# **NEW STABLE GERMENES**

# M. LAZRAQ, C. COURET,\* J. ESCUDIE\* and J. SATGE

Laboratoire de Chimie des Organominéraux, URA 477, Université P. Sabatier, 118 route de Narbonne, 31062 Toulouse Cedex, France

and

# **M. SOUFIAOUI**

Laboratoire de Cycloadditions, Département de Chimie, Faculté des Sciences, Université Mohamed V, Av. Ibn Batouta, Rabat, Morocco

Abstract—Two new stable fluorenylidene germenes 5 and 6 substituted on germanium with two bulky bisyls [ $(Me_3Si)_2CH$ ] or with a bisyl and a mesityl group have been synthesized by dehydrofluorination of the corresponding fluorogermanes by tert-butyllithium. The ditert-butylfluorenylidene germene 7 could not be obtained by this route, but its lithio precursor 8 can be used as its synthetic equivalent.

Alkenes are among the most important compounds in organic synthesis. Their heavier homologues should also be very useful, both as precursors of potentially interesting new kinds of polymers (such polymers including a Group 14 metal could present new and unexpected mechanical or electrical properties) and in organometallic synthesis. So the study of the compounds M=C (M = Si, Ge, Sn) appears very promising.

Some years ago, evidence for the formation of transient germenes (M = Ge) was presented by trapping reactions.<sup>1,2</sup> The first examples of stable germenes  $1^{3,4}$  and  $2^{5,6}$  were reported as recently as 1987. Both compounds are stabilized owing to steric (bulky groups on germanium, and to a small extent on carbon) and electronic effects, involving mesomerism between the germanium–carbon double

bond and the fluorenylidene group in the case of  $1,^{3,4}$  or delocalization in the free orbital of boron with an ylide type structure in the case of  $2.^{5,6}$ 

Very recently we have been able to stabilize two other compounds with a Ge=C double bond, the fluorenylidene germenes 3 and 4:<sup>7</sup>



The great interest of sterically hindered germenes is the stabilization of cycloadduct derivatives which are normally inaccessible. However,



\* Authors to whom correspondence should be addressed.

although substituted with two bulky mesityl groups,  $Mes_2Ge=N-N=CR'_2$  ( $CR'_2 = CR_2$ ,  $CPh_2$ ) (obtained by reaction of 1 with diazofluorene or diphenyldiazomethane) could not be stabilized. Very few stable germa-imines have been reported,<sup>9</sup> and their chemical behaviour is not well developed. Also germirane,  $Mes_2Ge=CH_2=CR_2^{10}$  (obtained from 1 and diazomethane), is unstable but would be of great interest in organometallic synthesis.

So we thought that such interesting but labile species (as well as germanones, Ge=O, and germathiones, Ge=S, which have been invoked in some reactions from 1) could be rendered kinetically inert by substituting the germanium starting materials with more sterically demanding ligands.

We report here the synthesis of the new fluorenylidene germenes, substituted on germanium by two very large bis(trimethylsilyl)methyl (bisyl) groups 5, and with one mesityl and one bisyl on germanium, 6. In 6 steric hindrance should be intermediate between that observed for 1 and 5. Moreover, owing to the prochiral germanium, 6 could be useful in mechanistic and stereochemical studies. We report also the attempted synthesis of ditertbutylfluorenylidene germene 7 and the use of the lithio compound 8 as its synthetic equivalent. menes R'R"Ge=CR<sub>2</sub> (5)-(7) would be the dehydrofluorination of fluorogermanes R'R"Ge(F) CHR<sub>2</sub> by tert-butyllithium (R'R" = tBu<sub>2</sub>, Bis<sub>2</sub>, BisMes; CR<sub>2</sub> = fluorenyl). The use of fluorine instead of other halogens eliminates some side reactions, such as direct alkylation of germanium by lithio compounds and lithium-halogen exchange. The first step in the synthesis of 15-17 involves the preliminary preparation of dimethoxygermane derivatives 9-11, which are obtained in good yields from tetramethoxygermane<sup>11</sup> and tert-butyllithium or bisyllithium, or from mesityltrimethoxygermane<sup>12</sup> and bisyllithium :





## **RESULTS AND DISCUSSION**

## Synthesis of fluorofluorenylgermanes (15)–(17)

Following our synthesis of germene  $1,^{3,4}$  it appeared that the most convenient route to ger-

The corresponding diffuoro derivatives 12-14 are nearly quantitatively obtained by treatment of 9-11 with solutions of hydrofluoric acid in water; then addition of fluorenyllithium leads to the fluorofluorenylgermanes 15-17, which are the immediate precursors of germenes 5-7:

R	'R"Ge(OMe) <sub>2</sub>	HF/H <sub>2</sub> O/40% -2MeOH	R'R"GeF2	LiCHR <sub>2</sub> -LiF	R'R''GeC   F H	<b>CR</b> 2     
R'R": tBu <sub>2</sub> Bis <sub>2</sub> BisMes	9 10 11		12 13 14		15 16 17	

Compounds 9–17 could be easily purified by crystallization and exhibit good air and moisture stability, probably because of the large steric hindrance at germanium.

### Dibisyl(fluorenylidene)germene (5)

The formation of germene 5 is extremely dependent on the experimental conditions. The best yield of 5 is obtained by using a 50:50 mixture of THF/Et<sub>2</sub>O as solvent and an excess of tert-butyllithium (1.7 equivalent), required due to the reaction of tert-butyllithium with THF<sup>13</sup> during the lithiation of fluorogermane 16 to afford the lithio compound 18. Contrary to the species Mes<sub>2</sub>Ge (F)CHR<sub>2</sub>, which on reaction with tert-butyllithium gives the corresponding lithio compound at low temperature, 18 is obtained only after 1 h at room temperature. This low reactivity of 16 compared with its dimesityl analogue could be explained both by steric hindrance and electronic effects.

Lithio compound 18 is stable to the reaction conditions and when quenched with methyl iodide affords, nearly quantitatively, the corresponding The solutions of germene 5 are highly air and moisture sensitive and they immediately turn from orange to green in the presence of traces of oxygen. Compound 5 can be obtained in pure form and physicochemically characterized by <sup>1</sup>H and <sup>13</sup>C NMR. However, it has not been possible to assign with certainty the <sup>13</sup>C NMR resonance of the carbon doubly-bonded to germanium. This carbon was expected in the chemical shift region of the fluorenyl carbon atoms and might be small, either because of its long relaxation time or due to quadrupolar coupling with germanium.

