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Dimesitylneopentylgermene, A New Stable Germene

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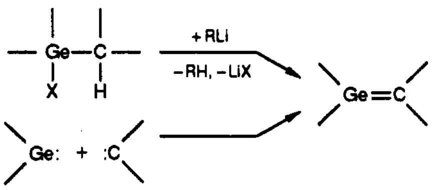
Summary: The dimesitylenopentylgermene $Mes_2Ge{=}CHCH_2\text{-}t\text{-}Bu$ (3) was synthesized in high yield by an addition–elimination reaction between dimesitylvinylfluorogermane and *tert*-butyllithium. It is stable at room temperature and is highly reactive toward electrophilic and nucleophilic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

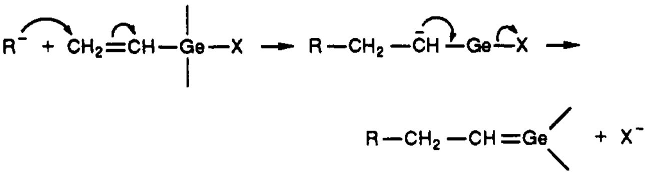
The dimesitylfluorenylidenegermane $Mes_2Ge{=}CR_2$ (CR_2 = fluorenylidene), isolated in 1987,[1] was the first example of a stable "organometallic alkene" with a formal germanium–carbon double bond. At about the same time,[2b] and more recently,[3,4] some other germenes have been described, with two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

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

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]

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

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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(1) Couret, C.; Escudié, J.; Satgé, J.; Lazraq, M. *J. Am. Chem. Soc.* **1987**, *109*, 4411.

(2) (a) Rivière, P.; Castel, A.; Satgé, J. *J. Am. Chem. Soc.* **1980**, *102*, 541. (b) Meyer, H.; Baum, G.; Massa, W.; Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 798.

(3) Anselme, G.; Escudié, J.; Couret, C.; Satgé, J. *J. Organomet. Chem.* **1991**, *403*, 93.

(4) Lazraq, M.; Couret, C.; Escudié, J.; Satgé, J.; Soufiaoui, M. *Polyhedron* **1991**, *10*, 1153.

(5) Jones, P. R.; Lim, T. F. O. *J. Am. Chem. Soc.* **1977**, *99*, 8447.

(6) (a) Auner, N. *J. Organomet. Chem.* **1987**, *336*, 59. (b) Auner, N. *J. Organomet. Chem.* **1988**, *353*, 275. (c) Auner, N. *Z. Anorg. Allg. Chem.* **1988**, *558*, 87. (d) Auner, N.; Grobe, J.; Schäfer, T.; Krebs, B.; Dartmann, M. *J. Organomet. Chem.* **1989**, *363*, 7. (e) Auner, N. *J. Organomet. Chem.* **1989**, *377*, 175. (f) Grobe, J.; Schröder, H.; Auner, N. *Z. Naturforsch., B* **1990**, *45B*, 785. (g) Auner, N.; Seidenschwarz, C.; Sewald, N. *Organometallics* **1992**, *11*, 1137. (h) Yoo, B. R.; Jung, I. N.; Lee, M. E.; Kim, C. H. *Bull. Korean Chem. Soc.* **1991**, *12*, 517.

(7) The transient germene [$Me_2Ge{=}CHCH_2\text{-}t\text{-}Bu$] 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 $Mes_2Ge(F)CH(CH_3)CH_2\text{-}t\text{-}Bu$, 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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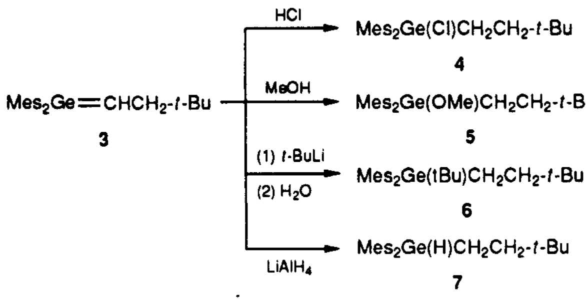
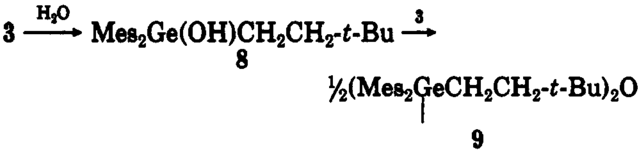
(HCl, MeOH, *t*-BuLi, $LiAlH_4$), which react rapidly and almost quantitatively:



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:



$$3 \xrightarrow{H_2O} \underset{8}{Mes_2Ge(OH)CH_2CH_2\text{-}t\text{-}Bu} \xrightarrow{3} \underset{9}{{}^1\!/_2(Mes_2GeCH_2CH_2\text{-}t\text{-}Bu)_2O}$$

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 ($CDCl_3$): ^1H (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 ^1H 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): ^1H (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, =C*H*), 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 (=*C*H), 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 ($CDCl_3$): ^1H (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 (*C*H_3, *t*-Bu), 29.82 (*C*, *t*-Bu), 38.00 (*C*H_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 ($CDCl_3$): ^1H (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 (*C*H_2Ge), 27.35 (*o*-Me), 28.82 (*C*H_3, *t*-Bu), 29.38 (*C*, *t*-Bu), 44.10 (*C*H_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 ($CDCl_3$): ^1H (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 (*C*H_2Ge), 20.89 (*p*-Me), 25.04 (*o*-Me), 28.94 (*C*H_3, *t*-BuCH_2), 29.78 (*C*, *t*-BuGe), 29.90 (*C*H_3, *t*-BuGe), 31.40 (*C*, *t*-BuCH_2), 40.47 (*C*H_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 ($CDCl_3$): ^1H (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 (*C*H_2Ge), 21.04 (*p*-Me), 23.74 (*o*-Me), 28.92 (*C*H_3, *t*-Bu), 32.02 (*C*, *t*-Bu), 41.40 (*C*H_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 ($CDCl_3$): ^1H (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 (*C*H_2Ge), 21.08 (*p*-Me), 23.41 (*o*-Me), 28.94 (*C*H_3, *t*-Bu), 31.25 (*C*, *t*-Bu), 37.80 (*C*H_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 ($CDCl_3$): ^1H (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 (*C*H_2Ge), 20.93 (*p*-Me), 24.41 (*o*-Me), 28.69 (*C*H_3, *t*-Bu), 29.75 (*C*, *t*-Bu), 31.15 (*C*H_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.