94(19), Cl3C1C2Cl4 = 174.23(18).

$$\mathrm{H_2FGe{-}C(Cl){=}C(Cl){-}GeClH_2 + CH_3Li = H_2FGe{-}C(Li){=}C(Cl){-}GeClH_2 + CH_3Cl} \quad (4a)$$

$$\Delta H = -170.35 \text{ kJ mol}^{-1}$$

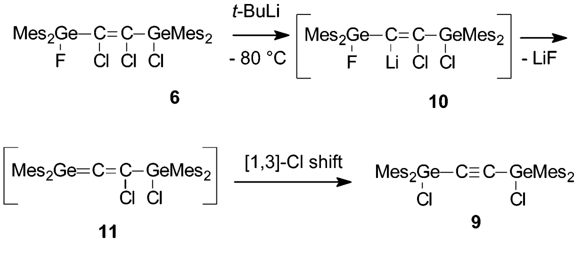
$$\mathrm{H_2FGe{-}C(Cl){=}C(Cl){-}GeClH_2 + CH_3Li = H_2FGe{-}C(Cl){=}C(Li){-}GeClH_2 + CH_3Cl} \quad (4b)$$

$$\Delta H = -148.72 \text{ kJ mol}^{-1}$$

The exclusive formation of bis(chlorogermyl)alkyne **9** rules out the formation of the triple bond by elimination of lithium chloride from alkene **10**, which would have given the 1,2-(chlorogermyl)(fluorogermyl)alkyne $\mathrm{Mes_2(F)Ge{-}C{\equiv}C{-}Ge(Cl)Mes_2}$.

The formation of **9** likely involves the selective LiF $\beta$-elimination from **10** to give the transient germaallene **11**. A [1,3]-chlorine shift then would lead to the observed bis(chlorogermyl)-alkyne **9** (Scheme 3).

**Scheme 3**



The barrier of the [1,3]-Cl shift from **11** to **9** estimated on the models **11H** and **9H** (Figure 3) is slightly higher than that of the similar rearrangement in $\mathrm{H_2FGe{-}CCl_2{-}C(Cl){=}GeH_2}$.

ONIOM B3LYP/6-31G(d):PM3 calculations on **9** and **11** also reveal a conspicuous difference in energy (170.71 kJ mol$^{-1}$) in favor of **9**.

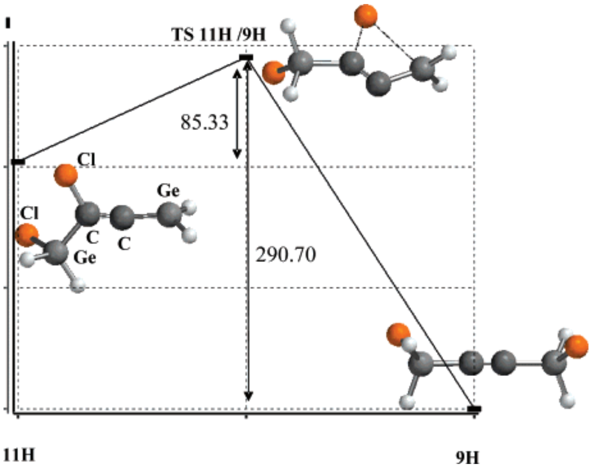


**Figure 3.** B3LYP/6-31G(d)-calculated pathway of the [1,3]-Cl migration in $\mathrm{ClGeH_2{-}CCl{=}C{=}GeH_2}$.

Allenes to alkynes rearrangements are well-known in carbon chemistry[13] but have been neither observed nor postulated in germanium chemistry. Two stable germaallenes, $\mathrm{Tip_2Ge{=}C{=}C(Ph)(}t\mathrm{\text{-}Bu)}$ (Tip = 2,4,6-triisopropylphenyl)[14] and Mes(Tbt)-Ge=C=CR$_2$ (Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl, CR$_2$ = fluorenylidene),[15] were isolated by West[14] and Tokitoh,[15] but isomerization of these species to the corresponding germylalkynes was not observed. The only examples of such a rearrangement in group 14 element chemistry were reported by Barton[16] in a silaallene (migration of a hydrogen atom) and by Ishikawa[17] in the case of a nickel complex of a silaallene ([1,3]-phenyl shift). Note that a reverse silylalkyne/silaallene rearrangement also has been reported by Ishikawa.[18]

## Conclusion

[1,3]-Chlorine shifts in both transient germene $\mathrm{Mes_2(F)Ge{-}CCl_2{-}CCl{=}GeMes_2}$ and allene $\mathrm{Mes_2Ge{=}C{=}CCl{-}Ge(Cl)Mes_2}$ account for the formation of the isolated *E*-dichlorodigermylalkene and digermylalkyne, respectively. No precedent of such rearrangements has been reported in germanium chemistry.