The presence of the germanium-carbon double bond is chemically unambiguously proven by addition of MeOH to afford the corresponding methoxygermane 20, as expected from the polarity  $Ge^{\delta+}=C^{\delta-}$  of the double bond. Addition of tertbutyllithium to 5, followed by quenching with MeOH or methyl iodide, respectively, leads to germanes 22 and 23. The reaction is best explained by a single-electron transfer mechanism involving the intermediates 21 and 21', because it seems that the addition of tert-butyllithium across the double bond is unlikely due to the high steric hindrance on germanium.



germane 19 after 1 h at room temperature. Elimination of lithium fluoride produces the expected germene, 5, only after heating for 1 h at  $40^{\circ}$ C.

Using  $Et_2O$  instead of a mixture of THF/ $Et_2O$  in the synthesis of 5 from 16, gives this germene in



Germene 5 is first obtained complexed with one molecule of THF, but free germene is easily synthesized by heating  $5 \cdot \text{THF}$  at about  $80^{\circ}\text{C}$  in vacuo.



material 16, in about the same ratio. This result can be explained by the slow formation of lithio compound 18, followed by a rapid elimination of LiF to give germene 5 (in  $Et_2O$ , 18 is much less stabilized than in THF). Compound 5 may then react with tert-butyllithium, according to the single-electron transfer mechanism previously described.

#### Bisyl(mesityl)fluorenylidenegermene (6)

Germene 6 is obtained in a good yield by dehydrofluorination of fluorogermane 17 by tert-butyllithium in  $Et_2O$ . Addition of tert-butyllithium was performed at low temperature, and the lithio compound 24 was formed rapidly. Contrary to the case of 18, THF was not necessary.

Methanolysis immediately after the reaction mixture has reached room temperature affords methoxygermane 25 and starting fluorogermane 17 in the ratio 30:70, indicating only partial elimination of lithium fluoride. The complete elimination occurred only after heating the lithio compound 24 for 0.5 h at 35°C. Under these conditions, addition of MeOH to germene 6 leads quantitatively to formation of 25: adducts, and also as free compounds. This complexation is, of course, due to the polarity of Si=C or Si=N double bonds. In contrast, analogous adducts have never been observed in symmetrical doubly-bonded derivatives such as disilenes,<sup>16</sup> digermenes,<sup>2</sup> distannenes,<sup>17</sup> diphosphenes,<sup>18</sup> or in unsymmetrical sila-,<sup>19</sup> germa-<sup>12,20</sup> or stannaphosphenes,<sup>21</sup> in which the double bond is only slightly polarized and the metal has a weaker electrophilic character.

The study of the reactivity of **6** with various unsaturated compounds is now in progress.

# Attempted synthesis of ditert-butyl(fluorenylidene) germene (7)

Addition of one equivalent of tert-butyllithium to the ditert-butyl(fluoro)fluorenylgermane 15 leads exclusively to the corresponding lithio derivative 8. Attempts to eliminate lithium fluoride, by using various solvents (Et<sub>2</sub>O, THF, pentane) or by thermolysis, were unsuccessful. Formation of 8 is proved by its reaction with methyl iodide or benzyl chloride, leading quantitatively to 26 and 27:



As for germene 5, orange solutions of 6 are highly air- and moisture-sensitive, but crystals can be handled in air for short periods. In nitrogen or argon atmosphere, 6, like 5, is stable and can be stored for long periods.

Germenes 5 and 6 can be isolated as  $Et_2O$  or THF adducts, but also free of complexing solvents. The same phenomenon exists in silicon chemistry: silenes Si=C, <sup>14</sup> and sila-imines Si=N, <sup>15</sup> have already been isolated as ether or amine Therefore, there is a great difference of stability of fluorogermyllithio derivatives, Ge(F)—C(Li), depending on the substituents on germanium : with one or two aryl groups (mesityl, <sup>3</sup> fluorenyl<sup>7</sup>) lithium fluoride is easily eliminated at low temperature, whereas with two alkyl groups such as tert-butyl this elimination did not occur. A rather similar phenomenon has been observed in the synthesis of germaphosphenes, Ge=P-, in which elimination of lithium fluoride is much easier for Mes<sub>2</sub>Ge (F)P(Li)Ar than for  $tBu_2Ge(F)P(Li)Ar^{12}$  (ca  $-40^{\circ}C$  instead of 24 h at room temperature). The easy formation of dibisylgermene 5 from its lithio fluoro precursor 18 could be partly due to the electrophilic assistance of silicon by interaction with fluorine:



However, lithio compound 8 can be considered to some extent as a synthetic equivalent of germene 7. For example, addition of benzaldehyde to 8 leads to the three derivatives 28, 29 and 30 which have been obtained in a pure form by fractional crystallization. Formation of 28 and 29 involves the preliminary formation of the four-membered ring germaoxetane 31, followed by a  $[4] \rightarrow [2+2]$  cycloreversion, and dimerization of the germanone intermediate 32. The formation of the sixmembered ring derivative 30 can be explained by insertion of the germanone 32 into the germaniumoxygen bond of the germaoxetane intermediate 31. This reaction is additional proof of the initial formation of this heterocycle.

## **EXPERIMENTAL**

## General procedures

All the experiments were carried out under argon or nitrogen with flame-dried apparatus. Solvents must be freshly distilled over sodium/ benzophenone. <sup>1</sup>H NMR spectra were recorded on a Bruker AC 80 at 80.13 MHz or on a Bruker AM 300 WB at 300.1 MHz; <sup>13</sup>C NMR spectra on a Bruker AC 200 at 50.3 MHz (TMS internal standard); and <sup>19</sup>F NMR spectra on a Bruker AM 300 WB at 282.4 MHz (CF<sub>3</sub>COOH external standard). IR spectra were recorded on a Perkin-Elmer 457 grating spectrometer. Mass spectra were measured on a Nermag R 10 010 spectrometer (EI). Melting points were determined on a Reichert apparatus. Elemental analyses were performed by the "Service de microanalyse de l'Ecole de Chimie", Toulouse (France). Carbon atoms of fluorenyl groups are numbered  $C_1$  to  $C_{13}$  according to the scheme shown in the introduction.

