Dimesitylneopentylgermene, A New Stable Germene

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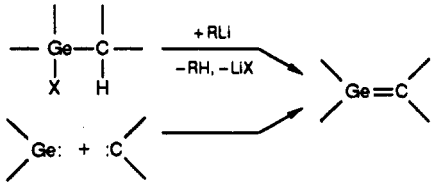
Summary: The dimesitylneopentylgermene $Mes_2Ge{=}CHCH_2$-*t*-Bu (**3**) was synthesized in high yield by an addition–elimination reaction between dimesitylvinylfluorogermane and *tert*-butyllithium. It is stable at room temperature and is highly reactive toward electrophilic and nucleophilic reagents.

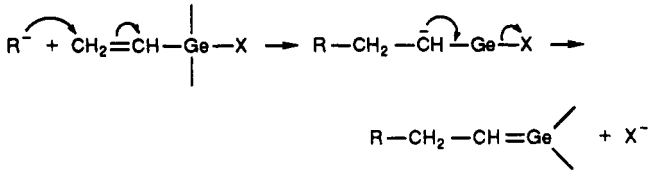
The dimesitylfluorenylidenegermane $Mes_2Ge{=}CR_2$ (CR_2 = fluorenylidene), isolated in 1987,[1] was the first example of a stable "organometallic alkene" with a formal germanium–carbon double bond. At about the same time,[2b] and more recently,[3,4] some other germenes have been described, with two of them having a prochiral germanium atom.

We report here the preparation and our initial studies of the reactivity of dimesitylneopentylgermene (**3**), the first stable germene with a prochiral carbon.

Two methods have been used to synthesize germenes, the dehydrohalogenation of halogermanes by organolithium compounds[1,3,4] and a germylene–carbene coupling reaction:[2]



For **3** we have used the addition–elimination reaction, i.e., addition of an organolithium compound to a vinylhalogermane:



This route was described first by Jones[5] and then widely used by Auner[6a–g] and, more recently, by Yoo[6h] to prepare silenes from vinylchlorosilanes.[7]

In order to limit the side reactions often observed in the case of vinylchlorosilanes,[6] we performed the reaction with a vinylfluorogermane, $Mes_2Ge(F)CH{=}CH_2$ (**1**); because of the strong germanium–fluorine bond energy (114 kcal/mol),[8] lithium/fluorine exchange generally does not occur with fluorogermanes. Moreover, it is well-known that mesityl groups on germanium increase the stability of germenes.[1,4]

Dimesitylvinylfluorogermane (**1**) was prepared in one step by the reaction of vinylmagnesium bromide with dimesityldifluorogermane[9] in THF:

$$Mes_2GeF_2 + CH_2{=}CH{-}MgBr \xrightarrow{THF} Mes_2Ge(F)CH{=}CH_2$$
1

Addition of 1 molar equiv of *tert*-butyllithium (1.7 M in pentane) to an Et_2O solution of **1** cooled to −78 °C gave the α-lithiogermane **2**;[10] the reaction, followed by ^1H NMR spectroscopy, involved the elimination of lithium fluoride at −50 °C and the nearly quantitative formation (yield >90%) of the expected germene **3**:[11]

$$1 \xrightarrow[Et_2O/-78\ °C]{t\text{-BuLi}} \underset{\mathbf{2}}{Mes_2Ge(F)CH(Li)CH_2\text{-}t\text{-Bu}} \xrightarrow[-LiF]{-50\ °C} Mes_2Ge{=}CHCH_2\text{-}t\text{-Bu}$$
3

After elimination of solvents in vacuo, the yellow solid was analyzed by NMR (solvent toluene-d_8), which showed the expected characteristic signals, both in the ^1H (2 unequivalent mesityls and the triplet of ethylenic proton at 6.10 ppm) and in the ^{13}C NMR spectrum (doubly bonded carbon at 124.2 ppm).