## Experimental Part

All manipulations were carried out under Ar using standard Schlenk techniques with solvents freshly distilled from sodium benzophenone. $^1$H, $^{13}$C, and $^{19}$F NMR (external ref CF$_3$COOH) spectra were recorded in CDCl$_3$ on Bruker AC 200 ($^1$H, 200.1 MHz; $^{13}$C, 50.1 MHz; $^{19}$F, 188.30 MHz) and Bruker Avance 300 ($^{13}$C, 75.46 MHz) instruments. $^{13}$C NMR signals were assigned by

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Attached Proton Test. Mass spectra were measured on a Hewlett-Packard 5989 A spectrometer by EI at 70 eV, except that of compound **1**, which was measured on a NERMAG R10-10 spectrometer by CI (NH$_3$). Melting points were determined on a Leitz microscope heating stage 250.

Molecular orbital calculations were performed at the B3LYP/6-31G(d) level[19−21] on the model compounds mentioned in the text. In addition, full geometry optimization of **9** and **11** was carried out by using an ONIOM B3LYP/6-311G(d):PM3 model[22,23] (heteroatoms included in the high level, the organic radicals form the lower level shell) by resorting to the Gaussian 98 system.[24]

**Mes$_2$(F)Ge−CCl$_3$, 1.** A mixture of Mes$_2$GeF$_2$ (4.00 g, 11.47 mmol) and CHCl$_3$ (1.38 g, 1 equiv) in THF (50 mL) was cooled to −110 °C, and 9 mL of a 1.6 M hexane solution of *n*-BuLi (14.4 mmol) was added. The reaction mixture was slowly warmed to room temperature under magnetic stirring for 4 h; after removal of LiF by filtration and of the solvents in vacuo, crystallization from pentane afforded 3.50 g (60%) of **1** (mp 147 °C). $^1$H NMR: $\delta$ 2.28 (s, 6H, *p*-Me), 2.53 (d, $^4J_{HF}$ = 1.7 Hz, 12H, *o*-Me), 6.89 (s, 4H, arom H). $^{13}$C NMR: $\delta$ 21.18 (*p*-Me), 23.88 (d, $^4J_{FC}$ = 3.5 Hz, *o*-Me), 94.96 (CCl$_3$), 129.64 (*m*-C), 131.04 (d, $^2J_{FC}$ = 9.1 Hz, *ipso*-C), 141.20 (*p*-C), 143.44 (*o*-C). $^{19}$F NMR: $\delta$ −96.1. MS: 429 (M − F, 6), 331 (Mes$_2$GeF, 100), 311 (Mes$_2$Ge − 1, 30), 191 (MesGe − 2, 35), 91 (PhMe − 1, 90). DCI: 483 (M + N$_2$H$_7^+$, 21), 466 (M + NH$_4^+$, 76), 449 (M + H$^+$, 31). Anal. Calcd for C$_{19}$H$_{22}$Cl$_3$FGe: C, 50.90; H, 4.95. Found: C, 51.10; H, 4.85.

**Mes$_2$(MeO)Ge−CHCl$_2$, 3.** To a solution of **1** (0.70 g, 1.56 mmol) in THF (10 mL) cooled to −110 °C was added 1 mL of a 1.7 M in hexane solution of *t*-BuLi (1.7 mmol). The reaction mixture was stirred at −80 °C for 30 min. Methanol (in excess) was added, and the reaction mixture was slowly warmed to room temperature within 2 h. After filtration, the solution was concentrated in vacuo to remove the solvents. Cooling the crude product in pentane to −20 °C gave **3** as a yellow, waxy product (0.53 g, 82%) in about 95% purity. $^1$H NMR: $\delta$ 2.31 (s, 6H, *p*-Me), 2.47 (s, 12H, *o*-Me), 3.54 (s, 3H, OMe), 6.11 (s, 1H, CH) 6.90 (s, 4H, arom H). $^{13}$C NMR: $\delta$ 22.24 (*p*-Me), 25.03 (*o*-Me), 52.26 (OMe), 65.25 (CHCl$_2$), 128.66 (*m*-C), 130.62 (*ipso*-C), 138.92 (*p*-C), 142.22 (*o*-C). MS: 426 (M, 5), 343 (M − CCl$_2$H, 46), 311 (Mes$_2$Ge − 1, 33), 191 (MesGe − 2, 18), 84 (CCl$_2$H + 1, 98).