### Dibisyl(dimethoxy)germane (10)

A solution of bis(trimethylsilyl)methyllithium [prepared from bis(trimethylsilyl)bromomethane<sup>22</sup>



# CONCLUSION

The germenes 5 and 6 and the lithio derivative 8 described in this paper present a particular interest for the following reasons. Compound 5, the most hindered germene isolated to date, may stabilize otherwise unstable adducts or low coordination number species. Studies of its chemistry are now in progress. Compound 6 is the first example of germene with a prochiral germanium atom suitable for stereochemical studies at the Ge=C double bond and 8 can be used as a synthetic equivalent of the ditert-butylfluorenylidene germene 7.

(16.8 g, 70 mmol) and 44 cm<sup>3</sup> of a solution 1.6 M of butyllithium in hexane] in Et<sub>2</sub>O (50 cm<sup>3</sup>) was added to a solution of tetramethoxygermane (6.6 g, 33.3 mmol) in Et<sub>2</sub>O (20 cm<sup>3</sup>). After the end of the addition, the reaction mixture was refluxed for 4 h. MeOLi was eliminated by filtration; **10** can be recrystallized in small amounts of pentane at  $-20^{\circ}$ C: 9.19 g (61%); m.p. 55°C. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): 0.22 (s, 36H, Me<sub>3</sub>Si), 1.82 (s, 6H, OMe). <sup>13</sup>C NMR (CDCl<sub>3</sub>): 3.31 (Me<sub>3</sub>Si), 12.03 (CHSi), 52.42 (OMe).

## Dibisyl(difluoro)germane (13)

To a solution of 10 (8.6 g, 18.9 mmol) in Et<sub>2</sub>O (100 cm<sup>3</sup>) was added a solution of hydrofluoric acid in water (40%, 5.5 g, 50% excess). The reaction was slightly exothermic. The reaction mixture was heated at reflux of Et<sub>2</sub>O for 4 h, then the organic layer was extracted with Et<sub>2</sub>O and dried overnight over Na<sub>2</sub>SO<sub>4</sub>. Removal of solvent *in vacuo* led to crude 13 which can be recrystallized from pentane to afford 6.16 g (76%) of white crystals; m.p. 59°C. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): 0.18 (s, Me<sub>3</sub>Si). <sup>19</sup>F NMR (C<sub>6</sub>D<sub>6</sub>): -58.05 (t, <sup>3</sup>J<sub>HF</sub> 18.6 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>): 2.42 (Me<sub>3</sub>Si), 14.24 (t, <sup>2</sup>J<sub>CF</sub> 8.12 Hz, CHSi).

# Dibisyl(fluoro)fluorenylgermane (16)

Fluorenyllithium was prepared by addition of a solution 1.6 M of butyllithium in hexane (11.3 cm<sup>3</sup>, 18.0 mmol) to a solution of fluorene (3.0 g, 18.0 mmol) in a 50 : 50 mixture of THF/Et<sub>2</sub>O (100 cm<sup>3</sup>). The lithio compound was stirred for 1 h at room temperature, then this red solution was slowly added to a solution of 13 (7.75 g, 18.0 mmol) in  $Et_2O$  (50 cm<sup>3</sup>) at room temperature. The reaction mixture was heated for 8 h at reflux, then filtered through silica (eluent, THF). The volatile components were removed in vacuo and crude 16 was recrystallized in pentane to afford 8.08 g (78%) of white crystals; m.p.  $339^{\circ}$ C. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): 0.04 (d,  ${}^{5}J_{HF}$  0.3 Hz, 18H, Me<sub>3</sub>Si), 0.18 (d,  ${}^{5}J_{HF}$  0.7 Hz, 18H, Me<sub>3</sub>Si), 4.71 (broad s, 1H, CHR<sub>2</sub>), 7.25-7.96 (m, 8H, CR<sub>2</sub>). <sup>19</sup>F NMR (CDCl<sub>3</sub>): -87.4. <sup>13</sup>C NMR (CDCl<sub>3</sub>): 3.46 (Me<sub>3</sub>Si), 4.04 (Me<sub>3</sub>Si), 12.27 (d,  ${}^{2}J_{CF}$  12.8 Hz, CHSi), 47.73 (d,  ${}^{2}J_{CF}$  10.3 Hz, CHR<sub>2</sub>), 120.17 (C<sub>4</sub>, C<sub>5</sub>), 125.87, 126.44, 126.57 (C<sub>1</sub>, C2, C3, C6, C7, C8), 141.42 (C12, C13), 143.45 (d,  ${}^{3}J_{CF}$  1.0 Hz, C<sub>10</sub>, C<sub>11</sub>). MS (EI, 70 eV,  ${}^{74}Ge$ ), m/z: 557 (M-F, 7), 411 (Bis<sub>2</sub>GeF, 3), 393  $(Bis_2Ge+1, 1), 165 (R_2CH, 70), 73 (Me_3Si, 100).$ Found: C, 56.6; H, 8.3. C<sub>27</sub>H<sub>47</sub>FGeSi<sub>4</sub> requires C, 56.3; H, 8.2.