Germene **3** is yellow in solution and stable at room temperature. It is extremely air- and moisture-sensitive and has not yet been isolated but was obtained sufficiently pure to study its chemical behavior. It is highly reactive, particularly toward electrophilic or nucleophilic reagents

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(7) The transient germene [$Me_2Ge{=}CHCH_2$-*t*-Bu] was trapped, in low yields, by 2,3-dimethylbutadiene in the reaction of dimethylvinylchlorogermane with *t*-BuLi: Auner, N. Conference, Toulouse, 1989.
(8) Purcell, K. F.; Kotz, J. C. *Inorganic Chemistry*; W. B. Saunders: Philadelphia, PA, 1977; p 271.
(9) Rivière, P.; Rivière-Baudet, M.; Castel, A.; Desor, D.; Abdennadher, C. *Phosphorus, Sulfur Silicon Relat. Elem.* **1991**, *61*, 189.
(10) α-Lithiogermane **2** was evidenced by addition of methyl iodide to the reaction mixture, at −60 °C, leading to the fluorogermane $Mes_2Ge(F)CH(CH_3)CH_2$-*t*-Bu, which was not isolated in pure form but was fully characterized by NMR (^1H, ^{13}C, ^{19}F) spectroscopy and mass spectrometry. NMR ($CDCl_3$): ^1H (80.1 MHz) δ 0.89 (d, $^3J_{H-H}$ = 7.7 Hz, 3 H, CH_3), 1.32 (s, 9 H, *t*-Bu), 1.34 (m, 2 H, CH_2), 2.12 (s, 6 H, *p*-Me), 2.34 (d, $^5J_{H-F}$ = 2.5 Hz, 12 H, *o*-Me), 6.72 (s, 4 H, *m*-H, Mes); ^{13}C (50.3 MHz) δ 23.54 (*p*-Me), 25.4 (*o*-Me), 26.65 (d, $^2J_{C-F}$ = 13.7 Hz, CH), 28.88 (CH_3, *t*-Bu), 29.82 (CH_3), 32.40 (*C*, *t*-Bu), 40.46 (CH_2-*t*-Bu), 128.73 (*m*-C), 136.10 (*p*-C), 142.20 (*o*-C), ipso C undertermined; ^{19}F (75.4 MHz) δ −112.9. MS (EI, 70 eV, *m*/*z* (%)): 354 (M − F − *t*-Bu, 65), 311 (M − Mes, 27), 292 (M − F − Mes, 81), 235 (M − F − Mes − *t*-Bu, 79), 193 (MesGe, 18), 119 (Mes, 15), 57 (*t*-Bu, 100).
(11) The reaction performed in a toluene–pentane mixture (50/50) leads to similar results; in this case, lithium fluoride elimination occurs at −30 °C.

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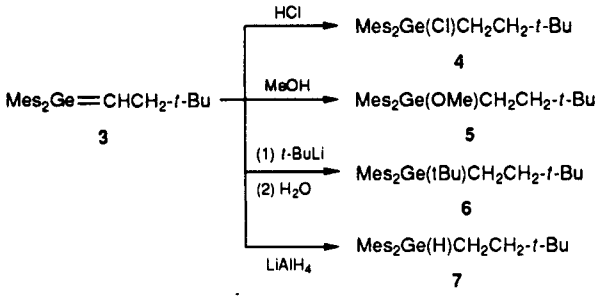
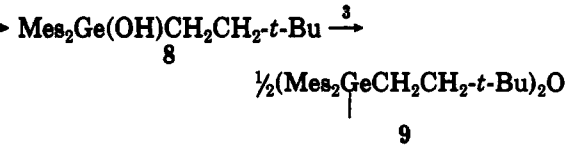
(HCl, MeOH, *t*-BuLi, $LiAlH_4$), which react rapidly and almost quantitatively:



Hydrolysis of **3** gives different products that depend on the experimental conditions. Rapid addition of an excess of water affords nearly exclusively the germanol **8**, whereas the addition of $^1/_2$ molar equiv of water leads to formation of digermoxane **9** via reaction of **8** with still unreacted germene **3**:



All compounds isolated in this work were fully characterized.[12]

In conclusion, **3** is the first example of a germene that is stable at room temperature and is not resonance-stabilized. It is easily available in high yields and appears to be an excellent model for wide investigations of germene chemistry; some aspects of its reactivity are now being examined.

