

Articles

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

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Received December 29, 2006

Dimesitylfluoro(trichloromethyl)germane (**1**) has been synthesized from difluorodimesitylgermane, chloroform, and *n*-butyllithium. Addition of *n*-butyllithium to compound **1** gave the lithium carbenoid Mes₂(F)Ge–C(Li)Cl₂ (**2**), which behaves as a synthetic equivalent of the *C*-dichlorogermene Mes₂Ge=CCl₂ (**5**). Warming **2** to room temperature afforded the 1,2-digermylalkene Mes₂(F)Ge–CCl=CCl–Ge(Cl)Mes₂ (**6**) possibly by an unprecedented [1,3]-Cl shift from the transient germene Mes₂(F)Ge–CCl₂–CCl=GeMes₂ (**8**). Addition of *tert*-butyllithium to **6** gave bis(chlorogermeryl)alkyne Mes₂(Cl)Ge–C≡C–Ge(Cl)Mes₂ (**9**) probably via a 3-chloro-1-germaallene/(chlorogermeryl)alkyne rearrangement.

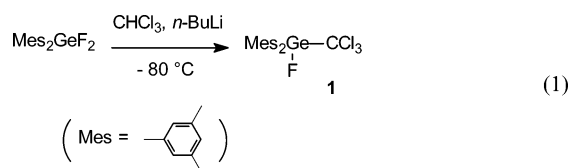
Introduction

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 sp² carbon atom should greatly increase the synthetic utility of such compounds. The *C*-dihalophosphaalkenes Mes*P=CX₂² and arsaalkenes Mes*As=CX₂³ (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 phospho(or arsa)alkenes,⁴ phosphoalkynes,⁵ and phospho(or arsa)allenes.⁶ In contrast to their pnictogen counterparts, *C*-dihalometallaalkenes >M=CX₂ derivatives (M = Si, Ge, Sn) are still unknown.

Here we describe the preparation of the lithium compound Mes₂(F)Ge–C(Li)Cl₂, a potential synthetic equivalent of the *C*-dichloro compound Mes₂Ge=CCl₂, and its conversion on warming to room temperature into the digermylalkene Mes₂(F)Ge–CCl=CCl–Ge(Cl)Mes₂. The reaction of the latter with *tert*-butyllithium afforded the digermylalkyne Mes₂(Cl)Ge–C≡C–Ge(Cl)Mes₂. 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 difluorodimesitylgermane⁷ and chloroform afforded the air- and moisture-stable dimesitylfluoro(trichloromethyl)germane (**1**) (eq 1). The struc-



ture of **1** was proven by its NMR spectra. The high-field shift in the ¹⁹F NMR spectrum (δ ¹⁹F = –96.1 ppm) lies in the expected range for a fluorine atom bonded to a Mes₂Ge–CR₃ moiety (for example –105.2 ppm in Mes₂(F)Ge–CH₂CN⁸). Moreover a ¹³C NMR signal at 94.96 ppm was observed for the carbon atom bearing three chlorine atoms (comparable to δ ¹³C = 77.7 ppm for CHCl₃). The molecular peak was observed in the mass spectrum of **1** (chemical ionization with NH₃).

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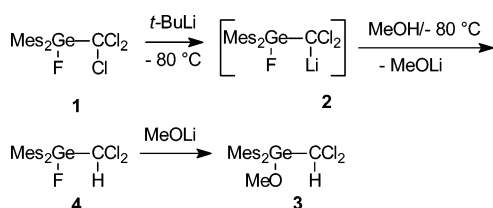
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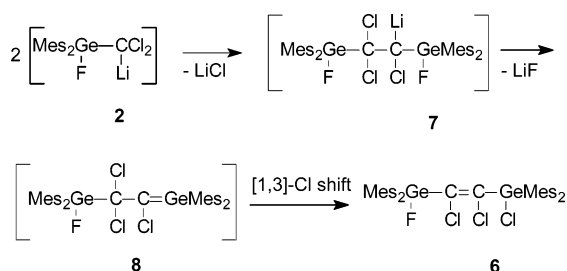
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Scheme 1



Scheme 2



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

Formation of **3** by successive elimination of lithium fluoride from **2** to give $\text{Mes}_2\text{Ge}=\text{CCl}_2$ **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/(Chlorogermeryl)alkene Rearrangement. Warming lithium compound **2** to room temperature surprisingly afforded the 1,2-dichloro(chlorogermeryl)(fluorogermeryl)ethene **6** in nearly quantitative yield (eq 2). The formation



of **6** can be reasonably explained by the selective β -elimination of LiF from **7**, leading to the transient germene $\text{Mes}_2(\text{F})\text{Ge}-\text{CCl}_2-\text{CCl}=\text{GeMes}_2$ **8** (Scheme 2). Compound **7** could be formed by an "eliminative dimerization" of two molecules of carbenoid **2** (as $\text{Cl}_2(\text{H})\text{C}-\text{CCl}(\text{H})\text{Li}$ from $\text{Cl}_2(\text{H})\text{CLi}^9$) or by insertion of the carbene $\text{Mes}_2(\text{F})\text{Ge}-\text{CCl}$ into the carbenoid **2**. Germene **8** then undergoes an unprecedented [1,3]-chlorine shift (Scheme 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 (chlorogermeryl)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}).