# Dibisylfluorenylgermane (22)

To a solution of **16** (2.00 g, 3.5 mmol) in  $Et_2O$  (30 cm<sup>3</sup>), cooled in a dry ice-acetone, were added 2.7 molar equivalents of tert-butyllithium, 1.7 M in pentane. The reaction mixture was then warmed to room temperature and became an intense red. Addition of an excess of MeOH immediately decolorized the solution. Solvents were removed *in vacuo* and 20 cm<sup>3</sup> of pentane were added; lithium salts were filtered off, and crude **22** was recrystallized

from pentane; 1.65 g (85%) of white crystals of **22** were obtained; m.p. 118–119°C. <sup>1</sup>H NMR (CDCl<sub>3</sub>): -0.21 (d, <sup>3</sup>J<sub>HH</sub> 3.0 Hz, 2H, CHSi), 0.01 (s, 18H, Me<sub>3</sub>Si), 0.22 (s, 18H, Me<sub>3</sub>Si), 4.52 (s, 1H, CHR<sub>2</sub>), 4.75 (t, <sup>3</sup>J<sub>HH</sub> 3.0 Hz, 1H, GeH), 7.18–7.55 (m, 8H, CR<sub>2</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>): 1.08 (CHSi), 2.95 (Me<sub>3</sub>Si), 3.40 (Me<sub>3</sub>Si), 42.58 (CHR<sub>2</sub>), 119.68 (C<sub>4</sub>, C<sub>5</sub>), 125.20, 125.59, 126.36 (C<sub>1</sub>, C<sub>2</sub>, C<sub>3</sub>, C<sub>6</sub>, C<sub>7</sub>, C<sub>8</sub>), 140.60 (C<sub>12</sub>, C<sub>13</sub>), 146.63 (C<sub>10</sub>, C<sub>11</sub>). IR (KBr): v(Ge—H) 2068 and 2076 cm<sup>-1</sup>. MS (EI, 70 eV, <sup>74</sup>Ge), *m*/*z*: 557 (M–1, 2), 543 (M–15, 10), 393 (Bis<sub>2</sub>GeH, 100), 165 (CHR<sub>2</sub>, 25).

## Dibisylfluoro(methylfluorenyl)germane (19)

To a solution of 16 (0.50 g, 0.87 mmol) in THF (5 cm<sup>3</sup>)-Et<sub>2</sub>O (5 cm<sup>3</sup>) was slowly added 1.7 equivalents of tert-butyllithium 1.7 M in pentane. The reaction mixture, warmed to 0°C, turned gradually yellow. After 1/2 h stirring at 0°C, MeI (0.12 g, 0.87 mmol) was added. After 1 h at room temperature the reaction mixture was practically colourless; LiI was filtrated and solvents were removed in vacuo, and crude 19 was crystallized in pentane; 0.44 g of **19** (86%) were obtained; m.p. 112–113°C. <sup>1</sup>H NMR  $(CDCl_3): -0.16 (d, {}^{5}J_{HF} 0.6 Hz, 18H, Me_3Si), 0.18$ (d,  ${}^{5}J_{HF}$  0.9 Hz, 18H, Me<sub>3</sub>Si), 1.77 (d,  ${}^{4}J_{HF}$  0.6 Hz, 3H, MeCR<sub>2</sub>), 7.38-7.88 (m, 8H, CR<sub>2</sub>). <sup>13</sup>C NMR  $(CDCl_3)$ : 3.95 (Me<sub>3</sub>Si), 4.31 (d,  ${}^{4}J_{CF}$  1.8 Hz, Me<sub>3</sub>Si), 14.10 (d,  ${}^{2}J_{CF}$  13.1 Hz, CHSi<sub>2</sub>), 25.40 (d,  ${}^{3}J_{CF}$  27 Hz, MeCR<sub>2</sub>), 52.17 (d, <sup>2</sup>J<sub>CF</sub> 12.6 Hz, CR<sub>2</sub>), 120.25  $(C_4, C_5)$ , 125.00, 125.05, 126.93  $(C_1, C_2, C_3, C_6, C_7)$  $C_8$ ), 140.61, 149.61 ( $C_{10}$ ,  $C_{11}$ ,  $C_{12}$ ,  $C_{13}$ ).

# Dibisyl(fluorenylidene)germene (5)

To a solution of 16 (2.0 g, 3.48 mmol) in  $Et_2O/$ THF (50:50) (15 cm<sup>3</sup>) cooled to  $-78^{\circ}$ C were slowly added 3.48 cm<sup>3</sup> of a 1.7 M solution of tertbutyllithium in pentane (5.92 mmol). The reaction mixture was warmed to room temperature then heated at reflux for 1 h. A slight precipitate of LiF appeared and the reaction mixture turned orangered. After elimination of LiF by filtration and of the solvents in vacuo, crystallization in pentane afforded orange crystals of germene 5 complexed with one mole of THF; the free germene 5 was obtained by heating 5 · THF in vacuo at 80°C; 1.53 g of orange crystals (79%) of 5 were obtained ; m.p. 149–150°C. 5 · THF, <sup>1</sup>H NMR ( $CD_2Cl_2$ ): 0.43 (s, 36H, Me<sub>3</sub>Si), 1.87 (m, 4H, CH<sub>2</sub>), 3.74 (m, 4H, CH<sub>2</sub>O), 7.20–7.46 (m, 4H, CR<sub>2</sub>), 7.79–8.00 (m, 4H,  $CR_2$ ). 5, <sup>1</sup>H NMR ( $C_6D_6$ ): 0.46 (s, 36H,  $Me_3Si$ ), 7.27-8.23 (m, 8H, CR<sub>2</sub>).

#### Dibisyl(methylfluorenyl)germane (23)

Two molar equivalents of a solution 1.7 M of tert-butyllithium in pentane were added to a solution of 16 (2.00 g, 3.5 mmol) in  $Et_2O$  (30 cm<sup>3</sup>) cooled to  $-78^{\circ}$ C. The reaction mixture was then warmed to 20°C and became red; on the addition of a twofold excess of methyl iodide, it turned gradually colourless. After 1 h stirring, solvents were eliminated in vacuo and 20 cm<sup>3</sup> of pentane were added to precipitate LiF and LiI. After filtration, cooling of the solution at  $-20^{\circ}$ C gave white crystals of 23, 1.20 g (60%); m.p. 160–161°C. <sup>1</sup>H (CDCl<sub>3</sub>): -0.1(s, 18H, Me<sub>3</sub>Si), 0.14 (s, 18H, Me<sub>3</sub>Si), 1.79 (s, 3H, MeC), 4.96 (t,  ${}^{3}J_{HH}$  1.5 Hz, 1H, GeH), 7.30–7.84 (m, 8H, CR<sub>2</sub>).  ${}^{13}C$  (CDCl<sub>3</sub>): 3.51 (Me<sub>3</sub>Si), 3.72 (Me<sub>3</sub>Si), 4.51 (CHSi), 25.48 (MeC), 47.94 (CR<sub>2</sub>), 120.24 (C<sub>4</sub>, C<sub>5</sub>), 124.13, 126.26, 126.74 (C<sub>1</sub>, C<sub>2</sub>, C<sub>3</sub>, C<sub>6</sub>, C<sub>7</sub>, C<sub>8</sub>), 139.97, 151.63 (C<sub>10</sub>, C<sub>11</sub>, C<sub>12</sub>, C<sub>13</sub>). IR  $(KBr): v(Ge-H) 2056 \text{ cm}^{-1}$ . MS (EI, 70 eV, <sup>74</sup>Ge), m/z: 557 (M-15, 2), 393 (Bis<sub>2</sub>GeH, 35), 179 (R<sub>2</sub>CMe, 59), 73 (Me<sub>3</sub>Si, 100). Found : C, 59.1 ; H, 9.0. C<sub>28</sub>H<sub>50</sub>GeSi<sub>4</sub> requires : C, 58.8; H, 8.8.