**Mes$_2$(F)Ge−CCl═CCl−Ge(Cl)Mes$_2$, 6.** A 6 mL amount of a 1.5 M hexane solution of *t*-BuLi (0.9 mmol) was added to a solution of Mes$_2$(F)Ge−CCl$_3$ (**1**) (4.00 g, 8.84 mmol) in THF (50 mL) cooled to −110 °C to form Mes$_2$(F)Ge−C(Li)Cl$_2$. The reaction mixture was slowly warmed to room temperature within 2 h. After filtration and removal of solvents in vacuo, 20 mL of Et$_2$O was added. Cooling to −20 °C gave 2.06 g (60%) of **6** as a crystalline product (mp 207 °C). $^1$H NMR: $\delta$ 2.28 (s, 12H, *o*-Me), 2.35 (s, 12H, *p*-Me), 2.42 (s, 12H, *o*-Me), 6.86 (s, 8H). $^{13}$C NMR: $\delta$ 21.07 and 21.17 (*p*-Me), 23.10 (d, $^4J_{FC}$ = 12 Hz, *o*-Me), 23.99 (s, *o*-Me), 129.31 and 129.74 (*m*-C), 131.75 (d, $^2J_{FC}$ = 45 Hz, *ipso*-C MesGeF), 133.80 (*ipso*-C MesGeCl), 140.15 and 140.51 (*p*-C), 143.13 and 143.34 (*o*-C), 146.34 (d, $^2J_{FC}$ = 57 Hz, ═CGeF), 147.53 (═CGeCl). $^{19}$F NMR: $\delta$ −101.5. MS: 772 (M, 5), 561 (M − F − 2Cl − Mes + 1, 7), 494 (M − 2MesH − HCl, 80), 331 (Mes$_2$GeF, 100), 191 (MesGe − 2, 25), 120 (MesH, 95). Anal. Calcd for C$_{38}$H$_{44}$Cl$_3$FGe$_2$: C, 59.17; H, 5.75. Found: C, 59.19; H 5.81.

**Mes$_2$(Cl)Ge−C≡C−Ge(Cl)Mes$_2$, 9.** To a solution of **6** (1.00 g, 1.30 mmol) in THF (10 mL) cooled to −110 °C was added 0.9 mL of a 1.5 M hexane solution of *t*-BuLi (1.35 mmol). The mixture was slowly warmed to room temperature within 2 h. After filtration, the solvents were removed in vacuo and 5 mL of pentane was added. Cooling to −20 °C led to 0.73 g (79%) of **9** as a white solid (mp 111 °C). $^1$H NMR: $\delta$ 2.26 (s, 12H, *p*-Me), 2.41 (s, 24H, *o*-Me), 6.80 (s, 8H arom H). $^{13}$C NMR: $\delta$ 21.15 (*p*-Me), 24.04 (*o*-Me), 114.12 (C≡C), 129.72 (*m*-C), 132.46 (*ipso*-C), 139.80 (*p*-C), 142.86 (*o*-C). MS: 681 (M − Cl, 6), 371 (Mes$_2$(Cl)Ge−C≡C, 20), 347 (Mes$_2$GeCl, 28), 335 (Mes$_2$Ge−C≡C − 1, 100), 191 (MesGe − 2, 25), 120 (MesH, 85). Anal. Calcd for C$_{38}$H$_{44}$Cl$_2$Ge$_2$: C, 63.67; H, 6.19. Found: C, 63.37; H 6.08.

**Crystal Data for 6.** C$_{38}$H$_{44}$Cl$_3$FGe$_2$, $M$ = 771.26, monoclinic, $P2_1/c$, $a$ = 8.447(1) Å, $b$ = 28.130(3) Å, $c$ = 15.094(1) Å, $\beta$ = 95.896(2)°, $V$ = 3567.5(6) Å$^3$, $Z$ = 4, $T$ = 193(2) K; 20 785 reflections (7328 independent, $R_{int}$ = 0.0483) were collected. Largest electron density residue: 0.527 e Å$^{-3}$, $R_1$ (for $I > 2\sigma(I)$) = 0.0442 and $wR_2$ = 0.0947 (all data) with $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $wR_2 = (\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2)^{0.5}$.

All data for the structure 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 K$\alpha$ radiation ($\lambda$ = 0.71073 Å). The structure was solved by direct methods,[25] and all non hydrogen atoms were refined anisotropically using the least-squares method on $F^2$.[26]

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**Supporting Information Available:** CIF files, total energies, and optimized coordinates of the investigated systems. This material is available free of charge via the Internet at http://pubs.acs.org.

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