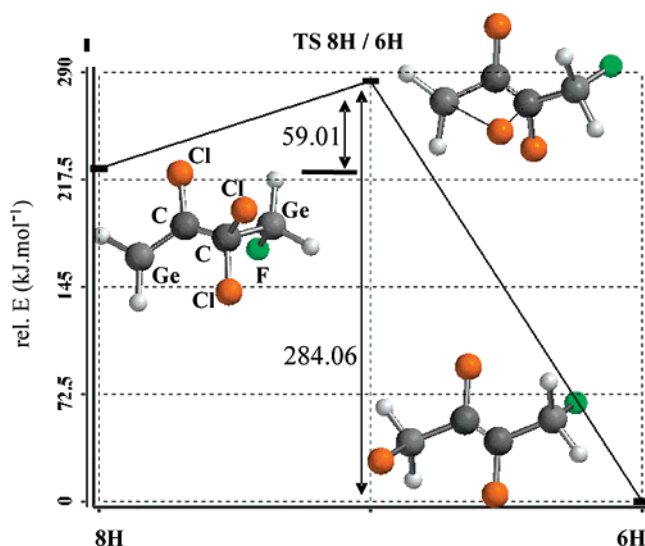


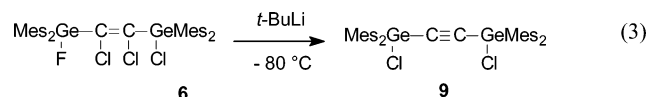
Figure 1. B3LYP/6-31G(d)-calculated energies along the [1,3]-Cl shift reaction path in $\text{H}_2\text{Ge}=\text{CCl}-\text{CCl}_2-\text{GeH}_2\text{F}$, **8H**.

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**.

That alkene **6** is favored over germene **8** could also be expected by consideration of the bond energies involved: the $\text{C}=\text{C}$ π -bond energy (250 kJ mol^{-1}) is greater than the $\text{Ge}=\text{C}$ π -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 ^1H NMR spectrum for the nonequivalent $\text{Mes}_2\text{Ge}(\text{Cl})$ and $\text{Mes}_2\text{Ge}(\text{F})$ groups and one singlet and one doublet (coupling with fluorine) at 147.53 and 146.34 ppm ($^2J_{\text{CF}} = 57 \text{ Hz}$), 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 ($\text{Ge1C1C2Ge2} = 160.94(19)^\circ$, $\text{Cl3C1C2Cl4} = 174.23(18)^\circ$), 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 $\delta^{13}\text{C} = 114.12 \text{ ppm}$), as well as the absence of a fluorine atom (eq 3).



The preference for the lithium/chlorine exchange reaction to take place at the carbon atom bearing the $\text{Mes}_2\text{Ge}(\text{F})$ 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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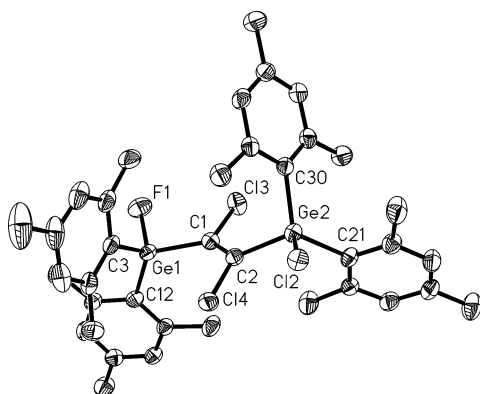
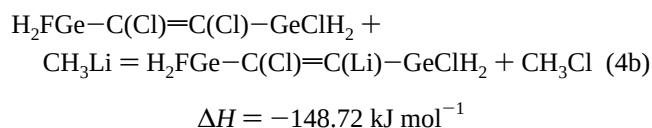
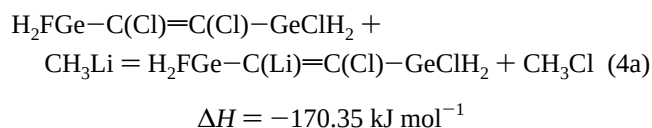
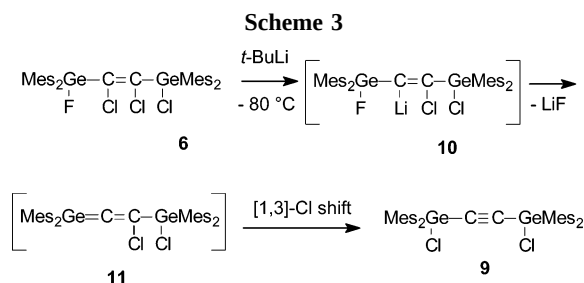