# Dibisyl(methoxy)fluorenylgermane (20)

To a solution of 16 (1.0 g, 1.74 mmol) in Et<sub>2</sub>O (20 cm<sup>3</sup>) and THF (20 cm<sup>3</sup>) at  $-20^{\circ}$ C was slowly added a solution of tert-butyllithium 1.7 M in pentane (1.02 cm<sup>3</sup>, 1.74 mmol). The reaction mixture immediately turned light yellow and after 1 h was allowed to gradually warm; it turned orange (probably due to the formation of lithio compound). After 1 h at reflux, a three-fold excess of MeOH (0.15 g, 5.20 mmol) was added, to afford a light vellow solution. Solvents were removed in vacuo and 30 cm<sup>3</sup> of pentane were added to precipitate MeOLi. Crystallization from pentane afforded white crystals of 2, 0.83 g (81%); m.p. 105-106°C. <sup>1</sup>H NMR (CDCl<sub>3</sub>): -0.10 (s, 1H, CHSi), 0.04 (s, 18H, Me<sub>3</sub>Si), 0.07 (s, 18H, Me<sub>3</sub>Si), 3.74 (s, 3H, MeO), 4.61 (s, 1H, CHR<sub>2</sub>), 7.29-7.91 (m, 8H, CR<sub>2</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>): 1.10 (CHSi), 4.16 (Me<sub>3</sub>Si), 4.34 (Me<sub>3</sub>Si), 46.23 (CHR<sub>2</sub>), 53.77 (MeO), 120.04 (C<sub>4</sub>, C<sub>5</sub>), 125.69, 126.05, 126.34 (C<sub>1</sub>, C<sub>2</sub>, C<sub>3</sub>, C<sub>6</sub>, C<sub>7</sub>, C<sub>8</sub>), 141.31, 144.48 (C<sub>10</sub>, C<sub>11</sub>, C<sub>12</sub>, C<sub>13</sub>).

# Bisyl(mesityl)dimethoxygermane (11)

A solution of BisLi [prepared from BisBr (10 g, 41.7 mmol) and a stoichiometric amount of butyllithium 1.6 M in hexane at  $-78^{\circ}$ C] in Et<sub>2</sub>O was added to a solution of MesGe(OMe)<sub>3</sub> (11.85 g, 41.7 mmol) in pentane (40 cm<sup>3</sup>) cooled to  $-78^{\circ}$ C. After the addition the reaction mixture was allowed to 1159

warm to room temperature and then refluxed for 4 h. MeOLi was removed by filtration and the solvents were evaporated *in vacuo* leading to nearly pure waxy 11, which is very soluble in common organic solvents and can be recrystallized from small amounts of pentane to give 17.17 g (91%) of white waxy crystals; m.p. 39°C. <sup>1</sup>H NMR ( $C_6D_6$ ): 0.15 (s, 1H, CHSi), 0.33 (s, 18H, Me<sub>3</sub>Si), 2.14 (s, 3H, *p*-Me), 2.62 (s, 6H, *o*-Me), 3.55 (s, 6H, OMe), 6.77 (s, 2H, arom. Mes). <sup>13</sup>C NMR (CDCl<sub>3</sub>): 2.61 (Me<sub>3</sub>Si), 10.50 (CHSi), 21.05 (*p*-Me), 22.73 (*o*-Me), 51.66 (OMe), 129.40 (*m*-C Mes), 131.33 (*ipso*-C Mes), 139.55 (*p*-C Mes), 143.56 (*o*-C Mes). Found: C, 52.6; H, 8.9. C<sub>18</sub>H<sub>36</sub>GeO<sub>2</sub>Si<sub>2</sub> requires: C, 52.3; H, 8.8.

### Bisyl(mesityl)difluorogermane (14)

A solution of hydrofluoric acid in water (40%, 4.0 g, 50% excess) was added to 11 (5.28 g, 12.8 mmol) in benzene (30  $\text{cm}^3$ ). The reaction mixture was heated at reflux for 2 h, then the organic layer was extracted with Et<sub>2</sub>O and dried over Na<sub>2</sub>SO<sub>4</sub>. Solvents were removed in vacuo and 14 was recrystallized from pentane to afford 3.78 g (76%) of white crystals; m.p. 62–63°C. <sup>1</sup>H NMR ( $C_6D_6$ ): 0.23 (s, 18H, Me<sub>3</sub>Si), 1.99 (s, 3H, p-Me), 2.49 (s, 6H, o-Me), 6.62 (s, 2H, arom. Mes). <sup>19</sup>F NMR  $(C_6D_6)$ : -61.9 (d,  ${}^{3}J_{HF}$  8.2 Hz).  ${}^{13}C$  NMR  $(CDCl_3)$ : 2.22 (s, Me<sub>3</sub>Si), 13.79 (t, <sup>2</sup> $J_{CF}$  8.2 Hz, CH), 21.17 (s, p-Me), 23.30 (s, o-Me), 129.50 (s, m-C Mes), 141.50 (p-C Mes), 142.70 (o-C Mes). Found : C, 50.1; H, 7.8.  $C_{16}H_{30}F_2GeSi_2$  requires: C, 49.4; H, 7.8.