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(12) Synthesis of **1**: To a solution of Mes_2GeF_2[9] (2.0 g, 5.7 mmol) in Et_2O (20 mL) cooled to −78 °C was added 1 molar equiv of a solution of vinylmagnesium bromide (1 M in THF). The reaction mixture was warmed to room temperature and then was hydrolyzed (H_3O^+); the organic layer was dried over anhydrous Na_2SO_4. After distillation of solvents in vacuo, crude **1** was purified by crystallization from pentane at −20 °C; 1.70 g (yield 83%) of white crystals (mp 79 °C) was obtained. NMR ($CDCl_3$): ^{1}H (200.1 MHz) δ 2.26 (s, 6 H, *p*-Me, Mes), 2.33 (d, $^5J_{H-F}$ = 1.6 Hz, 12 H, *o*-Me, Mes), 5.79 (ddd, $^2J_{H-H}$ = 3.0 Hz, $^3J_{H-H}$(trans) = 19.3 Hz, $^4J_{H-F}$ = 0.9 Hz, 1 H, H trans CH_2), 6.12 (ddd, $^2J_{H-H}$ = 3.0 Hz, $^3J_{H-H}$(cis) = 13.2 Hz, $^4J_{H-F}$ = 1.5 Hz, 1 H, H cis CH_2), 6.79 (ddd, $^3J_{H-H}$(cis) = 13.2 Hz, $^3J_{H-H}$(trans) = 19.3 Hz, $^3J_{H-F}$ = 3.1 Hz, 1 H, C=CH_2), 6.84 (d, $^5J_{H-F}$ = 0.6 Hz, 4 H, *m*-H, Mes); ^{13}C (50.3 MHz) δ 15.82 (*p*-Me), 18.01 (d, $^4J_{C-F}$ = 2.9 Hz, *o*-Me), 123.30 (*m*-C), 123.39 (d, $^2J_{C-F}$ = 9.4 Hz, ipso C), 127.01 (d, $^3J_{C-F}$ = 4.3 Hz, =CH_2), 132.85 (d, $^2J_{C-F}$ = 14.0 Hz, HC=), 134.63 (*p*-C), 137.95 (*o*-C); ^{19}F (75.4 MHz) δ −109.3. MS (EI, 70 eV), ^{74}Ge; *m*/*z* (%)): 358 (M^+, 25), 339 (M − F, 15), 331 (M − CH=CH_2, 15), 238 (M − MesH, 100). IR ($CDCl_3$): ν(C=C) 1602.1 cm^{-1}. Anal. Calcd for $C_{20}H_{25}FGe$: C, 67.28; H, 7.06. Found: C, 67.35; H, 7.12. Synthesis of **3**: One equivalent of *t*-BuLi (1.7 M in pentane) was added under nitrogen to a solution of **1** (0.50 g, 1.4 mmol) in Et_2O (10 mL) cooled to −78 °C. The reaction mixture became pale yellow. Near −50 °C it turned an intense yellow. The reaction was followed by ^{1}H and ^{13}C NMR spectroscopy, which showed the formation of **3** at this temperature. The reaction mixture then was warmed to room temperature; after elimination of LiF by filtration and removal of solvents in vacuo, the yellow solid was dissolved in toluene-d_8 and analyzed by NMR. NMR (C_7D_8): ^{1}H (200.1 MHz) δ 0.98 (s, 9 H, *t*-Bu), 2.06 (s, 6 H, *o*-Me, Mes), 2.10 (s, 6 H, *o*-Me, Mes′), 2.41 (d, $^3J_{H-H}$ = 9.7 Hz, 2 H, CH_2), 2.44 (s, 6 H, *p*-Me, Mes, Mes′), 6.10 (t, $^3J_{H-H}$ = 9.7 Hz, 1 H, =*CH*), 6.66 (s, 4 H, *m*-H, Mes, Mes′); ^{13}C (50.3 MHz) δ 21.44, 24.61, 24.67, 25.09 (*o*-Me and *p*-Me, Mes, Mes′), 29.24 (CH_3, *t*-Bu), 30.78 (*C*, *t*-Bu), 46.31 (CH_2), 124.20 (=*CH*), 128.50 and 128.74 (*m*-C, Mes, Mes′), 135.27 and 136.11 (ipso C, Mes, Mes′), 139.03 and 139.26 (*o*-C, Mes, Mes′), 142.77 and 142.82 (*p*-C, Mes, Mes′). Synthesis of adducts **4**–**9**. Solutions of **3**, prepared as described above, were allowed to react with a 2-fold excess of the reactant. Compounds **4**–**9** then were purified by chromatography on silica. All compounds were obtained as waxy materials, very difficult to crystallize; thus, melting points were not reported. Data for **4** are as follows. NMR ($CDCl_3$): ^{1}H (80.1 MHz) δ 0.90 (s, 9 H, *t*-Bu), 1.30 (br s, 4 H, CH_2CH_2), 2.27 (s, 6 H, *p*-Me), 2.39 (s, 12 H, *o*-Me), 6.83 (s, 4 H, *m*-H, Mes); ^{13}C (50.3 MHz) δ 21.06 (*p*-Me), 23.53 (CH_2Ge), 23.74 (*o*-Me), 28.95 (CH_3, *t*-Bu), 29.82 (*C*, *t*-Bu), 38.00 (CH_2-*t*-Bu), 129.57 (*m*-C), 135.14 (ipso C), 139.29 (*p*-C), 142.33 (*o*-C). MS (EI, 70 eV; *m*/*z* (%)): 432 (M^+, 5), 397 (M − Cl, 4), 347 (M − CH_2CH_2-*t*-Bu, 100), 312 (Mes_2Ge, 68), 228 (MesGeCl, 87), 193 (MesGe, 26), 119 (Mes, 30), 57 (*t*-Bu, 78). Anal. Calcd for $C_{24}H_{35}ClGe$: C, 66.79; H, 8.17. Found: C, 66.89; H, 8.26. Data for **5** are as follows. NMR ($CDCl_3$): ^{1}H (80.1 MHz), δ 0.84 (s, 9 H, *t*-Bu), 1.52 (br s, 4 H, CH_2CH_2), 2.23 (s, 6 H, *p*-Me), 2.30 (s, 12 H, *o*-Me), 3.31 (s, 3 H, OMe), 6.77 (s, 4 H, *m*-H, Mes); ^{13}C (62.9 MHz) δ 21.01 (*p*-Me), 23.77 (CH_2Ge), 27.35 (*o*-Me), 28.82 (CH_3, *t*-Bu), 29.38 (*C*, *t*-Bu), 44.10 (CH_2-*t*-Bu), 62.82 (OCH_3), 128.82 (*m*-C), 134.87 (ipso C), 140.15 (*p*-C), 142.64 (*o*-C). MS (EI, 70 eV; *m*/*z* (%)): 428 (M^+, 1), 397 (M − OMe, 9), 343 (M − CH_2CH_2-*t*-Bu, 100), 312 (Mes_2Ge, 14). Anal. Calcd for $C_{25}H_{38}GeO$: C, 70.29; H, 8.97. Found: C, 70.45; H. 9.08. Data for **6** are as follows. NMR ($CDCl_3$): ^{1}H (80.1 MHz) δ 0.80 (s, 9 H, *t*-Bu), 1.23 (s, 9 H, Ge-*t*-Bu), 1.27 (br s, 4 H, CH_2CH_2), 2.19 (s, 12 H, *o*-Me), 2.22 (s, 6 H, *p*-Me), 6.75 (s, 4 H, *m*-H Mes); ^{13}C (50.3 MHz) δ 14.40 (CH_2Ge), 20.89 (*p*-Me), 25.04 (*o*-Me), 28.94 (CH_3, *t*-BuCH$_2$), 29.78 (*C*, *t*-BuGe), 29.90 (CH_3, *t*-BuGe), 31.40 (*C*, *t*-BuCH$_2$), 40.47 (CH_2-*t*-Bu), 128.74 (*m*-C), 136.90 (*p*-C), 139.26 (ipso C), 142.52 (*o*-C). MS (EI, 70 eV; *m*/*z* (%)): 397 (M − *t*-Bu, 56), 313 (Mes_2Ge + H, 100), 193 (MesGe, 15), 119 (Mes, 10), 57 (*t*-Bu, 63). Anal. Calcd for $C_{28}H_{44}Ge$: C, 74.20; H, 9.79. Found: C, 74.47; H, 9.91. Data for **7** are as follows. NMR ($CDCl_3$): ^{1}H (80.1 MHz) δ 0.87 (s, 9 H, *t*-Bu), 1.28 (br s, 4 H, CH_2CH_2), 2.26 (s, 6 H, *p*-Me), 2.34 (s, 12 H, *o*-Me), 5.25 (t, $^3J_{H-H}$ = 1.9 Hz, Ge–H), 6.81 (s, 4 H, *m*-H, Mes); ^{13}C (50.3 MHz) δ 13.34 (CH_2Ge), 21.04 (*p*-Me), 23.74 (*o*-Me), 28.92 (CH_3, *t*-Bu), 32.02 (*C*, *t*-Bu), 41.40 (CH_2-*t*-Bu), 128.60 (*m*-C), 134.25 (ipso C), 138.11 (*p*-C), 143.46 (*o*-C). MS (EI, 70 eV; *m*/*z* (%)): 398 (M^+, 1); 313 (M − CH_2CH_2-*t*-Bu, 39), 278 (M − MesH, 14), 221 (M − MesH − *t*-Bu, 7), 193 (MesGe, 35), 119 (Mes, 28), 85 (CH_2CH_2-*t*-Bu, 7), 57 (*t*-Bu, 80), 43 (Me_2CH, 100). IR ($CDCl_3$): ν(Ge–H) 2062.5 cm^{-1}. Anal. Calcd for $C_{24}H_{36}Ge$: C, 72.58; H, 9.14. Found: C, 72.37; H, 9.02. Data for **8** are as follows. NMR ($CDCl_3$): ^{1}H (80.1 MHz) δ 0.91 (s, 9 H, *t*-Bu), 1.49 (br s, 4 H, CH_2CH_2), 2.28 (s, 6 H, *p*-Me), 2.40 (s, 12 H, *o*-Me), 6.83 (s, 4 H, *m*-H, Mes); ^{13}C (50.3 MHz) δ 19.79 (CH_2Ge), 21.08 (*p*-Me), 23.41 (*o*-Me), 28.94 (CH_3, *t*-Bu), 31.25 (*C*, *t*-Bu), 37.80 (CH_2-*t*-Bu), 129.16 (*m*-C), 135.84 (ipso C), 138.81 (*p*-C), 142.79 (*o*-C). MS (EI, 70 eV; *m*/*z* (%)): 397 (M − OH, 3), 329 (M − CH_2CH_2-*t*-Bu, 71), 294 (M − Mes H, 13), 238 (M − Mes − *t*-Bu, 10), 193 (MesGe, 13), 119 (Mes, 46), 57 (*t*-Bu, 100). IR ($CDCl_3$): ν(OH) 3639.0 (free), 3451.8 (associated) cm^{-1}. Anal. Calcd for $C_{24}H_{36}GeO$: C, 69.77; H, 8.78. Found: C, 69.90; H, 8.93. Data for **9** are as follows. NMR ($CDCl_3$): ^{1}H (80.1 MHz) δ 0.61 (br s, 18 H, *t*-Bu), 1.53 (br s, 4 H, CH_2CH_2), 1.85 (br s, 24 H, *o*-Me), 2.17 (br s, 12 H, *p*-Me), 6.57 (br s, 8 H, *m*-H, Mes), ^{13}C (50.3 MHz) δ 16.52 (CH_2Ge), 20.93 (*p*-Me), 24.41 (*o*-Me), 28.69 (CH_3, *t*-Bu), 29.75 (*C*, *t*-Bu), 31.15 (CH_2-*t*-Bu), 129.14 (*m*-C), 136.63 (ipso C), 142.69 (*p*-C), 144.80 (*o*-C). MS (EI, 70 eV; *m*/*z* (%)): 793 (M − Me, 1), 397 ($Mes_2GeCH_2CH_2$-*t*-Bu, 6), 312 (Mes_2Ge, 100), 193 (MesGe, 17), 119 (Mes, 12). Anal. Calcd for $C_{48}H_{70}Ge_2O$: C, 71.33; H, 8.73. Found: C, 71.07; H, 8.58.