Figure 2. Molecular structure of **6** (thermal ellipsoids are shown at 50% probability level). Selected bond distances (Å), bond angles (°), and dihedral angles (°): Ge1C1 = 1.988(3), Ge2C2 = 1.987(3), C1C2 = 1.335(5), C1Cl3 = 1.749(3), C2Cl4 = 1.756(3), Ge1F1 = 1.778(9), Ge2Cl2 = 2.141(3), Ge1C3 = 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), Ge2C2C1 = 127.9(3), Ge1C1C2Ge2 = 160.94(19), Cl3C1C2C14 = 174.23(18).



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 $\text{Mes}_2(\text{F})\text{Ge}-\text{C}\equiv\text{C}-\text{Ge}(\text{Cl})\text{Mes}_2$.

The formation of **9** likely involves the selective LiF β -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).



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 $\text{H}_2\text{FGe}-\text{CCl}_2-\text{C}(\text{Cl})=\text{GeH}_2$.

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

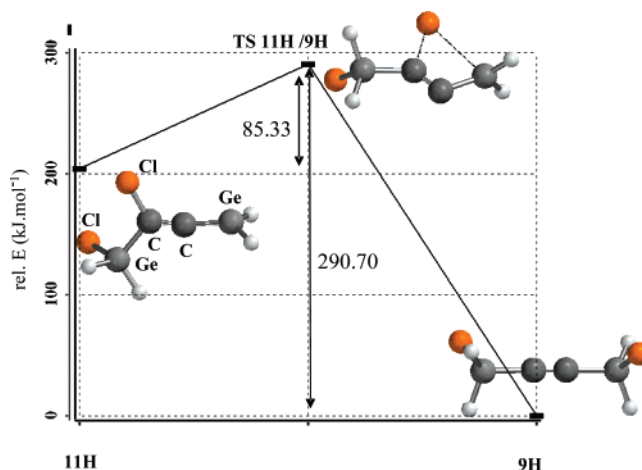


Figure 3. B3LYP/6-31G(d)-calculated pathway of the [1,3]-Cl migration in $\text{ClGeH}_2-\text{CCl}=\text{C}=\text{GeH}_2$.

Allenes to alkynes rearrangements are well-known in carbon chemistry¹³ but have been neither observed nor postulated in germanium chemistry. Two stable germaallenes, $\text{Tip}_2\text{Ge}=\text{C}=\text{C}(\text{Ph})(t\text{-Bu})$ (Tip = 2,4,6-triisopropylphenyl)¹⁴ and $\text{Mes}(\text{Tbt})\text{-Ge}=\text{C}=\text{CR}_2$ (Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl, CR_2 = fluorenylidene),¹⁵ were isolated by West¹⁴ and Tokitoh,¹⁵ but isomerization of these species to the corresponding germynalkynes was not observed. The only examples of such a rearrangement in group 14 element chemistry were reported by Barton¹⁶ in a silaallene (migration of a hydrogen atom) and by Ishikawa¹⁷ 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 $\text{Mes}_2(\text{F})\text{Ge}-\text{CCl}_2-\text{CCl}=\text{GeMes}_2$ and allene $\text{Mes}_2\text{Ge}=\text{C}=\text{CCl}-\text{Ge}(\text{Cl})\text{Mes}_2$ account for the formation of the isolated *E*-dichlorodigermynalkene and digermynalkyne, 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. ¹H, ¹³C, and ¹⁹F NMR (external ref CF_3COOH) spectra were recorded in CDCl_3 on Bruker AC 200 (¹H, 200.1 MHz; ¹³C, 50.1 MHz; ¹⁹F, 188.30 MHz) and Bruker Avance 300 (¹³C, 75.46 MHz) instruments. ¹³C 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 (NH₃). 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