### Bisyl(mesityl)fluorenylgermane (17)

A solution of fluorenyllithium [prepared from fluorene (3.0 g, 18.0 mmol) and a solution of butyllithium 1.6 M in hexane (11.3 cm<sup>3</sup>, 18.0 mmol) in 100 cm<sup>3</sup> of a 50:50 mixture of THF/Et<sub>2</sub>O] was slowly added to a solution of 14 (6.99 g, 18.0 mmol) in  $Et_2O(80 \text{ cm}^3)$  at room temperature. The reaction mixture was heated at reflux for 2 h then filtered on silica (eluent, THF). After removal of solvents in vacuo, crude 17 was recrystallized from pentane to afford 6.92 g (72%) of white crystals; m.p. 122-123°C. <sup>1</sup>H NMR (CDCl<sub>3</sub>): 0.01 (s, 9H, Me<sub>3</sub>Si), 0.49 (d,  ${}^{5}J_{HF} 0.5 \text{ Hz}$ , 9H, Me<sub>3</sub>Si), 0.50 (d,  ${}^{3}J_{HF} 21.0 \text{ Hz}$ , 1H, CHSi), 1.74 (s, 3H, *p*-Me), 1.98 (d, <sup>5</sup>J<sub>HF</sub> 2.2 Hz, 6H, o-Me), 4.73 (d,  ${}^{3}J_{HF}$  1.5 Hz, 1H, CH), 6.32 (s, 2H, arom. Mes), 7.00-8.27 (m, 8H, CR<sub>2</sub>). <sup>19</sup>F NMR  $(CDCl_3)$ : -95.27. <sup>13</sup>C NMR  $(CDCl_3)$ : 2.45 (s, Me<sub>3</sub>Si), 3.66 (s, Me<sub>3</sub>Si), 9.85 (d,  ${}^{2}J_{CF}$  15.2 Hz, CHSi), 20.89 (s, p-Me), 23.61 (d,  ${}^{4}J_{CF}$  6.0 Hz, oMe), 48.1 (d,  ${}^{2}J_{CF}$  11.3 Hz, CHR<sub>2</sub>), 119.62, 120.22, 124.02, 124.75, 124.79, 125.96, 126.38, 126.41, 128.66, 132.32, 132.49 (C<sub>1</sub>, C<sub>2</sub>, C<sub>3</sub>, C<sub>4</sub>, C<sub>5</sub>, C<sub>6</sub>, C<sub>7</sub>, C<sub>8</sub> and *m*-C Mes), 132.3 (d,  ${}^{2}J_{CF}$  8.0 Hz, *ipso*-C Mes), 138.94, 140.08, 141.47, 142.40, 143.35 (d, 5.0 Hz), 144.33 (C<sub>10</sub>, C<sub>11</sub>, C<sub>12</sub>, C<sub>13</sub>, *o*-C Mes, *p*-C Mes). MS(EI, 70 eV,  ${}^{74}$ Ge), *m*/*z*: 521 (M-15, 2), 371 [BisGe(F)Mes, 63], 165 (R<sub>2</sub>CH, 31), 119 (Mes, 11), 159 (Bis, 2). Found : C, 65.5; H, 7.4. C<sub>29</sub>H<sub>39</sub>FGeSi<sub>2</sub> requires : C, 65.1; H, 7.3.

## Bisyl(mesityl)fluorenylidenegermene (6)

An equivalent of tert-butyllithium 1.7 M in pentane (2.8 mmol) was added to a solution of 17 (1.50 g, 2.8 mmol) in Et<sub>2</sub>O (20 cm<sup>3</sup>) cooled to  $-78^{\circ}$ C. (Note: Et<sub>2</sub>O must be very carefully dried and deoxygenated and all the apparatus flame-dried in vacuo.) The reaction mixture was then allowed to warm to room temperature : it turned gradually yellow, then orange at room temperature, and orange-red on reflux of Et<sub>2</sub>O. Approximately 1/2 h of reflux was necessary for the complete formation of germene. LiF was eliminated by centrifugation. Solvents were removed in vacuo giving crude germene 6. Crystallization in pentane gave 0.88 g (61%) of orange crystals of 6; m.p. 60-61°C. Solutions of 6 are extremely air-sensitive: they turned green when traces of air were added. <sup>1</sup>H NMR ( $CD_2Cl_2$ ): 0.33 (s, 18H, Me<sub>3</sub>Si), 0.37 (s, 1H, CHSi), 2.45 (s, 3H, p-Me), 2.61 (s, 6H, o-Me), 6.96-8.05 (m, 8H, CR<sub>2</sub>), 7.14 (s, 2H, arom. Mes).

# Bisyl(mesityl)(methoxy)fluorenylgermane (25)

An excess of methanol (carefully dried and deoxygenated) was added to a solution of 6(1.14 g)2.2 mmol) in  $Et_2O$  (10 cm<sup>3</sup>). The orange solution of 6 turned immediately colourless.  $Et_2O$  and excess of MeOH were eliminated in vacuo and crude 25 was recrystallized in pentane to afford 0.91 g (86%) of white crystals; m.p. 134-135°C. <sup>1</sup>H NMR (CDCl<sub>3</sub>): 0.03 (s, 9H, Me<sub>3</sub>Si), 0.47 (s, 9H, Me<sub>3</sub>Si), 2.06 (s, 6H, o-Me), 2.18 (s, 3H, p-Me), 3.83 (s, 3H, OMe), 4.85 (s, 1H, CH), 6.59 (s, 2H, arom. Mes), 7.02-8.01 (m, 8H, CR<sub>2</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>): 2.92 (Me<sub>3</sub>Si), 3.83 (Me<sub>3</sub>Si), 7.36 (CHSi), 21.00 (p-Me), 23.14 (o-Me), 44.69 (CHR<sub>2</sub>), 53.10 (OMe), 119.67, 120.19 (C<sub>4</sub>, C<sub>5</sub>), 124.64, 124.97, 125.69, 125.99, 126.32, 126.44, (C<sub>1</sub>, C<sub>2</sub>, C<sub>3</sub>, C<sub>6</sub>, C<sub>7</sub>, C<sub>8</sub>), 128.65 (m-C Mes), 134.52, 138.40, 140.65, 141.70, 143.02, 145.04, 145.07 (C<sub>10</sub>, C<sub>11</sub>, C<sub>12</sub>, C<sub>13</sub>, ipso-C Mes, o-C Mes, p-C Mes). MS (EI, 70 eV, <sup>74</sup>Ge), m/z: 547 (M-1, 11), 383 [Bis(Mes)GeOMe, 100], 351  $[Bis(Mes)Ge - 1, 10], 193 (MesGe, 11), 165 (R_2CH,$ 

53), 119 (Mes, 10), 73 (Me<sub>3</sub>Si, 64). Found : C, 66.3 ; H, 7.9. C<sub>30</sub>H<sub>42</sub>GeOSi<sub>2</sub> requires : C, 65.8 ; H, 7.7.

## Ditert-butyl(fluoro)fluorenylgermane (15)

A solution of fluorenyllithium [prepared as previously described from fluorene (8.67 g, 52.2 mmol) and butyllithium (52.2 mmol) in 120 cm<sup>3</sup> of THF/Et<sub>2</sub>O (50:50)] was added to a solution of 12 (11.73 g, 52.2 mmol) in Et<sub>2</sub>O  $(100 \text{ cm}^3)$  at room temperature. The orange reaction mixture was heated at reflux for 2 h, then filtered through silica and the solvents were eliminated in vacuo. Recrystallization from pentane afforded 13.34 g (69%) of white crystals of 15; m.p. 90-91°C. <sup>1</sup>H NMR  $(CDCl_3)$ : 1.00 (d,  ${}^{4}J_{HF}$  1.0 Hz, 18 H, tBu), 4.52 (broad s, 1H, CH), 7.17–8.00 (m, 8H, CR<sub>2</sub>). <sup>13</sup>C NMR  $(CDCl_3)$ : 28.41 (s, Me), 31.84 (d, <sup>2</sup> $J_{CF}$  8.6 Hz, CMe), 41.40 (d,  ${}^{2}J_{CF}$  6.8 Hz, CH), 120.11 (C<sub>4</sub> C<sub>5</sub>), 125.35, 126.16, 126.48 (C<sub>1</sub>, C<sub>2</sub>, C<sub>3</sub>, C<sub>6</sub>, C<sub>7</sub>, C<sub>8</sub>), 140.93, 143.91 (C<sub>10</sub>, C<sub>11</sub>, C<sub>12</sub>, C<sub>13</sub>). MS (EI, <sup>74</sup>Ge), m/z: 372 (M, 15), 315 (M-tBu, 2), 238 (M-2tBu-HF, 15), 207  $(tBu_2GeF, 30)$ , 165 (HCR<sub>2</sub>, 100). Found: C, 67.5; H, 7.3.  $C_{21}H_{27}FGe$ requires : C, 68.0; H, 7.3.

## Ditert-butyl(fluoro)(benzylfluorenyl)germane (27)

To a solution of 15 (1.0 g, 2.7 mmol) in  $Et_2O$  (15 cm<sup>3</sup>) cooled to  $-78^{\circ}$ C was added one equivalent of tert-butyllithium 1.7 M in pentane. After warming to room temperature, the reaction mixture turned red. Benzyl chloride (0.34 g, 2.7 mmol) was added to the lithio compound  $tBu_2Ge(F)C(Li)R_2$  at room temperature; the solution immediately became light yellow. After 1 h stirring at room temperature, lithium chloride was removed by filtration and then the solvents were removed in vacuo. Crude 27 was recrystallized from pentane, affording 1.06 g (85%) of white crystals of 27; m.p. 157-158°C. <sup>1</sup>H  $(CDCl_3)$ : 1.06 (d,  ${}^{4}J_{HF}$  1.3 Hz, 18H, tBu), 4.06 (s, 2H, CH<sub>2</sub>), 6.41-8.18 (m, 13H, CR<sub>2</sub>Ph). <sup>13</sup>C  $(CDCl_3)$ : 29.73 (s, Me), 34.44 (d, <sup>2</sup> $J_{CF}$  8.6 Hz,  $C(Me_3)$ , 40.69 (s, CH<sub>2</sub>), 57.55 (d, <sup>2</sup> $J_{CF}$  8.6 Hz,  $CR_2$ ), 120.00 (C<sub>4</sub>, C<sub>5</sub>), 125.76–136.05 (C<sub>1</sub>, C<sub>2</sub>, C<sub>3</sub>, C<sub>6</sub>, C<sub>7</sub>, C<sub>8</sub>, Ph) 141.20, 146.62 (C<sub>10</sub>, C<sub>11</sub>, C<sub>12</sub>, C<sub>13</sub>). MS (EI, <sup>74</sup>Ge), m/z: 462 (M, 2), 328 [tBuGe(F)CR<sub>2</sub>CH<sub>2</sub>, 1], 257 [Ge(F)CR<sub>2</sub>, 13], 207 (tBu<sub>2</sub>GeF, 6), 57 (tBu, 100). Found : C, 72.4; H, 7.2. C<sub>28</sub>H<sub>33</sub>FGe requires : C, 72.9; H, 7.2.

#### Ditert-butyl(fluoro)(methylfluorenyl)germane (26)

To the lithic compound 8 [prepared from 17 (0.5 g, 1.35 mmol) and one equivalent of tert-butyllithium in Et<sub>2</sub>O] was added methyl iodide (0.19 g, 1.35 mmol) in solution in pentane (5 cm<sup>3</sup>). After 15 min at room temperature the orange reaction mixture turned yellow; solvents were removed *in vacuo* and 15 cm<sup>3</sup> of pentane were added; LiI was then eliminated by filtration. Crystallization from pentane afforded 0.31 g (48%) of white crystals of **26**; m.p. 87–88°C. <sup>1</sup>H NMR (CDCl<sub>3</sub>): 0.96 (s, 18H, tBu), 1.53 (s, 3H, CMe), 7.17–8.11 (m, 8H, CR<sub>2</sub>).