Mes₂(F)Ge–CCl₃, 1. A mixture of Mes₂GeF₂ (4.00 g, 11.47 mmol) and CHCl₃ (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). ¹H NMR: δ 2.28 (s, 6H, *p*-Me), 2.53 (d, ⁴J_{HF} = 1.7 Hz, 12H, *o*-Me), 6.89 (s, 4H, arom H). ¹³C NMR: δ 21.18 (*p*-Me), 23.88 (d, ⁴J_{FC} = 3.5 Hz, *o*-Me), 94.96 (CCl₃), 129.64 (*m*-C), 131.04 (d, ²J_{FC} = 9.1 Hz, *ipso*-C), 141.20 (*p*-C), 143.44 (*o*-C). ¹⁹F NMR: δ –96.1. MS: 429 (M – F, 6), 331 (Mes₂GeF, 100), 311 (Mes₂Ge – 1, 30), 191 (MesGe – 2, 35), 91 (PhMe – 1, 90). DCI: 483 (M + N₂H₇⁺, 21), 466 (M + NH₄⁺, 76), 449 (M + H⁺, 31). Anal. Calcd for C₁₉H₂₂Cl₃FGe: C, 50.90; H, 4.95. Found: C, 51.10; H, 4.85.

Mes₂(MeO)Ge–CHCl₂, 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. ¹H NMR: δ 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). ¹³C NMR: δ 22.24 (*p*-Me), 25.03 (*o*-Me), 52.26 (OMe), 65.25 (CHCl₂), 128.66 (*m*-C), 130.62 (*ipso*-C), 138.92 (*p*-C), 142.22 (*o*-C). MS: 426 (M, 5), 343 (M – CCl₂H, 46), 311 (Mes₂Ge – 1, 33), 191 (MesGe – 2, 18), 84 (CCl₂H + 1, 98).

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Mes₂(F)Ge–CCl=CCl–Ge(Cl)Mes₂, 6. A 6 mL amount of a 1.5 M hexane solution of *t*-BuLi (0.9 mmol) was added to a solution of Mes₂(F)Ge–CCl₃ (**1**) (4.00 g, 8.84 mmol) in THF (50 mL) cooled to –110 °C to form Mes₂(F)Ge–C(Li)Cl₂. The reaction mixture was slowly warmed to room temperature within 2 h. After filtration and removal of solvents in vacuo, 20 mL of Et₂O was added. Cooling to –20 °C gave 2.06 g (60%) of **6** as a crystalline product (mp 207 °C). ¹H NMR: δ 2.28 (s, 12H, *o*-Me), 2.35 (s, 12H, *p*-Me), 2.42 (s, 12H, *o*-Me), 6.86 (s, 8H). ¹³C NMR: δ 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). ¹⁹F NMR: δ –101.5. MS: 772 (M, 5), 561 (M – F – 2Cl – Mes + 1, 7), 494 (M – 2MesH – HCl, 80), 331 (Mes₂GeF, 100), 191 (MesGe – 2, 25), 120 (MesH, 95). Anal. Calcd for C₃₈H₄₄Cl₃FGe₂: C, 59.17; H, 5.75. Found: C, 59.19; H 5.81.

Mes₂(Cl)Ge–C≡C–Ge(Cl)Mes₂, 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). ¹H NMR: δ 2.26 (s, 12H, *p*-Me), 2.41 (s, 24H, *o*-Me), 6.80 (s, 8H arom H). ¹³C NMR: δ 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 (Mes₂(Cl)Ge–C≡C, 20), 347 (Mes₂GeCl, 28), 335 (Mes₂Ge–C≡C – 1, 100), 191 (MesGe – 2, 25), 120 (MesH, 85). Anal. Calcd for C₃₈H₄₄Cl₂Ge₂: C, 63.67; H, 6.19. Found: C, 63.37; H 6.08.

Crystal Data for 6. C₃₈H₄₄Cl₃FGe₂, *M* = 771.26, monoclinic, *P*2₁/c, *a* = 8.447(1) Å, *b* = 28.130(3) Å, *c* = 15.094(1) Å, β = 95.896(2)°, *V* = 3567.5(6) Å³, *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* > 2σ(*I*)) = 0.0442 and *wR*₂ = 0.0947 (all data) with *R*₁ = Σ|*F*_o| – |*F*_c|/Σ|*F*_o| and *wR*₂ = (Σ*w*(*F*_o² – *F*_c²)²/Σ*w*(*F*_o²))^{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 Kα radiation (λ = 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

Acknowledgment. We thank the CNCSIS (Romanian Council for Scientific Research grant no. 6/45/AT), the CNRS, and the Ministry of Foreign Affairs (AI Brancusi 2005 08581TK (Fr)–C18015 (Ro)) for financial support.

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>.

OM061188J

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