#### Reaction of lithio compound 8 with benzaldehyde

To a solution of lithio compound 8 [prepared as previously from 15 (1.0 g, 2.7 mmol), one equivalent of tert-butyllithium and Et<sub>2</sub>O (15 cm<sup>3</sup>) cooled to  $-78^{\circ}$ C] was added a solution of benzaldehyde (0.29 g, 2.7 mmol) in  $Et_2O$  (5 cm<sup>3</sup>). The reaction mixture turned brown-black, then was warmed to room temperature. During stirring at 20°C for 10 h, it progressively turned yellow. After filtration to remove lithium fluoride, solvents were evaporated in vacuo. Pentane (25 cm<sup>3</sup>) was added to the crude resulting mixture; cooling to  $-20^{\circ}$ C allowed the crystallization of alkene 29,<sup>23</sup> which was separated by filtration (0.38 g, 55%). The filtrate contained 28 and 30, which were separated by fractional crystallization in  $Et_2O$ /pentane (50:50). 28 was the first to crystallize. 28, <sup>1</sup>H NMR (CDCl<sub>3</sub>): 0.96, 1.21, 1.24 and 1.46 (4s). <sup>13</sup> C NMR (CDCl<sub>3</sub>): 27.43, 27.99 and 31.91. MS (EI, <sup>74</sup>Ge), m/z: 437 (M – 3tBu, 0.5), 381 (M-4tBu+H, 1), 367 (M-4tBu-Me+2H, 1)1), 293 (M $-tBu_2Ge=O-2tBu+H$ , 2), 204 (tBu<sub>2</sub>) Ge==O, 2), 57 (tBu, 100). 30, <sup>1</sup>H NMR (CDCl<sub>3</sub>): -0.04 (s, 9H, tBu), -0.03 (s, 9H, tBu), 0.11 (s, 9H, tBu), 0.12 (s, 9H, tBu), 4.60 (s, 1H, CH), 7.17-7.93 (m, 13H, CR<sub>2</sub> and Ph).  ${}^{13}$ C NMR (CDCl<sub>3</sub>): 20.92, 23.43, 24.14 and 28.10 (Me<sub>3</sub>C), 60.86 (CH), 62.59 (CR<sub>2</sub>), 119.05 to 145.67 (Ph, CR<sub>2</sub>).

### REFERENCES

- T. J. Barton, E. A. Kline and P. M. Garvey, J. Am. Chem. Soc. 1973, 95, 3078; P. Rivière, A. Castel and J. Satgé, J. Am. Chem Soc. 1980, 102, 541; N. Wiberg and Ch. K. Kim, Chem. Ber. 1986, 119, 2966 and 2980; N. Wiberg, P. Karampatses and Ch. K. Kim, Chem. Ber. 1987, 120, 1203.
- For a recent review on Ge=C compounds, see: J. Barrau, J. Escudié and J. Satgé, *Chem. Rev.* 1990, 90, 283.
- C. Couret, J. Escudié, J. Satgé and M. Lazraq, J. Am. Chem. Soc. 1987, 109, 4411.
- 4. M. Lazraq, J. Escudié, C. Couret, J. Satgé, M.

Dräger and R. Dammel, Angew. Chem. 1988, 100, 885; Angew. Chem. Int. Edn. Engl. 1988, 27, 828.

- H. Meyer, G. Baum, W. Massa and A. Berndt, Angew. Chem. 1987, 99, 790; Angew. Chem. Int. Edn Engl. 1987, 26, 798.
- A. Berndt, H. Meyer, G. Baum, W. Massa and S. Berger, *Pure Appl. Chem.* 1987, **59**, 1011.
- G. Anselme, J. Escudié, C. Couret and J. Satgé, J. Organomet. Chem. 1991, 403, 93.
- M. Lazraq, C. Couret, J. P. Declerq, A. Dubourg, J. Escudié and M. Rivière-Baudet, *Organometallics* 1990, 9, 845.
- C. Glidewell, D. Lloyd, K. W. Lumbard and J. S. McKechnie, *Tetrahedron Lett.* 1987, **28**, 343; J. Pfeiffer, W. Maringgele, M. Noltemeyer and A. Meller, *Chem. Ber* 1989, **122**, 245; H. G. Ang and F. K. Lee, *J. Chem. Soc.*, *Chem. Commun.* 1989, 310; H. G. Ang and F. K. Lee, *F. Fluorine Chem.* 1989, **43**, 435.
- M. Lazraq, J. Escudié, C. Couret, J. Satgé and M. Soufiaoui, J. Organomet. Chem. 1990, 397, 1.
- D. C. Bradley, L. J. Kay and W. Wardlaw, J. Chem. Soc. 1956, 4916.
- H. Ranaivonjatovo, J. Escudié, C. Couret and J. Satgé, New J. Chem. 1989, 13, 389.
- R. B. Bates, L. M. Kroposki and D. E. Potter, J. Org. Chem. 1972, 37, 560.
- N. Wiberg, G. Wagner, G. Muller and J. Riede, J. Organomet. Chem. 1984, 271, 381; N. Wiberg, G. Wagner and G. Muller, Angew Chem. Int. Edn. Engl. 1985, 24, 229.
- N. Wiberg, K. Schurz and G. Fisher, Angew. Chem. Int. Edn Engl. 1985, 24, 1053; N. Wiberg, K. Schurz, G. Reber and G. Muller, J. Chem. Soc., Chem. Commun. 1986, 591; N. Wiberg, G. Preiner, P. Karampatses, Ch. K. Kim and K. Schurz, Chem. Ber. 1987, 120, 1357.
- 16. R. West, Angew. Chem. Int. Edn. Engl. 1987, 26, 1201.
- 17. S. Masamune and L. R. Sita, J. Am. Chem. Soc. 1985, 107, 639.
- S. Lochschmidt and A. Schmidpeter, *Phosphorus and Sulfur* 1986, 29, 73.
- C. N. Smit, F. M. Lock and F. Bickelhaupt, *Tetrahedron Lett.* 1984, 25, 3011; C. N. Smit and F. Bickelhaupt, *Organometallics* 1987, 6, 1156.
- J. Escudié, C. Couret, J. Satgé, M. Andrianarison and J. D. Andriamizaka, J. Am. Chem. Soc. 1985, 107, 3378.
- C. Couret, J. Escudié, A. Raharinirina and J. Satgé, J. Am. Chem. Soc. 1985, 107, 8280.
- 22. N. Wiberg and G. Wagner, Chem. Ber. 1986, 119, 1455.
- M. Neuenschwander, R. Vogeli, H. P. Fahrni, H. Lehman and J. P. Ruder, *Helv. Chim. Acta* 1977, 60, 1073.